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MODERN SYNTHETIC RUBBERS

By the Same Author

MODERN RUBBER CHEMISTRY (1937)
MODERN PLASTICS (1945)

MODERN SYNTHETIC RUBBERS

BY

HARRY BARRON

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To

GRACE,

ANTHONY AND HELEN

Modern Synthetic Rubber

"The author hardly needs an introduction either to the plastics or rubber industries, and any work by him will undoubtedly arouse considerable interest. In spite of the world-wide interest in synthetic rubber, there has hitherto been very little published on the subject. This deficiency will be made good by Dr. Harry Barron's book. . . . It is certainly a very instructive and entertaining publication." *British Plastics.*

"To say that Dr. Barron has rendered good service to science in general is not enough. He has not only clarified what we have called the science of big molecules, but he has, scientifically and economically, more clearly than most writers, correlated the rubber, synthetic rubber and modern plastics industry into one coherent whole." *Plastics.*

". . . The first part gives a lucid coherent view of the entire field. It can be read with ease by an ordinary layman. It is in Part 2 that the rubber chemist will start to get his teeth into the chemical and physical problems to be met with in the manufacture of synthetics, while Part 3 interests not only the manufacturers of rubber, but also its users.

We believe that this publication is likely to be the textbook of synthetic rubbers in this country for some time to come."

Rubber Age.

PRINTED IN ... AND LONDON
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AUTHOR'S PREFACE

THE subject of synthetic rubbers is of the greatest National importance. It is a topic of everyday conversation, although very little is known about them, even in technical circles. It is regrettable that a great deal of nonsense has been published on the subject. Unfortunately there is no recent work of reference concerning synthetic rubbers

Oddly enough, neither the Germans nor the Americans have so far published any books on the subject. Information is scattered far and wide among the technical journals, the scientific magazines, and various commercial leaflets and brochures. I have endeavoured to bring together as much of the information available in as palatable a form as possible. The most comprehensive mass of information on synthetic rubber is published in the U.S.S.R., and I have only had access to those few articles which have been translated.

I have thoroughly enjoyed this very formidable task, for I have long been one of the most ardent advocates for a synthetic rubber industry to be established in this country. I foresaw its normal commercial expansion, and have wondered why we did nothing about it here. As long ago as October 27th, 1936, I wrote in the *Evening Standard*: "as a form of long-term insurance it would be well worth the while of the Government to take an interest in the production of synthetic rubber". As events have turned out this was almost prophetic. A few weeks later, on November 23rd, in the same newspaper, I wrote: "Vinyl resins obtained from acetylene will in the near future attain an industrial importance which at present it is not possible to estimate". But until recently all my endeavours to stir up active interest have fallen on deaf, not to say hostile, ears. It is very grievous that at the present time when the natural rubber position is so unhappy, Great Britain should be left high and dry without any synthetic rubber industry, and without one in sight.

If only the powers-that-be could understand what they are doing in holding up the development of such an industry! But I despair of making them appreciate the full significance, of making them conscious of the many considerations other than that of synthetic versus natural rubber. Let me have yet another try.

On all sides one hears the opinion expressed very glibly that we are entering upon a Plastics Age. I believe this to be the case, but what does it mean? If it means anything at all, it is that plastics will play a very great part in our life. But this does not mean an

existence dominated by the moulded articles with which we are so familiar. Not at all. It means that plastics will play a very important part in building aircraft, motor-cars, ships, houses, and structures generally. It means that they will have a great influence on many industries, such as the electrical industries, the engineering industries, and so on. Our livelihood, our comfort, and our happiness may be utterly bound up in their use. Already the design of many machines of war are deeply affected by the application of both synthetic rubber and plastics.

Where do synthetic rubbers come into this picture? Well, they have their own physical part to play: a very important part. Of that there can be no doubt. But the important thing is that in many cases precisely those plastics which will be of such pre-eminent importance are also involved in the production of synthetic rubber, either directly or as by-products. That single fact enables them to be produced on a very large scale and very cheaply, since all the major costs are borne by the synthetic rubber production. In other words, synthetic rubber paves the way for the Plastics Age. Together with the synthetic rubber industry you will have a healthy expanding plastics industry; without it, the thermoplastic industry will inevitably be a hothouse plant constantly requiring artificial stimulation. And those many dependent industrial activities will be correspondingly affected --adversely.

In Great Britain, the exigencies of war have brought home the fact that in many directions we are considerably behind in technical progress. We have certainly been travelling on the train of progress, but with our backs to the engine—and third class! There has been no money available for development. We can only see the receding landscape. Our technical men have not been encouraged to see the new horizons and opportunities that are continually being opened up. Our national inherent creative ability has been allowed to go to waste. Certainly a great part of it should be directed into the field of synthetic rubbers and the associated materials which will be the basis of the Plastics Age.

Advocacy of synthetic rubber in Great Britain has always been extremely unpopular. So much so, that on one occasion when I had the temerity to suggest such a thing, I was nearly thrown out of a meeting of the Institution of the Rubber Industry, early in 1939—an unprecedented occurrence. Oddly enough, that particular meeting was a Sales meeting for Buna rubbers!

But during the last year or two, the murmurings of synthetic rubber activity from abroad have begun to have some effect. The

worried rumblings of the uneasy American tyre manufacturers were very evident. The precautionary activity in the United States clearly showed the trend of things to those realistic people who realized the implications of bringing rubber so many thousands of miles under war conditions. It only needed the attack of the Japanese at Pearl Harbour to let loose the greatest torrent of scientific and technical development on synthetic rubbers that the world has yet seen. This work is going to have a most profound effect on world progress in the near future. It will certainly accelerate the arrival of the Plastics Age.

Early in 1941, a year before the need became so definite as to dispose of all doubts about the future of synthetic rubber, with commendable vision, the Editor of *The Rubber Age* agreed to my suggestion that he should publish a series of articles on synthetic rubbers. This series still continues. I have drawn freely on these articles in writing this book, and I must thank Mr. Pickett, Mr. Hunter, and Miss Fenn for their encouragement and enthusiasm.

The implications of synthetic rubber production on plastics development have always been quite clear to me, and I was able to persuade Mr. Wilkins of *British Plastics* to allow me to write a series of articles dealing with this aspect. I have to thank him for permitting me to draw freely on these articles.

The question of terminology has been a very thorny one. I expect to be assailed for indulging in a certain degree of dualism. But so far as nomenclature is concerned, I do not believe it is possible at any given moment to switch over from one set of terms to another. The only way is to change over gradually, which I have endeavoured to do.

I apologize in advance for any errors and omissions, but the work has been written under certain difficulties. For one thing, it has been a spare-time occupation. My days have been, and are, fully occupied in development work and large-scale manufacture of products involving many of the materials described in this book. The evenings and nights of these times, and in these parts, are not always conducive to constructive and creative work. All too often the pen has to be laid aside at the behest of the more urgent and insistent call of the air-raid siren.

Be that as it may, I present this book in the hope that it may be regarded as a contribution to knowledge in this sphere of activity. It will at least provide something to bite on, some basis on which, no doubt, many better books will be written.

HARRY BARRON.

SOUTHAMPTON,
1942.

AUTHOR'S PREFACE TO SECOND EDITION

AT the best of times a subject such as synthetic rubber would be difficult to handle. In these days events move so rapidly under the pressure of war conditions that by the time the first edition had been published it was already out-of-date. A flood of developments in the United States made it quite clear that another revised version would rapidly be required.

The book was written when the seriousness of the rubber situation had just made itself felt in the United States. An assortment of U.S. Senate Committees were examining different aspects of the problem. The earlier synthetic programmes had been impressive. When the true position became apparent, the programmes were stepped up until they became almost astronomical. The practical difficulties introduced a number of commercial by-products. Animosities were aroused. Competitive interests clashed.

Investigation of the patent position in the synthetic rubber field disclosed an unsatisfactory situation, hampering the war effort. This automatically led to the policy whereby patents in the synthetic rubber field were made generally available. One consequence of the disclosures made in this connection was to make the United States public fully conscious of the situation. It became clear that more intensive co-ordination was necessary. President Roosevelt appointed the Baruch Committee to sort the position out. Its recommendations were made public just as *Modern Synthetic Rubbers* was published. It laid down a programme which is now being pushed through with the greatest determination.

In the early days rubber from oil had all the limelight, and the major part of the programme was based on oil products. Another Senate Committee (the Gillette Committee) has since shown clearly that agriculture is perhaps an even better source of raw materials.

The difficulties of handling the new materials have been tackled with commendable American thoroughness. Moreover, what is perhaps even more laudable, the results have been published. New compounding ingredients have had to be developed. United States industry is all set to take the new materials in any quantities. There is the general determination to bring these materials on to a permanent basis.

And what of this country? We stand where we did—wondering

what may be retrieved from the Japs, and when! There are as yet few signs of activity in the synthetic rubber field.

Most people agreed with my strictures about our lack of research and development. Some disagreed violently. I stick to my opinion. Developments in plastics and associated chemical activities are keyed to a large synthetic rubber industry. We shall in due course regret our backwardness and reluctance to take the plunge.

It is heartening, however, to see the realization in all quarters that we must encourage development as far as possible. It is to be hoped that these will not remain as pious hopes, but will be put into practice.

Having stated that I regarded the book as something to bite upon, I could hardly expect to get away unscathed. Nor did I. It was well and truly "bitten" at—in most cases justifiably and constructively. Other critics just bit.

The first edition contained many errors. I am deeply grateful to those people who were kind enough to inform me of them. In particular I would express my gratitude to Mr. G. H. Wyatt, Ph.D., F.I.C., who has gone to a great deal of trouble in this respect. These errors have been rectified.

I wish to thank all those who have made constructive criticisms of various aspects. For example, Mr. W. H. Stevens, of the Monsanto Chemical Company, Ltd., has very kindly "vetted" my chapter on Thioplasts.

HARRY BARRON.

SOUTHAMPTON,
1943.

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PART I

GENERAL CONSIDERATIONS

CHAPTER I

NATURAL RUBBER AND SYNTHETIC RUBBER-LIKE MATERIALS

THERE are at the present time a large number of materials referred to as synthetic rubbers. They include many which have only lately come to be classed in this category. Table 1 lists many of these products. In one sense this represents only a summary, for each type divides up into variations on the main theme. It is evident, therefore, that the study of synthetic rubber is already a formidable task. And the really intensive universal interest has only just started.

Efforts to produce synthetic rubbers have passed through a number of distinct phases. The first and longest phase was the academic one, in which chemists endeavoured to break down natural rubber in order to determine its composition and structure, while at the same time endeavouring to utilize the breakdown products to rebuild the original material. They were able to obtain a number of interesting materials, but these were mere laboratory curiosities.

The second phase during the early part of the century coincided with the period during which the rubber plantations in the Far East were beginning to make some progress. It was marked by two outstanding technical developments. One was the discovery of useful starting materials in the form of coal and limestone, while the other was a better realization of and improvement in the process of polymerization. The climax of this phase came during the last war, during the final stages of which Germany was actually manufacturing with considerable difficulty some 300 tons per month of methyl rubber. The end of that war also saw the finish of this production. Thereafter there was complete stagnation until 1925, when the price level of raw rubber reached such a ridiculous height that the greatest possible stimulus was given for the production of synthetic material. This marks the third phase during which large-scale research in several countries yielded an increasing number of new synthetic materials. These were gradually combed out, and the more promising ones brought to the stage of practical application and nearer to the goal of

Table 1. Synthetic Elastic Materials

Name	Main ingredient	Other features	Manufacturer
Acronal	Polyacrylic ester		I.G. Farbenindustrie (Germany)
Agripol	Soya bean oil Ethylene glycol		Reichhold Chemicals, Inc.
A.X.F.	Copolymer of ethylene	Polyphenylene	U.S. Rubber Co. (U.S.)
Buna 85	Butadiene polymer	mol. wt. 85,000	I.G. Farbenindustrie
Buna 115	,, ,,	,, ,, 115,000	,, ,,
Buna N.	,, copolymer	acrylic nitrile.	,, ,,
Buna S.	,, ,,	styrene	,, ,,
Buna SS.	,, ,,	higher styrene content	,, ,,
Butyl	Olefine-diolefine copolymer		Standard Oil Co. (U.S.)
Chemigum	Butadiene copolymer	acrylic derivative	Goodyear Rubber Corpn. (U.S.)
Corvic	Polyvinyl Chloride		Imperial Chemical Industries Ltd.
Ethanite	Organic polysulphide		Belgium
Ethocel	Ethyl cellulose		Dow Chemical Co.
Ethyl Cellulose	,, ,,		Hercules Powder Co.
Flamenol	Plasticized polyvinyl chloride		G.E.C. of America (U.S.)
Flexon	Olefine-diolefine copolymer		Standard Oil Co.
Formvar	Polyvinyl formal		Shawinigan Corpn. of Canada
Hycar	Butadiene copolymer	acrylic derivative	Hydrocarbon Chemical Co. (U.S.)
Igelite	Polyvinyl chloride copolymer		I.G. Farbenindustrie
Ker	Butadiene polymer		Poland
Koroseal	Plasticized polyvinyl chloride		B. F. Goodrich (U.S.)
Mipolam	Plasticized polyvinyl chloride		Dynamit Akt. Troisdorf (Germany)
Neoprene	Chloroprene polymer		Du Pont de Nemours (U.S.)
Norepol	Soya Bean Oil Ethylene Glycol		U.S. Bureau of Agriculture
Novoplas	Organic polysulphide		Imperial Chemical Industries, Ltd. (Britain)
Oppanol	Isobutylene polymer		I.G. Farbenindustrie
P.V.A.	Polyvinyl alcohol		Du Pont de Nemours (U.S.)
Perbunan	Butadiene copolymer	acrylic nitrile	I.G. Farbenindustrie Standard Oil Co. Firestone Rubber Co. U.S. Rubber Co.
Perbunan Extra	,, ,,	higher acrylic nitrile content	,,
Plexigum	Polyacrylic ester		Röhm and Haas Akt.
Perduren	Organic polysulphide		I.G. Farbenindustrie
Polythene	Polymerized ethylene		Imperial Chemical Industries Ltd.
Saran	Polyvinylidene chloride		Dow Chemical Co. (U.S.)
S.K.A.	Butadiene polymer	from petroleum	U.S.S.R.
S.K.B.	,, ,,	from alcohol	U.S.S.R.
Sovprene	Chloroprene polymer		U.S.S.R.
Thiokol	Organic polysulphide		Thiokol Corpn. (U.S.)
Thionite	,, ,,		Japan
Vinidur	Plasticized polyvinyl chloride		I.G. Farbenindustrie
Vinylite	Polyvinyl chloride copolymer		Carbon & Carbide Corpn. (U.S.)
Vistanex	Isobutylene polymer		Standard Oil Co. (U.S.)
Vulcaplas	Organic polysulphide		Imperial Chemical Industries Ltd.

becoming commercial commodities. During this period extending up to 1933, the chief efforts were in the direction of finding suitable raw materials for large-scale production.

The fourth phase was the development of manufacturing establishments on an ever-growing scale in several countries, notably in the strongly nationalistic states where no hindrance was imposed and every encouragement given for large-scale production. This led up to a very considerable scale of manufacture with a somewhat questionable commercial prospect.

The fifth phase in which we have now entered is one in which large-scale production of synthetic rubber has become a necessity, and natural rubber plays a minor part.

Since synthetic rubber is now openly intended for use in the place of rubber the behaviour must be considered in relation to the behaviour and properties of natural rubber. This is necessary to bring the subject into true perspective. Synthetic rubber must be weighed up against the industrial and technical background of natural rubber.

What relationship is there between synthetic rubber and raw rubber? What is their commercial significance likely to be? Is there any real permanent threat to the interest of the plantation industry, etc.? These are all questions which must be examined and answered.

The Part played by Rubber in Modern Life. Rubber is indispensable to modern civilization. Its importance in every form of transport for tyres and tubes is self-evident. But in its other applications it plays equally important rôles. It is a revelation to consider to what extent industry in general, indeed life in general, is dependent upon rubber. About 80 per cent. of all rubber is used in the motor industry, mainly for tyres. This applies to passenger transport, goods transport, and private cars. A large proportion of the remainder goes into what are known as mechanical goods, which include such articles as belting, packings, moulded goods, hose, and innumerable other types of products. Most of these articles are absolutely vital to the operation of the industry in general. Without them industries could come to a standstill.

TABLE 2. UNITED STATES RUBBER CONSUMPTION, 1939

	Per cent.
Tyres	63·6
Tubes	9·2
Other tyre uses	3·1
Mechanicals	9·0
Boots and shoes	6·8
Druggists sundries and sports goods	5·0
Other uses	3·3

A large quantity of rubber is made into rubber footwear, into soles and heels, which all play an important part in the daily life and health of the community. Thousands of tons of rubber are used for covering wires and cables playing a vital part in communication and transmission. Lesser quantities of rubber find their way into such essential products as rubberized fabrics for rainproof and other sheetings, into numerous druggists' sundries, into rubber springs and mountings, into rubber thread, into sponge rubber, and many other vital types of products. In fact, rubber cushions the shocks of a turbulent world.

The Rubber Industry as a Service Industry. The rubber industry is chiefly a service industry. It produces indispensable parts required for the successful operation of nearly every other industry. The diversity is shown by the fact that one firm alone, B. F. Goodrich Co. in the United States makes more than 35,000 articles. Without rubber the various forms of transportation could not run, the communication system would break down, national health would be adversely affected, the shoe and clothing industry would suffer, etc. Rubber is of the greatest possible importance in tyres on tractors for agricultural use. The change-over from steel wheels to pneumatics has had a profound effect on agricultural development.

Importance in Warfare. This general statement applies to ordinary industrial obligations. Introducing military considerations merely emphasizes what has been stated. Present-day mechanized warfare implies rapid and smooth transport of armies and their supplies, which means that they must run on rubber. Modern mechanized warfare cannot be waged without rubber for transport.

But the fighting services rely on rubber for other activities than transport. Warfare is now a very scientific operation implying more instruments of control, more equipment, and more protective devices. In many of these aspects rubber has made profound contributions.

Vehicles such as lorries, cars, etc., must be equipped with tyres, or with rubber tracks, in many cases requiring to be bullet-proof and resistant to puncture. Tanks also must be equipped with various forms of rubber tracks, and other rubber articles. It has been stated that a 30-ton tank contains nearly a ton of rubber, while a modern battleship is said to use about 70 tons.

Another important development involving the use of rubber is in self-sealing petrol tanks and hose for aircraft. In war, as in peace, hosepipe of every description is of the greatest importance. Ordinarily hose is necessary for the transfer of petrol, oil, air, water and other fluids. The importance of fire hose notably for civil defence needs no emphasis. Rubber-insulated wires and cables make a particularly

important contribution to defence, apart from ordinary wiring, for innumerable purposes which defy recording. They are used as control cables for searchlights and anti-aircraft guns, for operating the electrical equipment on naval craft, and in the form of belts around ships for degaussing as protection against mines.

Special rubber pads of every description are employed in tanks and aircraft, to afford protection to the occupants against shock of warfare. Similar products are employed in parachute parts and as accessories to various instruments of war.

From the point of view of personal equipment of combatants, rubber also plays an important part. Rubber boots and shoes are necessary parts of the equipment of soldiers and sailors, special types being used for airmen. Rubber raincoats protect them from the weather, while rubber ground sheets are quite general. Rubber is also an indispensable part of gas-masks, both for military and civil purposes. Nearly every form of naval craft, aircraft, and military vehicles of war use hard rubber accumulator cases for their storage batteries. Pontoon bridges are built from rubber. Rubber dinghies and life jackets are also standard equipment for airmen. The barrage balloon is another familiar article which in great part depends upon the properties of rubber.

Growth in the Use of Rubber. Rubber has been in use for just over a century. Its really important and large-scale application runs parallel with the development of the motor-car, and is also bound up with the growth of the plantation industry in the Far East. The following table illustrates the growth in the consumption of natural rubber over a long period.

TABLE 3. CONSUMPTION OF NATURAL RUBBER

	Tons
1860	1,500
1875	9,000
1890	30,750
1900	48,000
1910	95,000
1915	155,000
1920	295,000
1925	525,000
1930	825,000
1935	873,000
1937	1,135,000

Rubber was necessary for the development of the modern car, the growing popularity of which has in turn greatly enlarged the rubber industry. The modern car contains about 200 different parts made chiefly of rubber. It has been estimated in the United States that an average car contains about 145 lbs. of rubber. It is used in prac-

TABLE 4. NET IMPORTS OF CRUDE RUBBER INTO PRINCIPAL MANUFACTURING COUNTRIES [6]

(Long Tons)

	United States	United Kingdom	Fr. [illegible] (c)	Germany	Canada (*ac*)	Japan (*da*)	Italy	Russia (*ce*)	Australia (*cd*)	Belgium (*d*)	Netherlands	Scandinavia (*abcdf*)	Spain (*g*)	Czechoslovakia (*abcd*)	Total
1929	[illegible]	42,671	17 [illegible]	5,584	6,[illegible]	9,753	9,894	75	1,002	3,995	2,771	3,[illegible]	2,418	9	343,[illegible]
1930	[illegible]	73,335	61 [illegible]	54,120	19,[illegible]	66,831	19,341	29,830	13,534	11,166	1,243	7,[illegible]	5,520	10,402	772,[illegible]
1931	[illegible]	158,482	49 [illegible]	59,330	28,[illegible]	69,905	21,398	47,271	9,642	9,115	3,758	12,[illegible]	6,900	10,999	926, [illegible]
1932	[illegible]	128,829	51.[illegible]	62,899	26,[illegible]	57,567	21,880	37,572	9,978	7,593	4,068	11,[illegible]	8,140	11,245	895,[illegible]
1933	[illegible]	—2,591	57	71,794	27,[illegible]	61,223	16,534	30,967	14,109	9,648	2,888	11,[illegible]	6,668	8,772	791,[illegible]
1934	[illegible]	92,707	59 [illegible]	98,170	36,[illegible]	62,311	24,733	30,462	19,164	14,970	4,343	4,[illegible]	2,400	13,063	1,055, [illegible]
1935	[illegible]	133,079	59,[illegible]	90,200	25,[illegible]	45,836	28,170	25,650	11,944	11,309	5,092	16,034	2,400	9,936	871,[illegible]
1936	[illegible]				31,[illegible]	42,352			15,426	9,612	7,051				
1937	[illegible]														
1940 :															
Feb.	41 797	7,500	5,000*	....	3,508	5,241	1,500*	2,000*	1,846	694	495	1,200*	200*	....	....
Mar.	58,302	14,200	5,000*	....	3,062	6,057	1,500*	2,000*	1,784	....	627	1,200*	200*	....	....
Apr.	70,135	16,400	5,000*	....	3,096	2,000*	1,500*	2,000*	1,612	....	....	1,200*	200*	....	....
May	50,610	10,000	5,000*	....	3,108	2,500*	1,500*	2,000*	2,128	....	....	1,200*	200*	....	....
June	53,,266	9,500	5,000*	....	1,062	3,000*	1,500*	2,000*	1,181	....	....	1,200*	200*	....	....
July	69,496	19,500	5,000*	....	5,112	3,000*	1,500*	2,000*	1,902	....	....	1,200*	200*	....	....
Aug.	72,612	21,250	5,000*	....	4,605	4,500*	1,500*	2,000	2,508	....	....	1,200*	200*	....	....
Sept.	78,306	25,940	5,000*	....	2,743	....	1,500*	2,000*	2,485	....	....	1,200*	200*	....	....
Oct.	74,400	.....	5,000*	....	8,336	....	1,500*	2,000*	590	....	....	1,200*	200*	....	....
Nov.	72,775	.....	5,000*	....	5,451	....	1,500*	2,000*	1,366	....	....	1,200*	200*	....	....
Dec.	97,794	.....	5,000*	....	7,437	....	1,500*	2,000*	721	....	....	1,200*	200*	....	....
1941 :															
Jan.	86,541	.....	5,000*	....	6,290	....	1,500*	2,000*	1,065	....	....	1,200*	200*	....	....
Feb.	73,647	.....	5,000*	....	3,770	....	1,500*	2,000*	1,717	....	....	1,200*	200*	....	....
Mar.	86,794	.....	5,000*	....	3,879	....	1,500*	2,000*	3,486	....	....	1,200*	200*	....	....
Apr.	64,521	.....	5,000*	....	2,531	....	1,500*	2,000*	2,326	....	....	1,200*	200*	....	....
May	101,034	.....	5,000*	....	5,596	....	1,500*	2,000*	1,549	....	....	1,200*	200*	....	....
June	64,101	.....	5,000*	....	2,818	....	1,500*	2,000*	1,373	....	....	1,200*	200*	....	....
July	96,658	.....	5,000*	....	4,143	....	1,500*	2,000*	2,003	....	....	1,200*	200*	....	....
Aug.	105,556	.....	5,000*	....	10,683	....	1,500*	2,000*	1,251	....	....	1,200*	200*	....	....
Sept.	81,742	.....	5,000*	....	....	....	1,500*	2,000*	4,392	...	....	1,200*	200*	....	....

a—Including gutta percha. *b*—Including balata. *c*—Re-exports not deducted in monthly statistics. *d*—Including some scrap and reclaimed rubber. *e*—Official statistics of rubber imports by Soviet Russia. *f*—Including Norway, Sweden, Denmark and Finland. *g*—United Kingdom and French exports to Spain except in years prior to 1925. *h*—French imports have been reduced in order to eliminate imports of gutta percha and to reduce to basis of net weight. †—United States imports of guayule are included in this compilation. *—Figure is provisional.

tically every available form as latex, cements, soft rubber, hard rubber, sponge rubber. Every important characteristic of rubber is utilized.

It is absolutely essential to realize that the importance of rubber is entirely due to its physical properties which have been so amazingly developed by the skill of the rubber technologist. Chemical properties play a comparatively minor part. This has an important bearing on the development of synthetic rubber.

It is of interest to view the chief physical properties which give rubber its importance. They may be summarized as follows[2]:

It has great flexing endurance, withstanding considerable distortion without injury.

It has a very high tensile strength which reaches about 30,000 lbs. per square inch at cross-section on break.

The elongation can be adjusted to almost any desired value over a very wide range.

It has a great range in properties from soft to hard rubber.

Hysteresis provides self-damping effects.

It has a high capacity for absorbing energy.

Its resistance to chemicals is outstandingly good.

It has high resistance to abrasion.

Its high dielectric strength makes rubber a splendid insulator.

It has a high coefficient of friction against nearly all surfaces.

It has excellent water-proofing properties.

It has low permeability to most gases and liquids.

It is a thermo-setting plastic, and is readily moulded.

It is available in a wide range of colours.

It is available in liquid condition as dispersion or cement.

In order to see synthetic rubbers in their true perspective, it is obviously desirable and necessary to make a brief study of the properties of natural rubber.

In considering the different uses of rubber, it is found that at least one, and usually several, of the outstanding properties have caused it to be chosen for any particular purpose. For example, in a motor tyre rubber is used in the inner tube because flexibility and low permeability to air are necessary. It is employed in the tyre carcase because of its outstanding flex resistance, and because it insulates the cotton cords and prevents them from chafing. In the tyre probably no other material than rubber affords the necessary resistance to abrasion, shock absorption, water-proofing, and friction against road surfaces.

The Scope for Synthetic Rubbers. In general the possibilities

for the use of synthetic rubber correspond to almost every use of natural rubber; in many applications where natural rubber is unsuitable synthetic rubbers have additional outlets. No single synthetic rubber has the versatility of rubber. It is in some specialized application that they score. As a result collectively the synthetic rubbers have a marked advantage over natural rubber.

For example, Buna S is at the present time the synthetic rubber generally used in Germany for tyres, Perbunan being applied chiefly where resistance to swelling is necessary. Buna S is cheaper to make, and has better adhesive properties than Perbunan, although not equal to natural rubber in this respect. Rubber is used for making the carcases of tyres, while Buna S is used for the tread. These two can be directly bonded, which is not possible with Perbunan and rubber. This lack of adhesive properties is a great disadvantage in tyre construction and similar applications. With the possible exception of neoprene this lack of tackiness is an outstanding defect of almost every synthetic rubber-like material.

The resistance to hydrocarbon liquids is responsible for the wide application of synthetic rubbers in hose and tubing, and in the handling of petroleum products. In oilfields, refineries, tankers, filling stations, and in the car itself petroleum products now are usually transported through hose and tubing made of synthetic rubber and into tanks which are sealed with it. Many other parts in cars which come into contact with oil are being made from one variety or another of synthetic rubber. For use in contact with oils, grease, fats, and so on, synthetic rubber is widely applied. Conveyor belts, industrial tyres, gaskets, and sealing devices are likewise made from synthetic rubber; soles and heels, aprons, gloves and other garments for use under similar conditions, also come into the same field of application. The great stability of synthetic rubbers towards liquids accounts for their growing use in printers' rolls and blankets, engraving plates, and similar articles. Pipes of spraying equipment for paints and lacquers are also made from synthetic rubbers. According to a fairly recent statistical survey made by the B.F. Goodrich Co.,[5] synthetic rubber can be substituted for natural rubber 769 times out of 1,000 in the mechanical goods field. Since rubber has been in short supply this proportion has become even greater.

There is an ever-growing application of synthetic rubbers in the electrical field. Those with super-electrical properties such as polyisobutylene and the Buna S type, are superior to natural rubber, and are being used in insulation for wires and cables. For many uses at low voltages, other types such as neoprene, Thiokol, and polyvinyl chloride

are also used for insulation. The big field so far has been in the form of sheathing over insulation of natural rubber or other materials. They are often used in this manner to protect rubber from the effects of light, air, ozone, oils, and other deteriorating influences. The low permeability of gases and resistance to sunlight accounts for the growing application of synthetic rubbers in balloons for every purpose. The impregnation of fabrics of every description with synthetic rubbers possessing better ageing properties than natural rubber has opened up the domestic field of application. For example, umbrellas, raincoats, tablecloths, shower curtains and so on, are typical products which have been made notably from polyvinyl chloride, possessing in addition to other merits a wide range of colours.

Disadvantages of Rubber. While rubber was unique its properties had to be good enough, but as soon as other elastic materials became available these properties were subjected to closer scrutiny.

The question has been posed as to whether the exceptional versatility of rubber is altogether desirable. For example, what use is outstanding elasticity to an electrical engineer who desires only an insulator? What properties are there in a rubber article of the mechanical type such as a doormat that might make it desirable for use as an eraser? What is the use of the outstanding insulating properties of rubber in a motor tyre or a pair of shoes? The general trend of product development is towards specialization. It is the functional aspect of materials which has become important.

In the case of rubber this has great point, because in spite of the excellent range of properties outlined above, these are unfortunately inevitably accompanied by an almost equally impressive number of serious disadvantages. For example, rubber deteriorates with age; it is attacked by oxygen, ozone and sunlight; minute amounts of such common metals as copper and manganese make it break down rapidly; it is attacked by strong acids; by oils and solvents. Chemically it is extremely reactive owing to its unsaturated character. The common feature of all these deleterious influences is that the elasticity is lost, which is fatal to most vulcanized rubber articles. In many instances the disadvantages of rubber for a particular purpose are in no sense compensated by the many superfluous virtues which do not come into operation.

With the passing of time the conditions under which rubber must work have become more and more strenuous and exacting. They are conditions which involve the poor properties rather than the good properties of rubber. For example, the increased trend towards mechanization of every description calls for contact with oil and petrol

under extreme conditions of temperature. Thus the internal combustion engine, involving all these considerations, is the fundamental feature in transport of every description; motor vehicles, aircraft, tanks and shipping. In some of these machines which are used in extremes of climatic conditions, exceptional temperature conditions are superimposed upon the internal heat and solvents present. Moreover, the rubber parts of the equipment must be adequate to withstand both extremes of heat and cold. Thus in aircraft products rubber parts must be suitable for the low Arctic temperatures and even worse sub-stratosphere temperatures, and yet the same equipment must be able to withstand tropical heat.

There are numerous conditions, notably in the electrical field, where ozone is present which has a disastrous effect on rubber, unless adequately protected. In many industries corrosive conditions abound in such a form that ordinary rubber compositions cannot withstand them. The numerous new industries have their own specialized requirements far in excess of the old standards for which rubber was regarded as an unsatisfactory but unavoidable expedient. Those consumers who have been dissatisfied with the deficiencies of rubber have accepted synthetic rubber with satisfaction; they have been willing to pay the high price. In order to satisfy this demand rubber manufacturers have become used to handling synthetic rubber.

It is unnecessary to stress at any length the importance of non-inflammability which is so essential for many purposes, especially under war conditions.

It is the failure of rubber to meet these requirements that has lent urgency to the search for synthetic substitutes. It has supplied the thin end of the wedge, and materials which have proved superior for such applications have met with ready demand even at far higher cost. Thus the immediate demand for neoprene and Thiokol when they appeared in 1931 came from the automobile industry.

Advantages of Synthetic Rubbers over Natural Rubber. Before the present situation of shortage of natural rubber arose, synthetic rubbers achieved popularity in spite of their high cost, because of possessing superior properties. The outstanding property that nearly all possessed was their resistance to the influence of solvents, particularly petroleum products. The only notable exceptions are Buna S and butyl rubber which, however, are superb in nearly every other respect. In general, it is not actual swelling which is a serious disadvantage so much as the loss of tensile strength, which almost invariably accompanies it. It is found that the tensile strengths of most synthetic rubbers are less affected even when the amounts of swelling

are comparable with rubber. Another feature is that in general more material is extracted from rubber mixes by solvents than from synthetic compositions.

Second only to the resistance to swelling is the resistance of synthetic rubbers to deterioration or ageing. This applies to nearly all the conditions which undermine the utility of natural rubber. These conditions include exposure to oxygen, to ozone from electric discharges, to ultra-violet light, or to high temperature. In this connection most of the disadvantages of rubber are explained by its unsaturation. Some credence is lent to this idea by the fact that saturated materials such as polyisobutylene and polyvinyl chloride are exceptionally resistant. Their flex resistance is also generally superior, and in some cases, e.g. butyl rubber, incomparably so.

Synthetic rubber compositions in general offer greater obstruction to the passage of liquids and gases than do rubber compounds. To some extent this is attributed to the absence of materials such as proteins and carbohydrate products which are present in rubber. Differences in structure also undoubtedly contribute to this.

Synthetic rubbers are far less permeable to gases, which is a factor of very great importance at the present time.

Buna S and the other Bunas are approximately about the same as natural rubber in this respect, but Perbunan is at least twice as good. Materials such as neoprene, and the polyvinyl chloride products have very great resistance to burning, largely due to their content of chlorine. This is a great advantage over rubber.

The position can be briefly summarized as follows:

Natural rubber is superior in :—

1. Processing properties.
2. Extensibility (in most cases) and elasticity.
3. Resilience (i.e. low hysteresis loss).
4. Maintenance of elastic properties at low temperature (in most cases).
5. Tear resistance.
6. Cutting resistance.

Synthetic elastic materials are superior in :—

1. Resistance to deterioration by oils and organic solvents.
2. Resistance to oxidation or ageing:
   (*a*) Induced by actinic rays (sunlight, etc.).
   (*b*) Induced by heat.
   (*c*) Induced by strong oxidizing agents or metals.
3. Lower permeability to gases and liquids.

According to Konrad,[4] Buna S in tyres has an advantage of 25 per cent. better abrasion resistance. Electrical properties of certain of the synthetic rubbers such as polyisobutylene, butyl rubber, and Buna S are superior to those of natural rubber. In other materials such as neoprene, Perbunan, and polyvinyl chloride, there are polar groups present which have an adverse influence generally on electrical properties.

It is the case that synthetic rubber-like materials are in general more difficult to process than natural rubbers. But it is a noteworthy fact that the art of compounding natural rubber has only really seriously been carried forward during the last twenty years. Compounding of synthetic materials has only a history of a few years. In the case of the oldest commercial type—neoprene—with a history of eleven years, there are now very few difficulties in processing. Other types have a shorter history and are not quite so far advanced. With the heavy pressure of intensified world-wide effort great advances can be anticipated during the next few years.

So far as suitability of synthetic materials for the major application —tyres—is concerned the most critical survey has been favourable. According to evidence obtained by the technical advisers to the Baruch Committee, Buna-S will give certainly 90 per cent. of the wearability obtainable from rubber. It is quite satisfactory for use in inner tubes. They concluded that a certain amount of crude rubber was necessary in making up carcases and sidewalls of tyres. However, not more than 20 per cent. of a heavy Buna-S tyre would need to be crude rubber.

There is another factor of outstanding importance—change in design. The chief cause of failure of synthetic rubbers in tyres has so far been the high heat build-up, with its adverse effect on the cotton in the tyre carcase and sidewalls. It has been shown that rayon carcases will withstand much higher temperatures—in fact for heavy-duty tyres there is a trend for rayon to replace cotton for this reason. Thus rayon is said to be as effective at 105° C. as cotton is at 75° C. It is considered very likely that the use of rayon together with synthetic rubbers may greatly alter the situation, and may overcome some of the difficulties now being experienced.

The Importance of Vulcanization. Considering rubber as a raw material, it owes its important position to two main causes: (1) the physical properties possessed by soft vulcanized rubber, and (2) the plastic characteristics of masticated unvulcanized rubber which makes it easily amenable to factory operations. It can be worked and manipulated in any desired manner. The fundamental change caused by vulcanization is of the greatest possible importance. It is a change in

condition usually affected by heating with sulphur, and is best defined by contrasting the difference in physical properties. The properties of unvulcanized rubber : [2]

(*a*) Low tensile strength	Change to	(*a*) High tensile strength
(*b*) Limited elasticity		(*b*) Extensive elasticity
(*c*) Low recovery		(*c*) High recovery
(*d*) High retentivity		(*d*) Low retentivity
(*e*) High flow		(*e*) Low flow
(*f*) Narrow temperature range		(*f*) Wide temperature range
(*g*) Plasticity-thermo-plastic		(*g*) Non-plasticity
(*h*) Solubility		(*h*) Lack of solubility
(*i*) Tack		(*i*) Lack of tack

Thus consider a normal rubber composition before and after vulcanization. Before vulcanization it is easily pulled apart, and if much extended does not tend to retract, although under impact the rebound is considerable. When heated it becomes softer and more plastic, being easily formed into any desired shape. If cooled below 0° C. it becomes stiff and boardy. It is readily soluble in hydrocarbon solvents. When two fresh surfaces are pressed together they adhere and become practically integral. This property of tack is extremely valuable in manufacturing operations.

After vulcanization (or " cure " as the process is technically known) rubber is tough and strong, and even after considerable distortion returns rapidly to its original shape. There is little tendency to flow, and hardly any tack. Hydrocarbon solvents make it swell, but it will not dissolve it. These characteristics do not vary greatly from — 40° C. to well above 100° C. This comparison illustrates how the elastic character of rubber is developed during vulcanization.

The general nature of the synthetic materials is often described by one of the three following terms : " vulcanizable ", " thermosetting " or " thermoplastic ". Each of these may be briefly defined as follows : vulcanization as in rubber, is a process by which the synthetic is changed from a thermoplastic substance, soluble in many organic solvents and susceptible to marked physical and chemical alteration within the range of ordinary atmospheric temperature, to a new material which is highly elastic, insoluble in most organic solvents and relatively insensitive to changes over a considerable temperature range. This change is brought about by the reaction, under the influence of heat, of the material with some added chemical, such as sulphur, zinc oxide magnesia or litharge.

A thermosetting synthetic resin will undergo a similar change, but this change is usually brought about by the action of heat alone, and

the products are seldom highly elastic, although in some instances sufficiently so as to warrant their consideration as synthetic rubber. The original physical and chemical properties of thermoplastics are not usually appreciably affected by changes in ordinary atmospheric temperature and these materials do not exhibit a permanent change in properties as do the vulcanizable and thermosetting types. Here the action of heat is merely to soften the material in order to facilitate extrusion or moulding and to relieve internal stresses. In other words, the same material may be milled or extruded repeatedly, whereas curing (heat treating) of the vulcanizable or thermosetting types renders the material non-thermoplastic and it can therefore not be re-milled or re-extruded.

The Status of Thermoplastics in the Synthetic Rubber Field. There are many thermoplastic materials having the rubber-like properties of soft vulcanized rubber. They tend to be applied more and more for products previously made of rubber. They differ fundamentally from rubber and elastomers (i.e. synthetic rubbers related to rubber) inasmuch as there is no chemical change from the plastic to the elastic state. That being the case there is a definite limiting temperature beyond which the characteristic plastic flow becomes appreciable. As Von Rosenberg [7] has pointed out, a satisfactory commercial material must be very plastic at the temperature at which it is processed, but it must have little plasticity, but much elasticity in the temperature range at which it is to be utilized. The ideal would be a material whose plasticity was nil during the working range but which at the top limit changed within a few degrees to the soft plastic state for processing. Rubber and elastomers once set or vulcanized no longer have the physical defects inherent in the plastic state.

The thermoplastics which have or can acquire rubbery properties during the normal working range of temperatures may be conveniently grouped as:

(1) Materials having rubber-like properties such as polyisobutylene, acrylic acid esters, polyvinyl butyrate, etc.
(2) Materials which are intrinsically hard and whose latent rubber-like properties are brought out by addition of plasticizers. These include: polyvinyl chloride, polyvinyl chloride-acetate, polyvinyl alcohol, etc.

It is interesting to note that the plasticizing effect is specific. Only certain plasticizers are effective. These are sometimes called elasticizers—an ugly word, but one whose meaning is quite clear.

There are, in addition, alkyd-condensation products which, however, do not really enter the rubber field and are not truly reversible thermoplastics. A case can be made out for cellulose ethers, e.g. benzyl cellulose and ethyl cellulose. In recent months a great deal has been heard about ethyl rubbers, based on ethyl cellulose.

It is interesting to review in brief some of the outstanding features of rubber-like materials in relation to natural rubber.

Rubber reinforced with channel black still has the highest tensile strength to be obtained with elastic materials. Several elastomers are not far behind in this respect. But in pure gum mixes, or those containing inert fillers, rubber is already equalled and surpassed by elastomers, and by thermoplastics such as polyisobutylene and plasticized polyvinyl chloride.

Polyisobutylene and butyl rubber have higher elongations at break than rubber, which is also equalled by elastomers such as Buna S, neoprene, Perbunan, etc.

Rubber and elastomers do not tend to undergo considerable permanent deformation under prolonged stress, whether in extension or compression. The thermoplastics all have a pronounced tendency to flow or " creep ", the effect being perhaps least pronounced in polyvinyl chloride, varying with plasticizer content, etc.

In resilience or rebound, rubber is as yet unequalled even by the elastomers.

Rubber Practice and Plant the Same throughout the World. Every industrial country in the world has a rubber-manufacturing industry. The equipment in every manufacturing establishment throughout the world is identical in principle, variations being largely a question of size, capacity, and newness. The procedure is likewise similar. Raw rubber, either crêpe or smoked sheet, is masticated or broken down on open rolls or in an internal mixer, the Banbury type being the most widely used. When it has been reduced to a plastic mass it is compounded, all the necessary ingredients being added on the mill or in the mixer.

It is interesting to note in connection with processing that the property of plasticity is of more fundamental importance than elasticity. During all manufacturing processes the important property is plasticity. Elasticity is required only in the final product, when vulcanization virtually eliminates plasticity.

Thereafter the processing depends upon the nature of the product being made. Compounded rubber may be calendered or extruded, or it may be moulded. It may be frictioned or skimmed on to fabric, or it may be fabricated in many ways; this flexibility in use is one of

its most valuable properties. To a great extent it is dependent upon the unique tackiness of rubber. It may also be converted into doughs or taken up into solutions and used in these forms.

The plastic rubber compound is then formed either in a mould, or by assembling, or by extrusion, and is then vulcanized either in a press or under open steam pressure, or in air, or by low temperature methods.

The important point which is brought out in this description is that all the plant required to handle rubber exists in very large quantities. A great deal of capital is sunk in this plant. Large numbers of skilled personnel are already available. Consequently it is essential, irrespective of any other merits that it may possess, that any substitutes for rubber should be suitable for handling on the same equipment. Failing this, it is hopeless to expect any rapid expansion in its use.

Other industries in which rubber is extensively used, and which have special equipment to handle it, are interested from the same angle. Obviously the highly specialized equipment of a tyre factory cannot be scrapped. It is for the new material to conform to the equipment. The same applies to plant for making boots and shoes. Another outstanding example is the longitudinal machine which is the backbone of insulated wire manufacture. Any new material suggested for the same purpose must be suitable for application on this machine. Many other examples can be brought to mind.

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CHAPTER 2

ECONOMICS OF SYNTHETIC ELASTIC MATERIALS

UNTIL recently the synthetic rubber position appeared to have fallen into a well-defined pattern. It was common knowledge that countries such as Germany, and the U.S.S.R. had proceeded with the synthetic rubber production to the virtual exclusion of the natural product. In contrast, United States production although small was geared to commercial demands, neoprene and Thiokol being well-established commercial materials. Until the rubber-producing areas of the Far East were overrun by the Japanese early in 1942, the position was that Russia and Germany already had large-scale synthetic rubber-producing industries; the United States production was relatively small. The position is now quite changed.

Synthetic rubber has now become a major factor in world affairs. All preconceived ideas have gone by the board, swept away by the rush of current events. The tolerant acceptance of these apparently expensive luxuries has given way to urgent insistence upon their necessity. Criticism of the " ersatz " materials of the totalitarian countries and of Russia has been completely stilled. Sources of supply of more than one million tons per annum of natural rubber have passed out of the hands of the chief consumers. Nevertheless, the necessity for rubber not only exists, but has become even greater and more urgent. Synthetic rubber must be considered against the dramatically changed background of a shortage of rubber available to the leading rubber consumers. Production schedules for synthetic rubber in the United States for example are now aimed at the enormous total of 1,100,000 tons per annum. That this scheme having once been started, will be carried through seems beyond reasonable doubt. The repercussions and implications of this programme are serious and inescapable.

Before the war spread to the Far East synthetic rubber was an insignificant competitor of natural rubber. It had indeed become something of a bogey to rubber growers. For the last fifty years it had been a somewhat abstract long-distance threat to them, but in recent years it had become a definite tangible reality which had to be faced. The full realization of this has only finally come about after the loss of the rubber-growing area. Now of course the position has changed considerably, so that synthetic rubber is no longer insignificant as a competitor of natural rubber.

At the present time the position is one which shows up an economic

TABLE 5. EXPORTS OF CRUDE RUBBER FROM PRINCIPAL PRODUCING COUNTRIES [17]

(Long Tons)

	BRITISH MALAYA						British North Borneo		NETHERLAND INDIES						
	Gross Exports	Imports	Net Exports	Ceylon	India & Burma	Sarawak		Thailand	Java & Madura	Sumatra E. Coast	Other N.I.	Indo-China	American Valley	All Other	World Total
1923	252,016	70,[illegible]	181,584	39,[illegible]71	6,416	5,705	4,[illegible]37	1,718	32,930	46,344	57,822	5,067	16,[illegible]	7,[illegible]56	406,413
1933	573,412	167,	406,035	63,[illegible]51	4,527	10,874	7,[illegible]	7,765	73,851	91,861	149,659	18,394	9,[illegible]	2,[illegible]37	846,312
1934	677,361	211,[illegible]	465,558	79,[illegible]1[illegible]	10,492	17,233	11,[illegible]	17,545	87,400	112,058	175,470	20,170	8,[illegible]	2,[illegible]	1,008,663
1935	590,319	174,[illegible]	415,667	54,[illegible]16	13,968	19,465	8,[illegible]	28,327	57,488	78,325	139,297	28,816	11,[illegible]	8,[illegible]15	864,574
1936	520,286	167, [illegible]	352,487	49,[illegible]	14,724	21,243	8,[illegible]	33,702	61,307	84,577	152,205	40,782	14,[illegible]	11,[illegible]00	845,431
1937	681,638	213,[illegible]	468,192	70,[illegible]83	17,015	25,922	13,[illegible]3	5,551	84,085	139,632	207,863	43,399	15,[illegible]	13,[illegible]13	1,133,864
1938	526,911	156,[illegible]	370,810	49,[illegible]2[illegible]	15,178	17,792	9,[illegible]7	41,080	57,526	94,501	145,909	58,518	14,[illegible]3	12,920	887,892
1939	553,324	177,[illegible]51	375,473	61,[illegible]2[illegible]	15,881	24,014	11,864	41,266	72,786	117,791	181,272	65,140	13,892	22,224	1,002,629

	British Malaya [1]	N.E.I.	Ceylon [2]	India & Burma [2]	North Borneo	Sarawak	Thailand	Indo-China	Oceania	Africa [3]	Liberia	South America	Mexico (Guayule)	Grand Total
1940	540,417	536,740	88,894	23,317	17,623	35,166	43,940	64,437	2,267	10,103	7,223	17,601	4,106	1,391,834
1940:														
Aug.	45,872	45,078	8,139	1,332	1,593	2,640	4,545	7,337	285	800	308	1,233	327	120,729
Sept.	58,892	44,009	9,985	1,319	1,743	2,404	3,247	9,303	100	800	323	1,295	200	133,715
Oct.	52,767	50,139	8,127	1,841	1,693	2,564	3,355	2,082	200	800	600	1,860	200	126,228
Nov.	36,045	37,387	5,623	2,626	1,130	3,360	3,463	6,715	200	800	600	1,500	200	99,649
Dec.	56,263	35,325	10,700	3,405	1,028	3,520	5,343	9,000	200	600	813	1,427	392	128,216
1941:														
Jan.	37,804	58,[illegible]	7,[illegible]	1,486	2,085	2,445	2,137	9,058	333	667	[illegible]	2,103	288	125,608
Feb.	27,115	42,[illegible]	4,	1,421	1,686	2,922	4,137	1,995	96	854	[illegible]	1,814	414	89,705
Mar.	56,651	53,[illegible]	6,	1,770	1,154	3,726	5,712	6,286	117	636	[illegible]	2,835	355	130,506
Apr.	40,500	48,[illegible]	6,[illegible]	1,661	2,175	3,118	4,271	....	263	864	[illegible]	2,009	423	112,024
May	53,062	48,[illegible]	7,	1,831	1,237	3,849	1,841	6,225	156	800	[illegible]	1,080	334	126,332
June	51,247	48,[illegible]	8,	1,056	986	3,195	2,831	7,318	200	800	[illegible]	1,510	250	127,733
July	53,373	53,[illegible]	7,	939	1,803	3,799	3,614	3,445	200	800	[illegible]	1,253	250	131,042
Aug.	46,404	51,[illegible]	9,	725	1,812	3,086	4,852	6,496	200	800	[illegible]	1,288	250	127,634
Sept.	70,598	65,496	6,706	145	1,371	2,495	6,524	8,000	200	800	[illegible]	1,421	250	164,756

[1] Including Brunei and Labuan; figures shown represent rubber which has actually been shipped and include rubber from the free stocks in Singapore and Penang. [2] Exports of domestic produce. [3] Exclusive of Liberia. Notes: Figures shown prior to 1940 were furnished by the United States Department of Commerce. Figures since 1940 were furnished by the International Rubber Regulation Committee, which accounts for the difference in the principal producing countries shown. Many figures for current months are provisional only and are later revised when more definite statistics are available. Therefore, it is suggested that figures from the most recent issue should be taken as more reliable.

anomaly. Hitherto it has been the custom to refer to a material being in short supply when the price of that material was high. Now, however, there is a situation of absolute shortage, in which price is of little consequence. In such circumstances synthetic rubber is on an equal footing with the natural material. For it is an elementary fact that no matter what rubber costs, large tyre manufacturers must have a steady flow of rubber into their factories.

We are in an interim period during which consumers of natural rubber can continue only by effecting economies in its use, and by eking out their stocks. By the time these stocks have run low, synthetic rubber will be coming forward in ever-growing volume with the definite object of replacing natural rubber. Already the names of various forms of synthetic rubber, such as neoprene, Thiokol, and Buna are almost household terms.

The Future of Rubber. There are considerable grounds for doubt as to the future of natural rubber. Will the future position resemble that of cotton, in relation to rayon, where in spite of enormous production of rayon the consumption of cotton continues to expand ? Or will the situation tend to resemble that of natural indigo which has been virtually eliminated by synthetic indigo ? In this case, however, it should be clearly realized that the synthetic material is identical with the natural material ; this is a somewhat unusual occurrence, and certainly does not apply to synthetic rubber. Or will the position resemble that of shellac and natural gums and resins which are tending to be replaced by synthetic resins ?

It must be made quite clear, however, that rubber does a magnificent job in the form of tyres, which account for about 75 per cent. of requirements. So that when more normal conditions prevail, the perspective will again alter, and the questions of price and performance will become once again as important as availability.

What will the future position be regarding the availability of natural rubber ? At the present time the Japanese control the entire rubber-growing area. In order to derive any benefit from this, they must sell the produce. The United States is the biggest market, and always will be, followed by Europe as a unit.

The Japanese have only sufficient industrial capacity to handle 60,000 tons a year. This quantity is amply covered by the output of Indo-China and Thailand. What are they to do with the remainder ? It cannot be stored for any length of time under tropical conditions. Even in the United States it has been recognized that " a stock pile could not be accumulated without rotating the rubber at regular intervals to prevent deterioration ". [19]

Every effort will be made to prevent them from establishing contact with Europe. Consequently there is no great inducement for them to continue to take any strong interest in rubber plantations, but rather to concentrate on other activities.

Rubber is grown on large plantations and on numerous native small-holdings. The former produce high grade rubber; with the latter quality is not so important. However in recent years native growers have produced nearly half the entire output.

It is quite certain that a great deal of damage has been done to many plantations during the recent fighting. The chief form this damage would take would be the destruction of the factories attached to each plantation and their equipment. Where these have been damaged, the plantations attached to them must surely be written off, for with their other war commitments the Japanese can have no industrial capacity available at present to replace damaged equipment. It seems almost certain, therefore, that a very considerable proportion of the plantations will be completely neglected, and will become wild jungle. It is possible that the remaining portion may be maintained and looked after by the Japanese, assisted by French rubber experts. It would be foolish, however, to be unduly optimistic regarding future output from these plantations when the Japanese have once again been ousted. It seems utterly illogical to assume that when fighting once again develops in these areas, not only will the plantations remain undamaged, but that the Japanese will refrain from destroying these, and will timidly allow them to be taken over as going concerns once again. This incredible line of reasoning does, however, appear to have a fairly wide appeal.

It is evident from any examination of the facts of the situation that raw rubber will in the most favourable circumstances be in extremely short supply for the next ten years. The significance of this to synthetic rubber production is the fact that during the next ten years it is certain that there will be an absolutely clear field for these new products. The position is no longer one where synthetic rubber is a competitor for natural rubber. It is one where there is just insufficient material to go round, and anything that is produced must be used no matter what the cost.

No material could possibly have a better set of circumstances for really large-scale development. The large-scale production which is already in hand will inevitably bring with it considerable reduction in prices. So that even when rubber once again may become available it is by no means certain that it will have a price advantage over the synthetic material, by that time in large-scale fully established production.

The Economic Background of Rubber and Synthetic Rubber. The search for synthetic rubber is almost as old as the rubber industry. The intensity with which it has been carried on has varied with the price of natural rubber, slackening when the price was low, and becoming intensified when the price was high. It is only since 1925 that work on synthetic rubber has become virtually independent of the rubber market. There are many economic factors which have contributed considerable pressure towards the development of synthetic rubbers. They are all well worth close consideration.

Widely Fluctuating Price of Rubber. The fluctuating price of rubber has had a profound effect on the search for synthetic substitutes. The creation of intolerable commercial conditions supplied a great urgency. For large manufacturers, notably the American companies, there has never been any sense of security. It was equally unsatisfactory to them to have rubber at about 6*s.* per lb., as in 1925, as to have it as low as 1½*d.* per lb., as in 1932. They desired a stabilized price for the commodity. Appreciable rises and falls in the price were equally disastrous, since changes in the prices of their tyres and stocks could not follow with equal rapidity, and large sums had to be written off.

TABLE 6.—AVERAGE MONTHLY PRICE PER POUND OF STANDARD SMOKED RUBBER SHEET PRIOR TO THE INTERNATIONAL RUBBER REGULATING COMMITTEE [4]

	s.	*d.*
1919	2	0 25/32
1920	1	10 7/16
1921		9 9/16
1922		9 9/32
1923	1	3 5/16
1924	1	1 7/32
1925	2	11 1/16
1926	1	11 3/4
1927	1	6 7/16
1928		10 29/32
1929		10 1/4
1930		5 9/32
1931		3 1/8
1932		2 11/32
1933		3 1/4
1934		6 7/16

This represents only one of many grades of rubber, and the Table does not show highest and lowest prices reached.

When from a top price of about 6*s.* per lb., in 1925, rubber fell to 1½*d.* per lb. in 1932, the big American rubber companies in particular were very hard hit. In order to safeguard themselves they had to buy

rubber all the way down. For example, it has been stated that the General Rubber Company [11] had by 1934 written off 50 million dollars. It was these constantly recurring difficult economic situations which have been a major factor in the search for synthetic rubber. During the last fifteen years every large United States rubber firm has had a long-term programme in operation with this object in view.

One angle on the synthetic rubber position has been that no matter how dear it was, it established a definite ceiling for the price of rubber, which previously did not exist.

The Influence of Restriction upon Synthetic Rubber Development. The Stevenson Restriction Scheme started in 1922. Britain then controlled two-thirds of the world's output of natural rubber. Production was cut very drastically in order to bring the price up from 7½*d.* per lb. The process went on, until in 1925 rubber reached 6*s.* per lb. Then there was a fearful drop, due to the fact that the Dutch growers, outside the scheme, began to flood the market with rubber from Sumatra. The Stevenson scheme died in 1928, discredited. But one of its unexpected effects was the re-birth of synthetic rubber activity.

The folly of extorting an absurdly high price for rubber as a stimulant to the production of synthetic rubber is fully demonstrated by the experience of the German I.G. Farbenindustrie. From the end of the last war until 1925 they took no further interest in the synthetic rubber field, an activity in which one of the subsidiary companies, the Bayer concern, had always taken a leading part. But at the peak of the Stevenson Restriction Scheme, commercial prospects became very bright for synthetic materials, and consequently they re-entered the field. The same considerations prompted chemical concerns such as Du Pont de Nemours to examine the possibilities of materials which possessed rubbery properties. The financial prospects justified the expense of large-scale long-term research work.

In recent years there has been a more successful method of restriction. The International Rubber Regulating Committee included Dutch and French representatives as well as British, and began to function in 1934. It has put up a very creditable performance, keeping rubber at a reasonable level by maintaining rubber production in line with rubber consumption. The great drawback was the fact that the greatest rubber consumer in the world—the United States—had no official say in the deliberations, although its advice was sought and acted upon. Nor were other large consuming countries, such as Germany and Russia, represented. It is to be noted that these countries form the vanguard of synthetic rubber producers.

Centralized Production. Although the centralized location of the rubber plantations has been conducive to economic production, it has had grave disadvantages which are now all too apparent. Practically the whole of the industry (some 90 per cent.) was located in and around Malaya and the Dutch East Indies. In this area there were some 8,942,000 acres planted with rubber trees, of which 8,000,000 acres were bearing.

The average daily yield of a *Hevea* tree has been calculated at 1½ ounces, according to Crane,[8] giving an annual yield of 5 lbs. per tree for a tapping season of 140 days.

This meant that the United States, consuming more than half of all rubber produced, had to have rubber transported 12,000 miles, taking two months to arrive. This was a most unsatisfactory position in ordinary times; it became precarious when Britain and Holland became involved in war, and utterly disastrous when Japan took a hand. Considering one minor aspect of rubber activity, the transportation of large amounts of water (in the form of latex) across such vast distances was also manifestly absurd.

Other Sources of Rubber. Rubber growers occupied a position of almost complete monopoly. British and Dutch growers could dictate their own policy, a state of affairs which had serious repercussions on American industry, since the entire American economy was based upon the motor-car, in turn dependent on the tyre. This monopoly extended so far that even when United States firms were able to purchase plantations, e.g. in Sumatra, they had to conform to the regulations which generally applied, and could only produce up to their quotas. Among other areas the United States Rubber Co. had 135,000 acres in Sumatra, while Goodyear Rubber Corporation owned 550,000, plus experimental areas in Panama, Costa Rica, and Phillipines. Firestone Tyre Co. have 110,000 acres in Liberia. The B.F. Goodrich Co. have never gone in for rubber growing, having for many years believed in the inevitability of synthetic rubber. Consequently they have utilized resources, that others have sunk into plantations, for the development of synthetic rubber, with considerable success, e.g. with Koroseal and Ameripol.

Attempts to develop other sources of supply have not been very successful. Brazil is the obvious example which springs to mind. It is the home of rubber, moreover it supplies the best quality rubber in the world. But this rubber is all wild. There are 2½ million square miles of rubber-growing area in the Amazon basin, mainly inaccessible. Attempts to develop plantations in Brazil have not been successful. The Ford Company has worked a concession on more than a million

acres, but in spite of systematic efforts, including the provision of every conceivable amenity, has not been able to achieve any notable success. It is difficult to foresee any considerable expansion in the output from Brazil. During the last few years there has been considerable economic encouragement for such expansion, but no comparable results have been forthcoming.

African sources of supply produce only limited amounts of satisfactory material; but the quantities of all these secondary producers is ludicrously small in relation to the demands. Firestone have developed successful plantations in Liberia. There are a number of plantations under British control in Nigeria; otherwise African sources of supply are wild.

The Americans have always felt unhappy about a position which has offered them no sense of security. From a political point of view it has always been essential for their welfare that the Far Eastern plantations should be in the hands of friendly nations. With this position in jeopardy during the last few years, it is not surprising that the realistic appreciation of these disadvantages has stimulated their interest in synthetic rubber.

Cultivation of Other Rubbers. Actually about 500 plants are known which give rubber latex. These rang from milk weed with 1 per cent. to tropical *Hevea* containing about 35 per cent. There have been efforts to develop the production of the less satisfactory types of rubber in areas contiguous to the United States. For example, guayule is being extensively cultivated in Mexico, but the quantities which are likely to be available in the near future are not very considerable, while the quality of the rubber is far inferior to ordinary commercial rubber.

According to McCullum,[11] guayule is a native of North Mexico, and is a heavy woody shrub, which has supplied about 5,000 tons of dry rubber per year for many years. The rubber is not obtained in the form of latex by tapping as in the case of *hevea* rubber, but is found in the living cells, other than the leaves. The best varieties have 22 per cent. of the weight of the plant as rubber. In the past the greatest Mexican output was 10,000 tons in 1912.

There is a scheme in the United States for growing guayule in the southern part of the country. Plants five or six years old weigh about 1 lb. and contain about 16 per cent. of rubber. The crop has to be harvested and the material deresinated. Immediate planting of 45,000 acres in 1942 would yield 1,500 tons in 1943, 5,400 tons in 1944, and 21,300 tons in 1946.

The U.S.S.R. are cultivating a type of dandelion known as *tau-sagyz* on large tracts of land in Turkestan. These give a rubber which is

adequate for many purposes. The yield is said to be between 30 to 150 lbs. per acre.[15]

Another type known as *kok-sagyz* is grown on the largest possible scale. In 1942 there were 625,000 acres under cultivation. Precessing developments had further increased yields. Thus whereas previously the entire plant was crushed to recover the rubber, latterly the yield has been doubled by cutting the tap root from time to time, allowing latex to flow and collecting it.[18]

Variation of Natural Rubber. One of the great difficulties rubber manufacturers have had to contend against has been the variation in the quality of rubber. For one thing, in common with all natural products rubber is never obtained pure. There are always impurities present which vary in amount according to the source of the rubber. This variation is encountered in rubber obtained from one plantation to another. It has caused a great deal of difficulty to the manufacturer and the consumer. It is extremely difficult to achieve uniformity in the case of a product such as rubber where marked differences arise according to the age and condition of trees, agricultural variations, climatic variations, etc.

In spite of the enormous amount of money at the disposal of rubber growers, until recently no really adequately financed scheme for fundamental research on rubber has ever been organized. As against this according to Wilson,[29] the British Rubber Producers Research Association now spends about £40,000 a year on fundamental research. Without this fundamental research a thorough knowledge of their own material was thus denied them. It is a fact that nearly all the great technical developments associated with rubber has emerged from the consumers and not from the growers. Rubber owes its eminence and importance almost entirely to the efforts of the tyre manufacturers (notable in the U.S.A.) whose technical developments have been amazing.

Little is known fundamentally about rubber, and in this respect natural rubber interests are no better off than those concerned with synthetic rubber. In fact, the latter are perhaps more favourably placed since, working from pure materials, they can produce a material of definite properties and characteristics. Synthetic rubbers can virtually be made to specification.

These fundamental rubber problems are extremely difficult, but there has never been any attempt to tackle them on a proper scale. For example, the author contends that the oil resistance of rubber could be made satisfactory, provided that really large-scale fundamental research were attempted. If this had been attempted and achieved, it would have removed the chief *raison d'être* of synthetic rubber. Such a scheme

necessitated employing the best technicians in the world, involving the expenditure of considerable sums. Instead of this, the same technicians have been allowed to concentrate their efforts on the development of synthetic rubber. Geer [10] posed the problem some years ago: "The rubber industry is at the cross roads with two courses before it, either to keep on along the present lines or to branch out upon a broad intensive programme of fundamental research. This idea is really but a change from the practical to the fundamental." Rubber producers took the practical path as being the route more likely to give rapid returns. It has never been properly appreciated that it is not rubber that is wanted but the properties of rubber.

Economic Nationalism. The causes already mentioned have contributed in part to the growth of the production of synthetic rubber. Of course, the greatest stimulus, the chief accelerating influence, has been a purely artificial one, namely the growth of economic nationalism. The grim determination of some nations to make themselves completely independent of outside sources of supply has been the powerful driving force in its production. In this respect the lead has come from Germany and Russia. The Germans well remember their experiences in the last war when lack of rubber imposed an almost unbearable strain on their war machine.

The monopolistic position with regard to supplies of raw rubber naturally encouraged such action on the part of fiercely national countries experiencing commercial difficulties. They have considered a high price within the country to be of little importance by comparison with expenditure of foreign currency for natural rubber. The development of large-scale synthetic rubber industries in these countries has been extremely costly, but they have had their compensations. For example, although the cost of the plants has been extremely high, as also was the cost of production, yet the labour concerned in such production has been productive, and has not been allowed to stand idle. Apart from this, over a period of years large-scale production inevitably results in a lowering of costs. There is also the unpredictable influence of unexpected discoveries and new developments, tending always to bring the cost down. During critical periods such as the present, those opportunities arise which enable the millstone of the early heavy capital cost to be wiped off very cheaply.

Before the war the trend had reached Poland, Czechoslovakia, Italy and even Japan. All were interested in the possibility of producing synthetic rubber. In Japan, for example, the output in 1938 was 100 tons, and a scheme was being considered to start production of Buna in Manchuria.[5] According to one source [16] the Pirelli concern

carrying out trials at Milan was using a modified German process from acetylene. The price was said to be twice that of natural rubber. They also made a product derived from alcohol. Poland was making synthetic rubber based on alcohol obtained from agricultural products.

It has been stated that in Switzerland [24] a satisfactory synthetic rubber has recently been produced based on charcoal as raw material.

So far as the countries with large synthetic industries were concerned, the pressure of war finally supplied the emphatic necessity of getting these into as large-scale production as possible.

Russia has led the way in large-scale synthetic rubber production, having been the only country which has maintained continuous research work on the subject, even from before the last war. The same Prof. Lebedev who first polymerized butadiene in 1910 was still leading technical development and organization until quite recently. In fact the U.S.S.R. is still the only country which publishes a technical journal dealing exclusively with synthetic rubber. The Russians have also been conducting large-scale long-term experiments in the growth of rubber-bearing plants, such as *tau-sagyz*, notably in Turkestan.

While comparatively little is known in detail about the scale of production yet it is considerable. Nor is there much information about the location of their plants.

The first announcements of large-scale production in 1933 were met with derision. Yet in 1939, the U.S. Bureau of Commerce [2] stated that U.S.S.R. production was 50,000 tons, German production was 20,000, while United States production was 3,000 tons. No further official information has since become available. The Russians make many types of synthetic rubber. One large establishment is known to be at Yaroslav. Sovprene is made at Erevan in Trans-Caucasia. The following table shows the production of synthetic rubber in relation to their imports of raw rubber. In view of the indisputable evidence of enormous industrial projects adequate to support a vast military machine, it is clear that synthetic rubber production must be on a great scale.

TABLE 7. U.S.S.R. FIGURES [28]

Year	Crude	Synthetic Rubber
1933	30,000	2,204
1934	47,000	11,139
1935	37,600	25,581
1936	31,000	44,200
1937	30,400	25,000
1938	26,219	53,000

German Progress. The following account explains the development of the German synthetic rubber industry.[12] Serious research was resumed in 1925 by the I.G. Farbenindustrie ; it was greatly intensified in 1933. As the result of this work in the following year the production of Buna was announced for the first time. By the latter part of 1936 the Bayer pilot plant of the I.G. at Leverkusen was producing 80 tons per month. In line with this activity the Continental Gummifabrike at Hanover was manufacturing 200 tyres per day and 25 per cent. of their mechanical goods from synthetic rubber. Also in 1937 it was announced that large-scale production of Thiokol had commenced at Saaru. In 1937 the plans were announced for the first really large-scale production unit at Schkopau, which was to produce 25,000 tons per year. The finance was secured by imposing a heavy import duty on raw rubber, calculated to bring in 25 million pounds, adequate to finance any synthetic rubber schemes.

In May, 1939, the Schkopau plant began production, to be followed a year later by a second similar plant at Hüls in Westphalia.

The ultimate objective was said to be 6,000 tons per month, which would make Germany independent of external sources of rubber. It was estimated that production in 1934 was 10 tons, in 1935 less than 100 tons, in 1936 1,500 tons, in 1937 4,000 tons, in 1938 10,000 tons, 1939 25,000 tons, and by late 1940 about 60,000 tons.

It is of great interest to consider some of the important factors considered by the Germans. Here is an extract from a description of the Schkopau works by Ambros.[1]

The Schkopau Buna Works is one of the most characteristic products of the four-year plan, not only because when it was begun there was no plan or model for the large-scale production, and a completely new technique had to be developed, but also when the beginning of the building programme began in 1936, it was essential that definite production should be rapidly achieved.

A great help in the development of the new works came from the fact that a pilot plant making 200 tons a month was already finished only ten months after laying the first stone, that is to say at the beginning of 1937. This small works was able to carry out valuable experiments, but it also served as a school for the training of key personnel. This is a point of extraordinary importance. In view of the complicated chemical technique it is essential to have absolutely fully trained skilled men who must be well acquainted with the technical processes, to ensure the proper handling of the apparatus and processes. The acquisition of such personnel was made possible only in this manner whereby the old I.G. Works supplied valuable personnel from their establishment near Schkopau. These key men acted as teachers in the expansion. Even so, this particular problem is not yet completely solved. The training of capable works' personnel is one of the most important features in the further expansion of the establishment.

According to Kluckow [13] the Germans are using besides vulcanizable synthetic rubbers like Buna-S, Perbunan, neoprene, Perduren and Thiokol, a number of non-vulcanizable thermoplastic products such as the polyisobutylenes, polyvinyl chlorides and methacrylic acid polymers.

It has also been suggested that they may be making and using butyl rubber since they have had all the technical information available on that subject.

United States Production. Until the virtual disappearance of sources of natural rubber United States production had been on a small scale, merely keeping in step with commercial demands. It has latterly become evident that advances were considerably retarded by patent complications. Nevertheless large-scale pilot plants have been functioning successfully for several years on many types of material.

TABLE 8. AMERICAN PRODUCTION OF SYNTHETIC RUBBER IN RECENT YEARS (in long tons) [3]

	Neoprene types	Butadiene types	Thioplasts
1939 . . .	1750	None	500
1940 . . .	2500	60	700
1941 (estd.) . .	6300	4000	1400

The latest American scheme [27] for the production of synthetic rubber deals with a prospective output of 1,100,000 tons per annum, the capital expenditure involved is estimated to be over 200 million pounds. Of this production about 70 per cent. is likely to be of the Buna types based on butadiene. It has been stated that Buna-S is to be adopted as the standard type. It is thought likely that the butadiene necessary for this scheme can be produced as a by-product in the 100-octane petrol plants under construction at the present time.

Materials produced to Government Specifications are to be known as :

GR–S which is Buna-S
GR–P which is Thiokol
GR–N which is Neoprene
GR–I which is Butyl rubber

The first of these is already widely used.

It is interesting to consider synthetic rubber activities in the United States in rather closer detail.

At the time of the débacle in the Far East Du Pont de Nemours were producing large quantities of neoprene from acetylene.

Buna rubbers were being produced by the Standard Oil Develop-

ment Company of New Jersey, by the Firestone Rubber Company, by the Hydrocarbon Chemical Corporation, and by the Goodyear Rubber Company. Thiokol was being produced by the Dow Chemical Company.

In the original programme for 1942 it was expected that 19,200 tons of neoprene and 18,000 tons of polyvinyl chloride would be made. In addition the U.S. government had authorized four plants to be run by Hydrocarbon Chemicals, Goodyear, United States Rubber Co., and Firestone from which 60,000 tons were expected. Hydro-carbon Chemicals had a private plant with 7,000 tons capacity, while Standard Oil of New Jersey were to make 10,000 tons Buna rubber and 5,000 tons butyl rubber.

In 1939 the only producer of butadiene was the Dow Company. In 1940 plants had been erected by the Shell Corporation, by Phillips Oil Company, by the Standard Oil Company, and by Carbide and Carbon Corporation. In 1941 Carbide and Carbon had built another plant, as had the Standard Oil Company of Louisiana, and the Shell Oil Company. The Monsanto Chemical Corporation had established equipment to produce auxiliary rubber chemicals, as had the United States Rubber Company, and the American Cyanamide Company.

The various rubber-like plastics were being produced by Du Pont Monsanto, Dow, Carbide and Carbon, Goodrich, Tennessee-Eastman, etc.

As a matter of fact it is interesting to note that until recently there has been considerable rivalry between petroleum interests, chemical interests, and rubber manufacturers, for leadership in these activities. This has been made quite clear in the reports of the Truman Committee. As has been pointed out, the interest of American rubber manufacturers has been one of sheer self-preservation. The extremely progressive chemical concerns, with their growing interest in synthetic resin production, could not help a lively interest in the development of the closely related synthetic rubbers. The gigantic oil concerns realized the possibilities of utilizing enormous quantities of materials which for years had been thrown away, and have taken a leading part in promoting production.

A trend has set in for co-ordination of effort and rationalization. This was essential in order to achieve the greatly expanded production programme. One excellent early example was the co-operation between Goodrich Rubber and the Phillips Oil Company, who jointly own the Hydrocarbon Chemical Corporation which produces Hycar.

It is very important to note the financial weight which these concerns can bear on the problem ; and it is a matter of considerable interest to

study the enormous sums which have been expended on research and development work towards producing synthetic rubbers.

However by the middle of 1942 the position was chaotic with many diverse interests pulling in different directions. Drastic measures were taken. President Roosevelt appointed the Baruch Committee to lay down a definite fixed programme.

The position at the present time has been defined in the report of the Baruch Committee. This report estimated that the supply of rubber available to the United States in 1944 will be:

TABLE 9. PROGRAMME OF THE BARUCH COMMITTEE

	Tons
Natural rubber	68,000
Buna-S	705,000
Neoprene	59,000
Butyl	132,000
Thiokol	60,000

with a recommendation for a further 140,000 tons of Buna-S.

No less than 400,000 tons of Buna-S is designed to come from grain.

Now of course the entire scheme is under direct Government control, and the financial aspect is likewise influenced by this factor. As a sidelight on this it is interesting to note the comment of the Baruch Committee

> Lest the influence of governmental policy serve to discourage the beneficial rivalries of the best brains of industry, we believe, that on the one hand there should be complete interchange of information, and on the other, as much competition in research, development and operation as possible.

Even Canada is to produce 25,000 tons per annum using petroleum products supplied from the United States by pipeline.[6]

It is a questionable point, when the Far Eastern position has been cleared up, whether it will be worth while investing the large sums that would be necessary to set up the plantation industry once again. Clearly the plantation industry could not be revived along the old anachronistic haphazard lines. It is quite certain that the enormous capital expenditure and effort involved in the American production of synthetic rubber will not be allowed to be wasted because natural rubber will once again become available. This is extremely unlikely. In fact, it seems much more probable that the synthetic rubber industry will be very much cherished and preserved owing to the insurance and freedom of action it confers upon the United States. Indeed this point has been reiterated time and time again *ad nauseum*.

TABLE 10. SET-UP OF THE UNITED STATES SYNTHETIC RUBBER PROGRAMME IN SEPTEMBER 1942 [26]

Name	Production capacity in short tons, per year	Scheduled Completion Date
Butadiene Plants—		
Shell Chemical	30,000	March 1943
So. Calif. Gas	25,000	Jan. 1943
Humble Oil	30,000	March 1943
Standard Oil (La.)	6,200	Sept. 1942
Standard Oil (La.)	15,000	March 1943
Carbide & Carbon	5,000	Sept. 1942
Carbide & Carbon	20,000	Jan. 1943
Carbide & Carbon	20,000	Feb. 1943
Carbide & Carbon	20,000	March 1943
Carbide & Carbon	20,000	April 1943
Carbide & Carbon	20,000	April 1943
Carbide & Carbon	20,000	May 1943
Carbide & Carbon	20,000	June 1943
Carbide & Carbon	20,000	May 1943
Carbide & Carbon	20,000	June 1943
Carbide & Carbon	20,000	July 1943
Atlas Oil & Ref.	12,000	Nov. 1942
Neches Butane	50,000	April 1943
Neches Butane	50,000	June 1943
Rubber synthetics	50,000	June 1943
Rubber synthetics	50,000	Aug. 1943
Koppers United	20,000	Aug. 1943
Sinclair Rubber	50,000	Oct. 1943
Cities Service	55,000	Aug. 1943
Total	648,200	
Styrene Plants—		
Dow Chemical	25,000	March 1943
Monsanto	10,000	Oct. 1942
Monsanto	10,000	Jan. 1943
Monsanto	10,000	Feb. 1943
Monsanto	5,000	March 1943
Carbide & Carbon	12,500	Jan. 1943
Carbide & Carbon	12,500	April 1943
Dow Chemical	4,200	Jan. 1943
Dow Chemical	25,000	April 1943
Dow Chemical	25,000	June 1943
Dow Chemical	25,000	June 1943
Dow Chemical	12,500	Aug. 1943
Koppers United	35,000	Aug. 1943
Total	211,700	
Copolymer Plants—		
Firestone	30,000	Feb. 1943
Firestone	15,000	June 1942
Firestone	15,000	Sept. 1943
Firestone	15,000	June 1942

TABLE 10—*continued*

Name	Production capacity in short tons, per year	Scheduled Completion Date
Copolymer Plants—continued		
Firestone	15,000	July 1943
Firestone	15,000	Aug. 1943
Firestone	60,000	Aug. 1943
Goodyear	15,000	May 1942
Goodyear	15,000	Aug. 1942
Goodyear	30,000	June 1943
Goodyear	30,000	April 1943
Goodyear	15,000	May 1943
Goodyear	20,000	June 1943
Goodyear	55,000	Oct. 1943
Goodrich	30,000	Nov. 1942
Goodrich	30,000	Jan. 1943
Goodrich	30,000	April 1943
Goodrich	15,000	May 1943
Goodrich	10,000	June 1943
U.S. Rubber	30,000	Jan. 1943
U.S. Rubber	30,000	March 1943
U.S. Rubber	30,000	May 1943
U.S. Rubber	15 000	Aug. 1942
U.S. Rubber	15 000	Nov. 1942
U.S. Rubber	15,000	June 1943
U.S. Rubber	15,000	July 1943
U.S. Rubber	15,000	Aug. 1943
Open	30,000	June 1943
Open	30,000	June 1943
Open	25,000	Aug. 1943
Total	700,000	
Butyl Plants—		
Standard Oil (La.)	7,000	Nov. 1942
Standard Oil (La.)	33,000	July 1943
Humble Oil	20,000	July 1943
Total	60,000 [a]	
Neoprene Plants—		
du Pont	10,000	Oct. 1942
du Pont	10,000	April 1943
du Pont	20,000	Oct. 1943
Total	40,000	

[a] Recently boosted to 132,000 tons by expanding existing plants.

Price of Synthetic Rubber. The question of cost is obviously an important one, and is worth some consideration. Neoprene, for example, started off in 1931 with an initial production of 250 lbs. per month, selling at $1 per lb. As the consumption and output has increased, so the price has dropped. Prices of synthetic rubbers in the United States in August 1941 were as follows:

TABLE 11. PRICES OF SYNTHETIC RUBBERS IN 1941 [7]

	Cents per lb.
Rubber	23
Neoprene GN	65
Buna S	60
Perbunan	70
Thiokol F.	45
Vistanex.	45
Hycar OR	70
Koroseal.	60

At this time all were at comparatively low rates of production hardly greater than pilot plant quantities. It is anticipated that when full-scale production has been achieved, particularly with the butadiene type of synthetic rubber, then the price per lb. will eventually come down to the order of 20 cents per lb.

Cramer [7] has given an interesting study of the prices to which the various materials must drop in order to be competitive with natural rubber.

TABLE 12. COMPARATIVE ECONOMIC PRICES

Product	Aug. 1941 Price	Density	Equivalent Price
Natural rubber	$0.23	0.92	0.23
Neoprene GN	0.65	1.24	0.17
Buna S	0.60	0.96	0.22
Perbunan	0.70	0.96	0.22
Thiokol F	0.45	1.38	0.15
Vistanex.	0.45	0.90	0.24
Koroseal (30 per cent. plasticizer)	0.60 (est.)	1.33	0.16
Hycar OR	0.70	1.00	0.23

At the time of writing the price of vinylidene chloride is 58 cents per lb. Polyvinyl chloride is at 40 cents, while ethyl cellulose is at 50 cents; in Britain these are 2*s.* 5*d.* and 3*s.* 9*d.* per lb. respectively.

Butadiene although only produced on a relatively small scale was being sold at about 10*d.* per lb., while styrene and acrylic nitrile also in small-scale production, were at 1*s.* 3*d.* and 1*s.* 6*d.* per lb., respectively. It is considered likely that when large-scale production is in progress butadiene will cost 5*d.* per lb., while finished polymer will be of the order of 10*d.* per lb.

There is little consolation to rubber growers in the fact that this price, which has not yet been attained, is likely to be considerably higher than the basic cost of natural rubber as it was, that is to say of the order of 4*d.* per lb. For according to the President of the Standard Oil Corporation,[20]

The basic raw materials for Buna rubbers are petroleum and natural gas which are worth less than 1 cent a pound in crude form. As a far-distant

goal we might look forward to finished synthetic rubber at a price under 10 cents a pound. This prospect is improved by experiments with butyl rubber in which the primary raw materials are easier to derive from petroleum than butadiene.

This means that the price of butyl rubber is likely to be round about 6*d*.

Farish [9] has stated :

Buna rubber at first will cost 30 c. a pound when made from butadiene derived from petroleum. When plants are running at maximum efficiency the cost will be reduced to 20 c. a pound or less. The first Butyl rubber will cost about 20 c. a pound but the price may eventually be reduced to between 10 c. and 15 c. a pound. Buna rubber plants at first originally estimated to cost $1000 a ton of annual capacity, are now figured to cost about $600. Butyl plants, first estimated to cost as high as $750 a ton are now expected to cost about $350 a ton of annual capacity.

The price of Government Buna-S rubber had been set at 50 c. per lb. At the time of writing the price has been cut sharply to 36 cents per lb. In England the price of GR-S (Buna S) at 1*s*. 4½*d*. per lb. is already lower than the price of natural rubber which is pegged at 1*s*. 6*d*.

Houdry recently quoted 6·421 cents per lb. as the cost of butadiene, while Dow Chemical Company are already selling polystyrene at 30 cents per lb.

In 1939 the Standard Oil Development Company [21] investigated the possibilities of butyl rubber in relation to crude rubber. They analysed the possible applications of butyl rubber (*a*) in fields where they believed butyl rubber to have a definite advantage, and (*b*) where they expected or hoped that it would have an advantage. At this time they estimated in each instance that butyl rubber would be available at between 30 to 40 cents per lb. as compared with natural rubber at 15 to 20 cents per lb. The following table gives the result of their investigation.

TABLE 13. POSSIBLE OUTLETS FOR BUTYL (AS AT OCTOBER 1939)

Uses (based on 1937–38 figures)	(*a*) lbs. per year	(*b*) lbs. per year
Cable insulation	13,000,000	—
Miscellaneous tubing	10,000,000	13,000,000
Tank car lining	(no data)	—
Packing, washers, gaskets	5,000,000	5,000,000
Inner tubes	—	100,000,000
Tyre curing bags	8,000,000	—
Coated fabric	5,000,000	5,000,000
Mechanical goods	50,000,000	50,000,000
Flooring	1,000,000	1,000,000
Sponge	—	10,000,000
Druggists' sundries	5,000,000	5,000,000
Total	97,000,000	189,000,000

At that time they were not sufficiently optimistic as to be certain that inner tubes would fall in the (*a*) group. As they pointed out even 10 per cent. of the inner tube business would amount to 10 million pounds per year.

It is clear that they were very conservative, since the most recent estimate, on the large scale costs butyl rubber at 6·6 cents per lb. while rubber stands at 22½ cents. Even a year later than when the above estimate was made, the possible field for butyl rubber, apart from tyres, was estimated at 250,000 tons per annum.

American Interest in Growing Rubber. The Standard Oil Development Company has studied every aspect of the synthetic rubber production and usage. These included comprehensive market surveys. In one such survey in 1940 [22] they considered the leading producers of tyres in the United States which consume a very large proportion of the total world production of rubber. The main objective was to show the salient facts of the tyre industry, those facts that would be of importance in [illegible] the rôle a competitive synthetic rubber might play.

One interesting angle was the financial interest of the large American Rubber Companies in growing their own rubber. They showed that Goodyear, United States Rubber, and Firestone, owned rubber plantations large enough to yield 20–25 per cent of their needs, as shown in the accompanying table. The Goodrich Company has never gone in for rubber growing.

TABLE 14. PRESENT VALUE OF RUBBER PLANTATIONS (ESTIMATED) [22]

	U.S. Rubber (dollars)	Goodyear (dollars)	Firestone (dollars)
A: Planted area	19,800,000	11,650,000	12,800,000
Unplanted	150,000	210,000	1,000,000
Book value	19,950,000	11,860,000	13,800,000
ACREAGE			
B: Acres owned	132,000	100,723	1,000,000
Acres planted	99,000	58,125	(1936) 64,000
Acres tapped	57,350	51,752	(1936) 16,000

To develop and use these plantations to their fullest extent, according to the survey, additional expenditures amounting to $200–$400 per acre, for a 5–7 year period when trees mature, would be necessary. At the lower cost the following expansion and additional expense would be involved:

TABLE 15. COST OF DEVELOPING PLANTATIONS

	Additional Rubber per year (lbs.)	Total production percentage of own demand	New investment (dollars)
U.S. Rubber	13,000,000	31	6,500,000
Goodyear	17,000,000	28	8,400,000
Firestone	21,000,000	30 [a]	13,000,000

[a] 30% production is taken for Firestone to be on a comparable basis with the other two.

Considering the out-of-pocket cost of growing rubber as 6 cents per lb., and adding other out-of-pocket charges, the following showed that these companies would be forced to stop growing rubber if the price in New York dropped permanently to about $8\frac{1}{2}$ cents per lb.

	cents per lb.
Cost of rubber at plantation (out-of-pocket)	6·0
Cost of container at 45 cents at 10 per ton (2,240 lbs.)	0·20
Ocean freight at $15.00–$18.00 per ton (2,240 lbs.)	0·67
All ocean risk at $22\frac{1}{2}$ cents per $100	0·04
Talc and labour for packing, Labour for handling, Exchange, export tax } Assumed	1·5
Out-of-pocket cost, New York	8·41

Cost at the point of consumption would be increased by freight and handling charges. Freight to Akron (the chief rubber manufacturing centre) is 0·43 cents per lb.

Financial statements of the U.S. Rubber plantations prior to absorption by the parent company in 1938 allowed the price picture to be developed from another angle:

TABLE 16. FINANCIAL STATEMENT OF UNITED STATES RUBBER COMPANY PLANTATIONS

Year	Produced pounds (millions)	Earnings		Rubber price New York (cents)	Total cost of Rubber (cents)
		Dollars (millions)	cents per lb.		
1934	50,986	1,735	3·4	12·9	9·5
1935	42,054	967	2·3	12·4	10·1
1936	42·185	1,913	4·6	16·4	11·8
1937	58,072	4,589	7·8	19·4	11·6
Average	48,324	2,301	4·7	15·4	10·7

The price of rubber at New York may be then broken down to:

	cents per lb.	%	%
Out-of-pocket cost	8·4	79	55
Other costs	2·3	21	15
Total cost, New York	10·7	100	
Earnings	4·7	—	30
Average price, New York	15·4	—	100

According to the Standard Oil Survey this earnings figure is probably somewhat higher than is actually the return to most growers, as brokerage and trading expenses must be deducted. Companies like U.S. Rubber, Goodyear, and Firestone should not be concerned with general trading expenses on their own production. The original investment on the U.S. Rubber Company's plantations was about $38,000,000, and the book value to-day is about half this sum. The productive life of the rubber tree is not known; some trees are still producing at seventy years. But taking forty years as the life and with a production of 50 million pounds per year, the investment amounts to 1·9 cents per lb. or 83 per cent. of the "Other costs" item (2·3 cents). On a basis of producing 50 million pounds per year the earning would be:

TABLE 17. PLANTATION EARNINGS

Rubber price, New York (cents)	Earnings per year (dollars)	Return on investment (%)	Book value (%)
12	650,000	1·7	3·4
15	2,150,000	5·6	11·2
20	4,650,000	12·2	24·4

which checks previous information that 12 cents was a living price for the plantations. This data actually shows 10·7 cents to be the breaking point for profits. Their main conclusion is of great interest. *Rubber permanently between 8 and 11 cents per lb., New York, should warrant shutting down the plantations if a satisfactory, abundant substitute were to become available.*

Cost of Equipping Plantations.—Trainer and Babcock of the Firestone Tyre & Rubber Co.[25], have given some interesting estimates of costs of natural rubber. In 1940 they estimated that rubber produced in a modern plantation could be delivered to New York at between 7 and 8 cents per lb. This figure would represent production costs and shipping costs. This was based on the assumption that the capital

investment of the plantation was being written off on a 20–25 year basis. They estimated that a plantation of 100,000 acres would cost about 40 million dollars completely equipped, and would produce about 25,000 long tons of natural rubber per year.

The Standard Oil Development Company, in considering the production of butyl rubber, examined these estimates. They concluded that the production of 100 tons of butyl rubber per day involved an investment of about 10 million dollars with production cost of 7·5 cents per lb. They estimated that the investment cost for the same quantity of rubber would be something over 50 million dollars, i.e. five times the investment required for an equal amount of butyl rubber. They deduced from this that if butyl rubber could be made as suitable as natural rubber for tyres, the manufacture of the material on a large scale would be economically sound. For the production of Buna-S on a corresponding scale they estimated a capital cost of something like 21 million dollars and a production cost of about 16 cents per lb.

It is as well to bear in mind that most rubber plantations will have to start from scratch once again. The above analysis gives an indication of the scale of finance likely to be involved.

There has been a great deal of scepticism in this country as to the likelihood of realizing the low costs of synthetic rubbers which have been suggested.

The pundits must remember their own oft-repeated predictions as to the impossibility of large-scale production. So far as price is concerned they have proved notoriously unreliable in forecasting the price of their own commodity. None forecast the possibility of rubber dropping from 6*s*. per lb. in 1925 to 1½*d*. per lb. in 1931 ; nor that during the depression the price of reclaimed rubber would be considerably higher than that of the raw material. It is therefore most unwise to be pontifical or dogmatic about the prospects of synthetic rubber. This is especially the case in view of the fact that American technicians have only just been permitted, or encouraged, to bring their full weight to bear on the problem, a state of affairs which is almost certain to produce astonishing results when it comes to fruition. As Stine, Vice-President of du Pont de Nemours said recently : " . . . under the pressure of a great war there may be compressed scientific, economic and social developments that might have taken many decades to achieve under less urgent conditions." [23]

To bring the matter into perspective it is just as well to point out that fifteen years ago there was no synthetic rubber on offer ; ten years ago synthetic rubber was at 5*s*. per lb., with a negligible production,

Five years ago production was of the order of 30,000 or 40,000 tons a year. To-day production is probably of the order of 400,000 tons per annum, and within a comparatively short space of time there is the promise of at least 1,100,000 tons of synthetic rubber to be made in the United States alone.

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PART II

CHEMICAL AND PHYSICAL BACKGROUND OF SYNTHETIC ELASTIC MATERIALS

CHAPTER 3

TERMINOLOGY

Synthetic Rubber Terminology. The number of materials having rubber-like properties increases at a steady rate. Many of these materials have no relation with one another, and certainly not with natural rubber; yet they are all referred to as "synthetic rubber", which has become something of an omnibus term.

For some time there has been growing confusion in rubber terminology. The arrival of numerous synthetic rubber-like materials has made matters considerably worse. It is very desirable to give close study to the definition of synthetic rubber.

The Approach of Rubber and Plastics.[1] It has been apparent for a long time that the gap between rubber and plastics has been filling in rapidly. The author has made a special point of stressing this during recent years.[2] Synthetic rubbers now fill the space. The result is that there is no very clear demarcation between rubber and synthetic rubbers on the one hand, nor between synthetic rubber and plastics on the other.[3] Thus Perbunan resembles rubber very closely in many respects, while no one has been bold enough to state categorically whether polyvinyl chloride is a synthetic rubber or a thermoplastic (although most opinion tends towards the latter). Yet again, what is polyisobutylene to be classified as? It is more rubbery than rubber yet is thermoplastic and cannot be vulcanized.

One important point is the matter of perspective. Since these new materials are no longer solely in the province of rubber technology, any system of nomenclature must be founded on lines which are much wider than apply for rubber alone. It is a grave error for rubber technologists to endeavour to impose their own extremely involved and unsatisfactory terminology on the new field. It is all very well to apply new expressions, for example, for the polyvinyl family of resins as if they were quite new, when all the time there exists a perfectly good and widely used name—"ethenoid" resins proposed by Redfarn.

The same reasoning applies to " thioplasts " which is a very satisfactory term for the polysulphide type of material.

For one thing all sorts of accessory materials are now employed which are novel in rubber technique, such as plasticizers, e.g. dibutyl phthalate, tricresyl phosphate, etc. They are, however, commonplace in the plastics industry, and in the lacquer industry.

The issue is not only a scientific one, but is complicated by commercial considerations which cannot be lightly set aside. At the present time anything having rubbery properties is immediately hailed as a synthetic rubber. It is impossible to take a completely detached view of the matter. It must be recognized that descriptions such as " synthetic rubber " always have strong public appeal. and it will require strong and persistent efforts to introduce any new terms.

Rubber is an Unsatisfactory Term. To start with, the very name " rubber " is a most unfortunate term. It is difficult to understand how the mere fact that it could erase marks from paper, could have developed into a generic term for the material. It should also be noted that rubber is not an international term, which is a grave disadvantage.

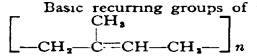
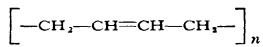
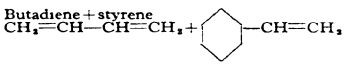
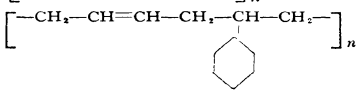
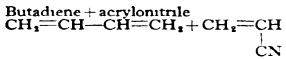
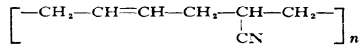
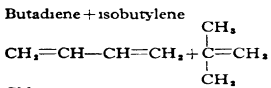
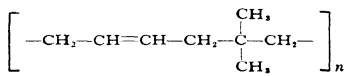
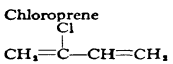
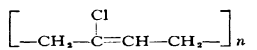
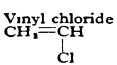
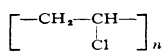
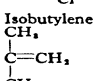
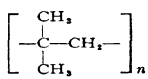
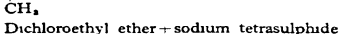
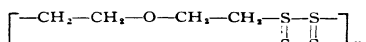
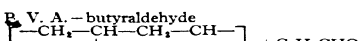
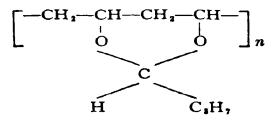
Rubber is the keyword of the industry, but as Dawson [7] has stated :

> It is commonly used without qualification to connote such diverse ideas as highly derived caoutchouc, raw or crude rubber of many botanical species, soft vulcanized rubbers in endless variety, hard rubbers, synthetic rubbers, and so-called synthetic rubbers. One has but to think of such common phrases as the empirical formula of rubber, sheet rubber, rubber-soled shoes, oil-resisting rubber, to appreciate how much is taken for granted every day.

In this connection the rubber industry cannot logically complain at the term " synthetic rubber ", for no efforts have been made to alter equally inaccurate designations such as " reclaimed " rubber.

Many of the troubles of rubber terminology arises from the fact that insufficient fundamental research has been carried out on rubber, and too little is known about it, and here it is perhaps appropriate to emphasize again that most work has been done not by scientists of countries interested in growing rubber, i.e. not by producers, but by consumers of rubber. Thus, while rubber is invariably a material having high molecular weight, which present methods are inadequate to define, there is as yet no real scientific basis for comparison between any two rubbers or between rubber and a synthetic material. The situation is further complicated by the fact that up to the present rubber has never been synthesized. None of the many materials based on isoprene has ever achieved this distinction. No commercial material can pretend literally to be synthetic rubber, for they all differ com-

TABLE 18.* STRUCTURAL RELATIONS AMONG MONOMERS AND POLYMERS

Monomers	Basic recurring groups of polymers	Nature of product
Isoprene 		Natural rubber
Butadiene 		Buna 85 and 115 (German) SKA and SKB
Butadiene + styrene 		Buna S, Buna SS
Butadiene + acrylonitrile 		Buna N, Perbunan, Hycar OR*, Chemigum*
Butadiene + isobutylene 		Butyl rubber*
Chloroprene 		Neoprene
Vinyl chloride 		Koroseal, Flamenol, Vinylite Q
Isobutylene 		Vistanex
Dichloroethyl ether + sodium tetrasulphide 		Thiokol B
B. V. A. – butyraldehyde 		Butacite, Butvar, Vinylite X

* Identity not disclosed by the manufacturer but reported to be of the type indicated.

pletely chemically from rubber. In any event rubber is itself a variable material.

Numerous Rubber-like Materials. The position at present is that there are numerous materials possessing rubber-like properties. Many are capable of undergoing a thermal change from the plastic to the elastic condition. In some cases this is promoted by the use of sulphur. In other instances materials other than sulphur are able to promote the change. Other rubber-like materials do not undergo the change, but remain permanently thermoplastic.

As regards the term " synthetic rubber ", Dawson has stated " The controversy centres around the choice between two interpretations :

(*a*) that a synthetic rubber should be identical with or at least closely related to natural rubber in a chemical state,

(*b*) that a synthetic rubber should reproduce the outstanding physical characteristics of rubber."

The first definition would limit the use of synthetic rubber to butadiene rubbers. The second term includes all materials that are rubbery. This second interpretation is the more widely accepted.

Yet these materials by virtue of possessing only some of the more evident rubbery properties are referred to as synthetic rubbers. Where can the line be drawn ?

A number of leading authorities have considered the question very closely. Definition of rubber has been a highly controversial subject. There is now a definite trend to get away from the use of the word " rubber " for substances other than where common usage applies. This trend is particularly marked for synthetic materials.

Definitions of Synthetic Rubber. Houwink [10] has supplied a very controversial definition of a rubber-like material ; " an organic material may be called a rubber when it shows a high elasticity of 100 per cent. or more at room temperature, and when it does not lose this property upon storage at room temperature during considerable periods." Yet this definition is hopelessly out of date, since many butadiene materials show little elastic behaviour at ordinary temperatures. Stevens [18] criticized this definition very strongly chiefly on the grounds that materials other than natural rubber come within its scope.

A more satisfactory general definition was given by Midgley [14] who considered the matter along these lines,

it is impossible at the present time to define synthetic rubber in chemical terms . . . expressed in physical terms the simplest definition is—" those substances which possess the physical properties of rubber ". Such a statement is functional, and should be revised in terms defining a unique physical property of rubber. Many organic substances of high molecular weight may

be stretched to many times their original lengths, examples being gums, tars, waxes, jellies, and so on, but only rubber forcibly retracts to substantially its original size and shape after stretching, so that the definition becomes " synthetic rubbers are those organic substances which possess the property of forcibly retracting to approximately their original size and shape after being greatly distorted, i.e. such as being stretched x per cent of their original length ". Here x is some arbitrary value. It should be over 100, probably 400, possibly 600, but certainly not higher.

This definition has the merits of including almost every type that has so far been put forward.

Wood [21] takes " synthetic rubber " to mean merely a synthetic substance which has physical properties resembling those of natural rubber, that is it can be stretched a considerable amount, e.g. 300 per cent., and when released will quickly and forcibly retract to substantially its original dimensions.

Bridgewater [5] described " synthetic substances with rubber-like properties " as substances that resemble rubber in the simple property of extensibility or deformability under moderate loads coupled with a tendency to recover their original form when the load is removed, although not necessarily to a degree comparable to the recovery exhibited by natural rubber.

Schade [17] has summarized the position in a very realistic fashion :

> The meaning of the word rubber has changed. It no longer signifies a particular hydrocarbon material but has been widely adopted to characterize a class of substances similar physically to natural rubber regardless of their chemical composition ; in order to qualify as a rubber a material should stretch readily to a considerable degree and after release retract forcefully and quickly ; but no specific criteria have been generally accepted limiting the values for these properties.

Trumbell and Sloan [20] suggested that the term " synthetic rubber " should be restricted to the polymers obtained from monomeric organic substances containing conjugated double or triple bonds or copolymers involving these materials. According to Fisher, it would be best to reserve the term " synthetic rubber " for products that are chemically related to natural rubber, that is to the various derivatives of butadiene.

It is desirable to have some single term to cover all rubber-like products. Among suggestions that have been put forward as generic terms for this type of material are " Collastics " by Barron,[4] " Lastics " by Ellis, " Elastoplasts " by Stevens, while Naunton [15] suggested " Elastoplastics ", and Patterson [16] has put forward the suggestion of " Cauchoid ". While all these have been favourably commented upon, the one which has received most general acceptance to date was actually suggested by

Fisher.[9] He suggested the use of the term " Elastomer ", and this has come into fairly wide usage. Moore [13] has put forward a companion term " Plastomer " to cover the non-elastic plastic substances, " Elastomer " being considered as referring to the elastic or rubber-like substances.

Terminology Suggested by Fisher. Fisher [9] extended his efforts in terminology to devising general terms for the more or less sharply defined groupings of materials which have rubber-like properties. For example, he suggested " Elastoprenes " to apply to the rubber-

TABLE 19. CLASSIFICATION FOR SYNTHETIC RUBBERS AND RUBBER-LIKE PLASTICS

ELASTOMERS	ELASTOPRENES (DERIVATIVES OF BUTADIENE)	Butadiene rubbers : Sodium butadiene rubber, Russia. Buna rubbers, Germany. Piperylene rubbers. Isoprene rubbers : Polyprene : natural rubber. Sodium isoprene rubber. Heat-polymerized isoprene rubber. Dimethylbutadiene rubbers : Cold polymer : methyl rubber H. Heat polymer : methyl rubber W. Haloprene rubbers : Polychloroprene rubber : neoprene. Polybromoprene rubber.
	ELASTOLENES	Polymers, such as polyisobutylene, formed in the presence of a catalyst—e.g. boron trifluoride : Vistanex, Oppanol B.
	ELASTOTHIOMERS	Polyalkylene sulphides: Thiokol, Perduren.
	ELASTOPLASTICS	Rubber-like polymers of acrylic and methacrylic esters : Acronal, Plexigum. Rubber-like mixed glyptals. Plasticized polyvinyl chloride : Koroseal, Igelite, Mipolam. Polyvinyl acetate, above 40° C. Polystyrene, above 65° C., and when partially solvated. Polyarylenethylenes or polyxylenes : AXF, from benzene, ethylene chloride, and aluminium chloride. Polyphosphonitrilic chloride $(PNCl_2)x$, an inorganic rubber.
PLASTOMERS	TRUE THERMOPLASTICS	Shellac, polystyrene, polyvinyl acetate, celluloid, cellulose acetate.
	THERMOSETTING PLASTICS	Bakelite, glyptals, formaldehyde-urea polymers, acrylic resins.

like polymers of butadiene and its derivatives, including chloroprene. He suggested " Elastolene " for materials similar to polyisobutylene. For the polyethylene sulphide type such as Thiokol, he suggested " Elastothiomers ", and for the growing class of rubber-like plastics which include polyvinyl chloride, methyl methacrylates, and the glyptals, he suggested using the term " Elastoplastics ". He pointed out that while many of the materials were not of a rubber-like nature, yet it was well worth bringing them under consideration in order to avoid inappropriate terminology.

Other systems have been put forward, for example Jacobs [11] devised four groupings for synthetic rubbers. He suggested (*a*) Halo Rubbers, as applying to the neoprene type, (*b*) Co-Rubbers, referring to the butadiene type, (*c*) Thio-Rubbers for the Thiokol and Perbunan, and (*d*) Plasto-Rubbers or Reso-Rubbers, which were intended to apply to vinyl polymers, and their unvulcanizable thermo-plastic polymers made from hydrocarbons.

Another scheme was that formulated by Kindscher.[12] He divided all rubber-like materials into three groups ; crude rubbers were referred to as Kautschukgene ; the second grouping, the synthetic rubbers from butadiene, etc., Thiokol, neoprene, and so on, being classified as Kautschukoide ; the third group, the rubber-like polyvinyl derivatives, polyisobutylene, and so on, being referred to as Gummoide.

In discussing this question of rubber terminology, Trumbell and Sloan submitted the classification of synthetic polymeric substances based upon the chemical composition as follows :

TABLE 20. SYNTHETIC POLYMERIC SUBSTANCES

I. Inorganic.
II. Organic.
  A. Saturated polymers with only carbon atoms in the chain.
    (*a*) Hydrocarbons.
    (*b*) Substituted hydrocarbons :
      1. Containing halogen (made from vinyl halide).
      2. Containing acid, ester, or nitrile groups.
      3. Co-polymers of (1) and (2).
  B. Unsaturated polymers with only carbon atoms in the chain.
    (*a*) Hydrocarbons (polymers of butadiene and its homologues, and of monomers containing more than one point of unsaturation.)
    (*b*) Co-polymers involving butadiene and its homologues.
    (*c*) Halogen containing polymers of butadiene and its homologues.
    (*d*) Alkoxy or Aryloxy-containing polymers of butadiene and its homologues.
    (*e*) Acid, ester, or nitrile derivatives of butadiene and its homologues.
    (*f*) Thioplastics.

C. Polymers in which oxygen, nitrogen, and perhaps sulphur, as well as carbon, enter into the formation of the chain.
   (*a*) Polymeric amides.
   (*b*) Polymeric esters.
      1. Aliphatic acid esters.
      2. Alkyd resins.
D. Derivatives of cellulose.
E. Derivatives of urea.
F. Reaction products of phenolic substances with aldehydes.
G. Derivatives of natural rubber.
   (*a*) Thermoprenes.
   (*b*) Reaction products obtained by the action of stannic chloride, aluminium chloride, etc.
   (*c*) Reaction products with halogen acids.
   (*d*) Reaction products with halogens.

As has already been pointed out this merely emphasizes the fact that there is no clear demarcation between rubber and plastics. In some of the instances quoted by Trumbell and Sloan, rubber-like properties of plasticity and elasticity are evident in the raw materials and are merely emphasized by the incorporation of plasticizers. In other instances these properties may be latent and will only become apparent after addition of suitable plasticizers. It is in these cases that plasticizers are referred to as " elasticizers ".

Highly polymerized rubber-like materials have been divided by Stöcklin [19] into two general classes; (1) synthetics capable of vulcanization—(*a*) butadiene copolymers and (*b*) reaction products of dihalogenated aliphatic compounds with sodium polysulphide ; (2) synthetics incapable of vulcanization—(*a*) polymerized isobutylenes (similar to Vistanex) and polymerized acrylic acid esters (similar to Plexigum and like materials) and (*b*) products having rubber-like properties in combination with certain plasticizing agents (for example, Koroseal).

Cramer [6] has outlined a scheme for defining these rubbery materials more closely. His scheme is as follows :

TABLE 21. DEFINITIONS OF SYNTHETIC RUBBERS

1. True synthetic rubbers, or elastoprenes, derived from butadienes, or these constituted homologues unsaturated :
   A. Simple butadiene polymers.
   B. Modified butadiene polymers.
      1. Butadiene plus styrene, as typified by Buna S.
      2. Butadiene plus acrylic nitrile, as typified by Perbunan.
   C. Substituted butadiene polymers.
      1. Polymers of isoprene.
      2. Polymers of methyl isoprene.
      3. Polymers of chloroprene, as typified by neoprene.
   D. Modified butylene polymers.
      1. Butylenes plus small amounts of butadiene or other diolefines, as typified by butyl rubber.

2. Synthetic rubber-like elastics or elasto-plastics saturated :
   A. Polyalkanes.
      1. Polybutylene as typified by Vistanex.
      2. Polyphenylene-ethylene as typified by A.X.F.
   B. Polyvinyl derivatives.
      1. Polyvinyl alcohol.
      2. Polyvinyl chloride-acetate copolymer, as typified by Vinylite.
      3. Polyvinyl chloride as typified by Koroseal, Vinylite Q, and Flamenol.
      4. Vinylidene chloride, as typified by Saran.
      5. Polyvinyl acetals, such as Formvar ; butyral, as typified by Butvar. Vinylite X, and Butacite.
   C. Reaction products of aliphatic halides plus alkali polysulphides.
      1. Ethylene dichloride, plus sodium tetrasulphide, as typified by Thiokol A.
      2. Dichlorethyl ether, plus sodium tetrasulphide, as typified by Thiokol B.
   D. Miscellaneous elasto-plastics.
      1. Plasticized polyacrylic esters as typified by the Acryloids.
      2. Alkyd condensation products as typified by Duraflex.
      3. Cellulose derivatives such as ethyl cellulose.

A Simple System. Actually all this has become rather complicated. More and more synthetic resins are coming into the synthetic rubber orbit. It is suggested that a perfectly workable scheme of nomenclature can be developed out of all the [illegible] so far put forward. It is submitted that the fundamental keyword, the generic term for all materials having rubber-like properties should be " elastics ". The term is in universal use as an adjective, to describe every form of rubber, so why not employ it as a name ? Everybody knows already what the word implies ; it is a familiar household term. Moreover, it is international. Using this there is therefore a very satisfactory division into the " natural elastics ", which includes ordinary rubber, and all the other secondary natural rubbers. Then there are the " synthetic elastics ", that is to say, those which are not found in nature, but have to be made chemically. These can be more closely defined in groups to some extent following the lines already suggested.

It is absolutely essential that some system of nomenclature should be decided upon immediately, and stressed by every possible means, for it must be realized that we are still only on the threshold of this field of activity. As new materials begin to pour in under the pressure of work dictated by present circumstances, an utterly chaotic situation may develop, unless [illegible] is done at an early stage to organize the terms of reference.

The nomenclature suggested here in many respects conforms to current practice which is a great advantage.

TABLE 22. ELASTICS

NATURAL ELASTICS:

1. *Rubber.*
   Hevea brasiliensis; Ficus elastica; Urceola elastica; Landolphia, Funtumia; Manihot glaziovii, Guayule, etc.
2. *Natural isomers of rubber.*
   Gutta-Percha; Balata, etc.

SYNTHETIC ELASTICS:

1. *Elastomers.*
   Materials which might reasonably be called synthetic rubbers, being unsaturated materials based on butadienes, or members of the butadiene family. These are vulcanizable. These would include Buna S, Perbunan, Hycar, Chemigum, Neoprene, etc.
2. *Elastenes.*
   Materials which are based on olefines and are virtually saturated. e.g. polyisobutylene, polythene, A.X.F., and butyl rubbers.
3. *Ethenoid.*
   Materials based on the polyvinyl grouping. e.g. polyvinyl chloride, acrylic esters, etc.
4. *Thioplasts.*
   Materials based on olefine dihalides and alkali polysulphides.
5. *Elastoplasts.*
   Plastics which have a very limited phase of elastic properties, either by physical or chemical changes, e.g. polystyrene, alkyd resins, cellulose esters, etc.

In this system, every general group name is already widely used except the term " elastene " which is here suggested for the first time.

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CHAPTER 4

HISTORICAL BACKGROUND OF SYNTHETIC ELASTICS

The Beginnings of Synthetic Elastics. The academic background of synthetic rubbers is similar in many respects to that of raw rubber. At first the main idea was to try to analyse rubber by breaking it down, and then to endeavour to build it up again. In spite of all attempts this has never been achieved. And, indeed, until it was realized that this approach to synthetic rubber was not a satisfactory one, production of synthetic rubber was in a complete rut, and never made much progress.

The chemistry of the rubber hydrocarbon isoprene is the basis upon which synthetic rubber chemistry is built. So it is desirable to briefly survey the work carried out on rubber, especially as in many instances it was associated with efforts to produce synthetic rubber. In fact, most of the work carried out until the last war had the dual purpose of learning about the structure of rubber, and by the use of this knowledge to synthesize rubber.

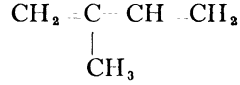
From about 1910 onwards these objectives became separated and diverged. Thereafter while rubber technologists made amazing strides in developing the physical properties of rubber compositions, the secrets of rubber structure have baffled all efforts and remain the subjects of speculation even to this day. Most chemical work was devoted towards the production of synthetic rubber-like materials.

The available information about rubber chemistry and structure, since it is in effect the behaviour of polymerized isoprene, is very pertinent to the study of synthetic rubber. Already similar chemical derivatives are being prepared from other butadiene polymers.

Action of Heat on Rubber. From quite early times rubber was subjected to heat and the products examined. Ordinarily rubber begins to soften at about 120° C., starts to decompose above 170° C., and as the temperature rises it changes into a thick brown oil with a characteristic odour, which is no longer rubbery. Above 300° C. cracking takes place, and breakdown occurs with the formation of numerous decomposition products.

Himly [13] obtained two fractions ; " faradayin ", and a high boiling fraction of " caoutchene ". Williams [43] distilled the former and isolated

a pure liquid hydrocarbon boiling between 37° and 38° C., which he called Isoprene. He found this to be empirically C_5H_8. Bouchardat [2] distilled rubber, and obtained in addition to isoprene other hydrocarbons such as dipentene and heveene. Empirical analysis showed them to be simple multiples of isoprene. Then Tilden [35] worked out the structure of isoprene which proved to be 2-methyl 1.3-butadiene.



It was subsequently demonstrated by Wallach [38] that dipentene could be derived from two molecules of isoprene on the basis of Thiele's [33] theory of partial valencies.

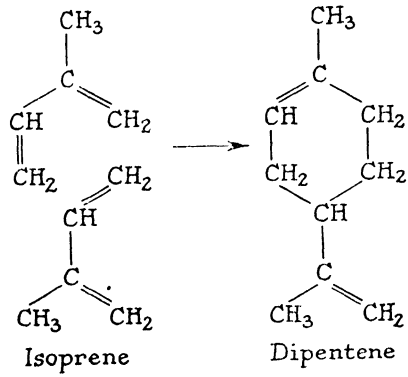


FIG. 1.

Polymerization of Isoprene. In the meantime it had been discovered that isoprene could be converted into rubber-like material. Williams discovered that on standing, isoprene tended to become viscous. Bouchardat [1] found that by heating isoprene with strong hydrogen chloride he obtained an elastic rubber-like product in a much shorter time than when the change was allowed to occur by standing. The possible industrial significance of the fact that isoprene could be polymerized was clearly noted for the first time by Tilden,[37] who wrote, "It is this character of isoprene which gives it a somewhat practical interest, for if it were possible to obtain this hydrocarbon from some other and more accessible source (than rubber) the synthetical production of India rubber could be accomplished." Tilden converted isoprene which he obtained from turpentine into a rubbery material

by the action of hydrogen chloride, a conversion which was also aided by the use of nitrosyl chloride. This change was found by Wallach in 1887 to be promoted very effectively by the use of ultra-violet light.

Isoprene monopolized all the attention in these early efforts at polymerization. In 1892 Tilden [36] reported that he had found isoprene to undergo spontaneous polymerization to caoutchouc. He stated that samples of isoprene, prepared from turpentine, which had been stored in bottles for several years, had given rise to solid masses of rubber.

> The artificial rubber [he wrote] like natural rubber, appears to consist of two substances, one of which is more soluble in carbon disulphide or benzene than the other. A solution of the artificial rubber in benzene leaves on evaporation a residue which agrees in all characteristics with a similar preparation from Para rubber. The artificial rubber unites with sulphur in the same way as ordinary rubber, forming a tough elastic compound.

It was only in 1900 that Kondakoff [18] discovered that dimethyl butadiene when heated with alkaline potash gave a rubber-like material.

Shortly afterwards Thiele [34] showed that piperylene, a material isomeric with isoprene, polymerized to a rubbery product when left in the dark for some time. It was then quite evident that the ability to form rubbery material was not specifically confined to isoprene, being shared at least by closely related materials. It is, therefore, strange that it was only in 1910 that Lebedev,[19] another Russian chemist found that the parent material of this group, namely butadiene, could be polymerized to produce an elastic material.

TABLE 23. BUTADIENE DERIVATIVES KNOWN AT THIS STAGE

		B.P.	Density
Butadiene . . .	$CH_2 \; CH{-}CH \; CH_2$	4° C.	—
Isoprene . . .	$CH_2 \; C(CH_3){-}CH \; CH_2$	33° C.	d^{20} 0·6804
Piperylene . . .	$CH_3{\cdot}CH{=}CH{-}CH{=}CH_2$	42° C.	d^{20} 0·679
Dimethyl Butadiene	$CH_2 \; C(CH_3){-}C(CH_3) \; CH_2$	69·5° C.	d^{20} 0·7273

Many workers showed when rubber was broken down by heat, that in addition to isoprene, many other materials were formed all isomeric with isoprene. This led to the inference that rubber was a polymer of isoprene having a composition expressed by $(C_5H_8)_x$. It was also inferred that the long-chain molecule formed broke up in

such a way as to give isoprene or polymers of isoprene. The highest recorded yield of isoprene obtained by destructive distillation of rubber has been obtained by Bassett and Williams,[3] amounting to 23 per cent.

Harries Ozone Reaction. By 1900 there was already a very lively interest in the production of synthetic elastic materials. But there was an obstinate determination to make synthetic rubber. Nothing else would do. Consequently it was necessary first to elucidate the structure of the natural material and criteria for the artificial materials. In this field the work of Harries was outstanding. The momentous study of the effect of ozone on rubber by Harries [11] is one of the classical features of rubber chemistry.

Harries showed that one molecule of ozone joined on to each double bond of an olefine to give an amorphous viscous material which was an ozonide. These were often explosive. When warmed

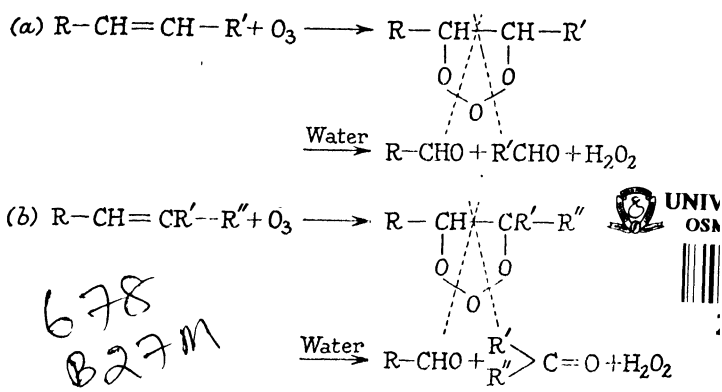


FIG. 2.

with water an ozonide decomposes in a regular fashion giving aldehydes and hydrogen peroxide, or ketones and hydrogen peroxide according to whether the carbon atoms at the double bond have hydrogen or alkyl groupings attached.

Thus rubber when subjected to ozone treatment yielded substantially levulinic aldehyde and levulinic acid. These are 1 : 4-dicarbonyl compounds, as are others such as succinic dialdehyde or acetonylacetone. It is essential for the formation of such compounds that a double bond should recur after each fourth carbon atom in a carbon chain.

If the double bonds are located in a different way or are removed by cyclization, then an abnormal rubber results. Consequently if

elastomers resemble rubber then comparable decomposition products will be obtained. It is the nature of these products in many instances which has lent support to the theory that many of them are long open-chain molecules comparable with the rubber molecule.

In his efforts to work out the structure of rubber Harries produced

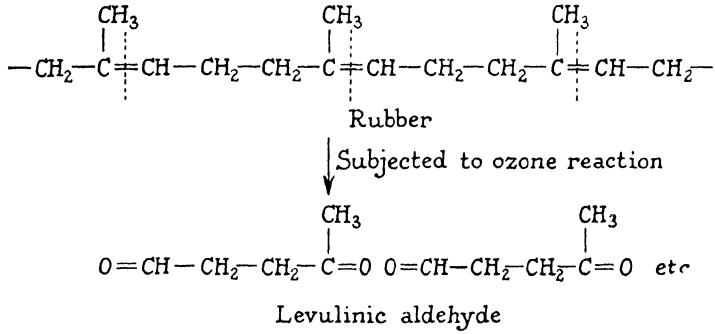


FIG. 3.

a number of materials having the same ultimate composition as rubber, but very different properties. These were the iso-rubbers, which were much less unsaturated than natural rubber.

The procedure was to convert rubber in benzene solution into rubber hydrochloride and then to remove hydrogen chloride. Although resembling rubber in some ways, it was a different material. In particular, the products he obtained after ozone treatment were different from those obtained with rubber. This meant that the double bonds were in different positions. By forming a hydrochloride with this iso-rubber, and again removing it, yet another different product was obtained which he called beta-iso-rubber. As a result of his work with ozone, Harries suggested an eight-membered ring structure for rubber.

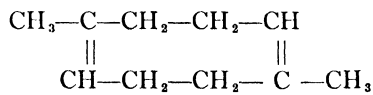
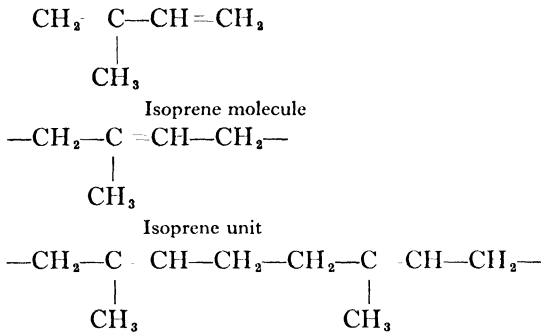


FIG. 4.—Harries' 8-membered ring.

Pickles [29] suggested that rubber is made up of a long chain of recurring isoprene units joined together by undergoing the Thiele transformation. By this an isoprene molecule becomes an isoprene unit,

i.e. forming a 1 : 4 conjugated system which joins up with other units to form the chain.



Isoprene units join together to form a chain of unknown length expressed as

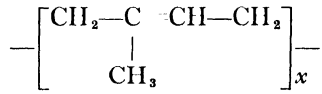


FIG. 5.

This conception that rubber is made up of a long chain of recurring isoprene units, i.e. as a polymer of isoprene, is the one generally accepted at the present time. It is no longer thought necessary to explain rubber properties and polymerization by means of the presence of secondary valencies. A good case for explaining such behaviour as being due to primary valencies was made by Whitby,[40] drawing on his work not only with rubber but with butadiene and polyethylene.

The work of Staudinger[31, 32] on the formation of high molecular weight in long-chain polymers also shows that the assumption of secondary valencies as connecting links is unnecessary. Carother's[6] work also tends to confirm this.

The Second Phase. The importance of Harries' work on the structure of rubber was that it paved the way for the first efforts to make synthetic rubber on a commercial basis. As already described, he established a number of criteria to distinguish rubber. To test these he had to make a number of synthetic rubbers. He was quite familiar with the synthetic rubber position, because in 1902 he had polymerized isoprene by heating it strongly, without getting really satisfactory products. He had shown that rubber was made up of isoprene units, which simplified the problem to one of obtaining isoprene and then developing a suitable method for making the isoprene molecules link up. The work he carried out had very important

repercussions. According to Memmler: [21] "These important degradation results which made possible the actual characteristics of a rubber substitute, together with the rising price of rubber in 1909 greatly stimulated attempts to produce artificial rubber."

As events turned out, the desire for absolute precision, i.e. to make artificial rubber, retarded the successful production of synthetic material, for subsequently it became evident that the rubbery properties were the important feature, not the exact composition. It is interesting to observe how in all his writings Harries particularly refers to "artificial" rubber, not "synthetic". He, more than anyone, realized that rubber had not been synthesized.

First Commercial Interest. Harries' work was of such great interest to the Bayer Company, and the Badische Anilin Fabrik in Germany, that they were prepared to sponsor extensive work aimed at the production of synthetic rubber.

The time was propitious, for natural rubber was at a very high price, and in 1910 reached nearly 15*s*. per lb. Also at that time the plantation industry had not yet become established, and rubber was a variable unsatisfactory raw material. So that the conditions at that time were very much different from the present, and any laboratory product that could be produced possessing rubbery properties had bright commercial prospects. Nowadays such materials would in the ordinary way be quite hopeless. They must have marked superiority in some properties.

In due course, working for the Bayer Company, Hoffman and Coutelle [15] were able to polymerize isoprene by heating it at temperatures below 200° C. for about eight days in the presence of catalysts. Hoffman claimed that prior to the work in 1909 no one had ever made synthetically "the tough, elastic, nervous caoutchouc colloid". Whitby and Katz [42] do not agree with this view.

> If the ground is taken that the synthesis of rubber has been achieved only when there has been made a product strictly identical with natural rubber in every particular respect, identical not only chemically but also in the degree of polymerization as indicated by the colloid and elastic properties before and after vulcanization—then, it must be declared that such synthesis has even yet to be accomplished; but, on the more reasonable ground that the production from isoprene of an elastic, vulcanizable product generally similar to natural caoutchouc constitutes a synthesis of caoutchouc, then the honour of having first made the synthesis must go to G. Bouchardat and Tilden.

Harries' earlier attempts along similar lines had failed because the temperatures that he employed were too high. Harries [10] eventually succeeded in effectively polymerizing isoprene at a much lower tem-

perature, namely 100° C., having acetic acid as catalyst and using pressure.

These discoveries inaugurated a really active era in the production of synthetic rubber. This concerted effort laid the foundations on which present-day production has been built.

Discovery of Rubber Accelerators. Arising out of this work there came many extremely important commercial developments. In fact, it cannot be stressed too much that although synthetic rubber may have only become practicable during recent years, yet numerous valuable by-products have emerged from the enormous amount of work directed towards its manufacture, and it has had profound effects on many other unrelated industries. An outstanding example of a profoundly important discovery in a closely related industry was the arrival of accelerators for rubber.

The synthetic materials which were in course of preparation were found to oxidize with great ease. Various materials were added to try to offset this tendency, some being extremely successful. But in addition to exerting a distinct retarding effect on oxidation they also increased the rate of vulcanization. The arrival of accelerators was the result, as described in the very important Bayer patent.[4]

According to Gottlob,[9] who was associated in all this work on synthetic rubber:

> There are certain kinds of synthetic rubber which decompose quickly from oxidation. These can be protected against oxidation very effectively if a small addition of organic base is mixed with them. As protective material, such bases as aniline, pyridine, quinoline, dimethyl aniline, and in certain cases piperidine were used. While the bases first mentioned in the above list produced no essential change during the vulcanization of the particular variety of rubber involved, the rubber in which 1 per cent. of piperidine was used showed a completely different behaviour after vulcanization. The determination of combined sulphur showed that about eight times as much sulphur had combined with the rubber as the accepted amount under normal conditions; a truly astonishing result. This observation made by Hoffman and Gottlob introduced us to investigating the action of piperidine on the vulcanization of natural rubber, whereby similar results were obtained.

This supplied the basis for the first Bayer patent on accelerators.

Organic accelerators of vulcanization, now universally used in rubber manufacture and which have contributed greatly to the advance of rubber-manufacturing technique and to the improvement in the quality of rubber goods, were first discovered in the United States by Oenslager and Marks.[23] Their use was kept secret. They were discovered independently and patented in Germany by the Bayer

Company. Their discovery followed directly out of work on synthetic rubber. The use of piperidine, originally applied to synthetic rubber as an antioxidant and later found to be an accelerator of vulcanization, was followed by the use of the compound prepared by the action of piperidine on carbon disulphide, viz. piperidine pentamethylene dithiocarbamate. If the dithiocarbamate is used with natural rubber in a simple rubber-sulphur mixture, it is in fact little more efficient as an accelerator than piperidine. If, however, it is used in the presence of zinc oxide, it is much more active than piperidine, causing vulcanization to occur at least twenty-five times as quickly as does piperidine.

Since zinc oxide is such a common component of technical rubber mixtures, it was inevitable that this fact should sooner or later be found out. And with its discovery the whole field of ultra-accelerators was opened up.

In course of time accelerators and the accompanying antioxidants moved out of the synthetic rubber orbit and materially contributed towards the development of rubber manufacture.

The results of the first great burst of activity towards synthetic rubber production can briefly be summarized as they seemed in 1910. Lebedev had just discovered that butadiene could be polymerized to give a rubbery material, and it was evident that the butadiene family of materials, distinguished by containing conjugated double bonds, could be turned into rubbery materials. Heat or ultra-violet light were effective in causing the change which was promoted by the presence of catalysts and by the use of pressure. This phase was very much concerned with the problem of polymerization and emphasis was laid on the importance of double bonds. Numerous materials had been discovered which acted as catalysts. It laid the groundwork on which subsequent successful production has been based.

Developments Preceding the Last War. Production of synthetic rubber was a matter of the greatest interest during the years immediately preceding the last war. This was the period of the second distinct phase in synthetic rubber development. There were three prominent groups of chemists working on the problem, in England, in Russia, and in Germany.

In view of the fact that in recent years British activity in the synthetic rubber field has been virtually non-existent, it comes as something of a surprise to realize that British chemists were extremely prominent in synthetic rubber development, and made great contribution towards its production. Very extensive and successful research work was carried out at Manchester under W. H. Perkin, junior.[27] Associated with him in the work were Matthews, Strange, and Weiz-

mann.[28] A number of laboratory processes were developed for making the various butadiene derivatives. Their most successful method was to make aldol from acetaldehyde which they obtained from ethyl alcohol. The aldol was reduced to butylene glycol which was then

$$\underset{\text{Acetaldehyde}}{CH_3.CHO} + CH_3.CHO \longrightarrow \underset{\text{Aldol}}{CH_3.CH(OH).CH_2.CHO}$$

$$CH_3.CH(OH).CH_2.CHO \xrightarrow{\text{reduce}} \underset{\text{Butylene glycol}}{CH_3.CH(OH).CH_2.CH_2OH}$$

$$CH_3.CH(OH).CH_2.CH_2OH \xrightarrow{\text{dehydrate}} \underset{\text{Butadiene}}{CH_2{=}CH{-}CH{=}CH_2} + 2H_2O$$

FIG. 6.

catalytically dehydrated. Singularly enough, this was essentially the method which the Germans ultimately adopted in 1928, to start their large-scale production. Another of Perkins' methods was to chlorinate butylene glycol and then to treat the product with soda-lime which also yielded butadiene.

Another method was based on butyl alcohol. This was dehydrated to 1.2-butylene by passing over phosphoric acid at 450° C., converted to the dibromide, and then passed over soda-line which removed hydrogen bromide and left butadiene. Fernbach [7] was associated with

$$\underset{\text{Secondary butyl alcohol}}{CH_3.CH(OH).CH_2.CH_3} \xrightarrow{\text{dehydrate}} \underset{\text{Butylene}}{CH_3.CH{=}CH.CH_3}$$

$$CH_3.CH{=}CH.CH_3 \xrightarrow{\text{bromine}} CH_3.CHBr.CHBr.CH_3$$

$$CH_3.CHBr.CHBr.CH_3 \xrightarrow{-2HBr} \underset{\text{Butadiene}}{CH_2{=}CH{-}CH{=}CH_2}$$

FIG. 7.

much of this work, having developed his famous process for the fermentation of starch to yield chiefly butyl alcohol. The modification of this process as worked out by Weizmann [39] to yield pure acetone was of outstanding assistance to Great Britain during the last war. Commenting on this work, Whitby and Crozier [41] have pointed out that

> although the processes which were developed in England prior to the war for the production of synthetic rubber have never established themselves commercially, the Fernbach fermentation process which was developed along with them has proved to be of great importance and may be said to represent a by-product of the programme of work on synthetic rubber which has more than justified the latter.

A good account of much of this work has been given by Schotz.[30] Many other important by-products since that time emphasize the wisdom of this attitude.

Perhaps the greatest achievement which emerged from this source was the discovery that the polymerization of the butadienes was profoundly accelerated by the use of sodium. Matthews and Strange [20] patented this discovery in 1910. Their method was to polymerize butadiene in the gaseous state in the presence of sodium wire.

It is a remarkable feature of almost every rubber development of major importance that simultaneous discoveries appear to be made elsewhere. So it proved in this case. Harries and the Bayer Company [12] had discovered almost the identical process at almost the same time. Harries' method essentially was to put butadiene with 3 per cent. sodium wire into a sealed tube. After a comparatively short period of heating at 40° C., a solid mass was formed, which when washed with alcohol to remove sodium, gave a light yellow rubber-like material. With isoprene treated in this way for five days an almost theoretical yield was obtained. Holt [16] found that the process was greatly facilitated and better products resulted by working in the presence of carbon dioxide.

As has almost become the custom in the rubber industry, long and involved litigation followed, the outcome of which was that the English chemists established in the Law Courts their priority in this discovery.

The Production of Raw Materials. It is of interest to consider briefly some of the methods utilized for the production of raw materials up to this time. This was the formative period in the production of synthetic rubbery materials. But it was also the formative time for many synthetic resins, such as polyvinyl chloride, etc. The difficulties being encountered in the production of synthetic rubbers applied equally well for these latter.

Isoprene was prepared by Tilden by passing rubber distillation products or turpentine vapours through red-hot tubes. Hoffman [14] hydrogenated *p*-cresol to methyl cyclohexanol, which was then oxidized to methyl adipic acid. This was converted into the diamide and then to the diamine, which was methylated. This diquarternary ammonium base was distilled to yield a pure isoprene. It is interesting to observe that even at this early stage the possibility of obtaining isoprene from petroleum had been studied. Thus Holt [17] obtained isopentenes from the pentane fractions, converted them into dihalides and then direct to isoprene.

Butadiene was extremely difficult to obtain. An interesting early

method was that of Berthelot,[5] who passed a mixture of acetylene and ethylene through heated tubes. Incidentally this work has recently been investigated again by Naragon, Burke and Laukelma,[22] who passed ethylene and ace ylene in the presence of steam through a tube at 610° C. obtaining chiefly butadiene. The method developed by Hoffman for isoprene was also used for butadiene except that phenol was the starting material. Matthews and Strange used the butyl alcohol method already described. Harries had a somewhat similar method starting from secondary butyl alcohol. These methods led to the really valuable methods based on alcohol, which will be described in due course. It is quite evident that none of these methods was suitable for the production of the quantities of monomers required for large-scale production of synthetic rubbers.

The Russian chemists, notably Lebedev and Ostromislensky, were making great advances. The former had found that butadiene could be polymerized to give a rubbery material, and he had also observed that substitution in the butadiene molecule had a profound influence on the rate of polymerization. The nature of the rubbery material formed depended on this substitution. Ostromislensky [24] published a book on his researches. He described a number of procedures for the preparation of isoprene by the removal of the elements of hydrogen chloride from the chloroisoamylenes and from 1.3-dichloropentane, but, in so far as the preparation of conjugated dienes is concerned, his attention seems to have been directed chiefly to butadiene. He investigated many cracking processes for the preparation of butadiene and concluded that at a high temperature all open-chain olefines and saturated cyclic hydrocarbons can be cracked to form butadiene and a saturated hydrocarbon. He also prepared butadiene by the catalytic removal of water and an acid from esters of di-glycols, of hydrogen chloride and water from chloroethers, of alcohol and water from acetals, etc. Ostromislensky [26] was the pioneer of a process which was the forerunner of some of the most modern methods. He passed a mixture of alcohol and acetaldehyde over a strongly heated catalyst such as kaolin, condensation and dehydration occurring at the same time, butadiene being formed thereby. He was also carrying out the extensive programme of work on polymerization of vinyl chloride, on which its present ever-growing application is based. In fact with the passing of time, it begins to appear that Ostromislensky is the outstanding figure in synthetic rubber history.

Thus in a patent, Ostromislensky [25] stated that polymerized vinyl chloride or bromide were identical in all properties with the chloride or bromide of butadiene rubber. The action of sunlight caused

complete polymerization. The reaction velocity was appreciably accelerated by using ultra-violet light and excluding air. Decomposition was averted by stirring strongly. He found that by heating solutions of vinyl chloride or bromide with zinc dust in the presence of alcohol he obtained the first member of a series homologous with that of natural rubber. Treatment of the polymerized vinyl halides with aromatic amines or caustic potash produced reactions analogous to those produced when butadiene halides were similarly treated.

Synthetic Rubber during the Last War. The last war provided the first real opportunity of testing the possibilities of synthetic rubber-like materials. All the work was carried out by the Germans under duress. No natural rubber was permitted to enter the country. Faced with an acute shortage of the strategic material, they were forced to inaugurate large-scale production of synthetic material. When this manufacture was actually commenced, it was based oddly enough not on the raw materials which had been so extensively studied in the preceding years in Germany, but upon the much earlier work of the Russian, Kondakoff. Their starting material was not isoprene, nor yet butadiene, which had monopolized so much attention, but dimethyl butadiene. Actually this was quite logical, because the latter material could be relatively easily obtained. Its production was based on pinacone which could be obtained from acetone, which in turn was made without great difficulty from calcium carbide. Pinacone was produced by reducing acetone with magnesium amalgam; two molecules of water were then removed by passing pinacone over heated dehydrating agents such as potassium bisulphate or clay.

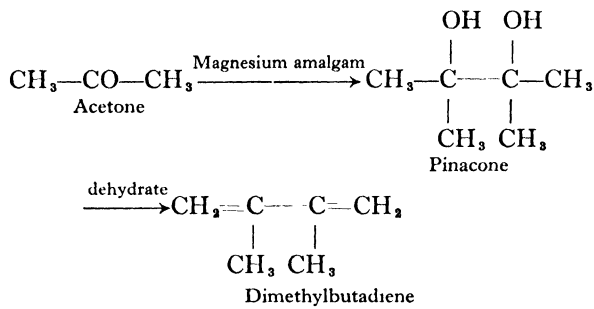


FIG. 8.

Two leading types of synthetic rubber were manufactured by the Bayer Company at Leverkeusen, known as Methyl H Rubber and Methyl W respectively.

Methyl H was manufactured by placing dimethyl butadiene in metal drums allowing plenty of air space over the liquid. It was maintained at 30° C. for about three months, after which time the liquid raw material had been transformed into a white solid crystalline product which became rubbery when milled. Small quantities of the finished product behaved as a very efficient catalyst for subsequent batches of material. This material yielded reasonably good hard products with good electrical properties. The physical properties were inferior to those of rubber.

The other product, Methyl Rubber W, was produced by heating dimethyl butadiene under pressure at 70° C., for long periods of time—six months or more. In due course the yellow rubbery product which was formed had to be cut out of the containers, a process involving some difficulty. It could be mixed and compounded in the usual manner. It was unsatisfactory as a substitute for rubber. The slow and laborious procedure involved in these forms of production made it fairly evident that there were no great prospects of these materials achieving any profound commercial significance. Another grade of methyl rubber was made at Ludwigshafen by the Badische Anilin und Soda Fabrik by the polymerization of dimethylbutadiene by means of metallic sodium in an atmosphere of carbon dioxide. Although this did not give stronger vulcanized products than Methyl Rubber H, it had an advantage over the latter in being more readily worked on the mill and giving a smooth product which could be extruded more easily.

Both Methyl Rubber H and Methyl Rubber W could be compounded and processed in the usual manner. According to Gottlob,[8] Methyl Rubber H was used for soft rubber goods, for packings, and so on. The working properties of both were not really satisfactory, and the vulcanization products were comparatively feeble compared with natural rubber. According to Gottlob production actually reached the order of 300 tons a month, and in all some 2,350 tons were made and used. Yet it is quite clear that they were quite unsatisfactory, for no sooner was natural rubber available once again than production ceased.

A careful examination of the products of these materials was subsequently carried out by Whitby and Crozier.[41] They concluded that the products were far inferior to those obtained from natural rubber. Methyl Rubber H was found to yield vulcanized products which were only one-third as strong and extensible as compared with rubber products.

The Methyl Rubber W, although its extensibility was good, had

only one-tenth of the strength of comparable natural rubber. Both types were very sensitive to temperature changes, were much more loggy and possessed much less nerve than products obtained from raw rubber.

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CHAPTER 5

CHEMICAL BEHAVIOUR AND STRUCTURE OF NATURAL RUBBER

In so far as it has had a very profound effect on the problem of making synthetic materials, the structure of rubber is of considerable importance. Much of the evidence regarding this has been derived from its chemical behaviour. The following account gives a brief résumé of the present position.[1, 2]

The singular feature about all the many interesting products is that as the degree of unsaturation is reduced, the elastic properties tend to disappear, so that in many cases these are completely absent, the product being invariably thermoplastic. Many of these synthetic thermoplastic materials have already found wide commercial application. They illustrate the other side of the picture, the approach of rubber to plastics. Already similar derivatives are being produced from butadiene elastomers, from polyisobutylene, etc.

Owing to its unsaturation, rubber is a very reactive material. This is responsible for many of its disadvantages. In this respect many synthetic elastic materials are of value precisely because they do not undergo these chemical changes. This chemical reactivity has also enabled a considerable amount of work to be carried on towards elucidating its structure.

Rubber and the Halogens. Rubber hydrocarbon is unsaturated and behaves like a typical olefine. Thus it reacts very readily with halogens and halogen acids; for example, it readily takes up chlorine, as was first shown in 1859 by Englehard and Day.[12] Not much interest was taken in this material until 1915, when Peachey [28] was able to obtain a product containing 65 per cent. of chlorine. Theoretically, rubber should only yield a product of 51 per cent. of chlorine by addition, so that considerable substitution takes place as well.

In recent years there has been a great deal of activity with chlorinated rubber, which is of great commercial value owing to its ability to dissolve in many solvents from which films may be obtained having great resistance to corrosion. It withstands both acids and alkalies. Films from it are unaffected by water, steam, sunlight, oxygen, etc.

One of the main trends has been to depolymerize the rubber prior to chlorination, making use of every method for degrading it.[6, 9, 10, 11, 20]

This has been effected either by excessive milling causing mechanical breakdown, or by the use of ultra-violet light or sunlight, or by the addition of oxidizing agents, or by the use of small quantities of the deleterious metals—copper, manganese, cobalt, etc. The material is available in several forms, giving solutions of different viscosity.

Films of chlorinated rubber are quite brittle and show no elasticity whatever. They have to be plasticized with materials such as chlorinated diphenyls, coumarone resins, dibutyl phthalate, tricresyl phosphate, etc. There is considerable literature on the subject both technical and commercial. Chlorinated rubber structurally is of considerable interest in relation to other chlorinated elastic materials such as chloroprene and polyvinyl chloride.

In connection with synthetic elastic materials it is of great interest, as wherever bonding to metal is required, that a solution of chlorinated rubber is frequently employed with great success, e.g. for Buna-S, Perbunan, neoprene, Hycar, etc. It is also miscible with polyvinyl resins and polyacrylic esters.

Gladstone and Hibbert,[17] in addition to their work with chlorinated rubber, examined the behaviour of rubber with bromine, and obtained a fully saturated compound, $C_{10}H_{16}Br_4$, which corresponded with the addition of bromine at the double bond.

The behaviour of rubber with halogen acids corresponds closely to its behaviour with the halogens themselves. Weber [40] obtained white products approximating to a composition of C_5H_8HCl. Harries [18] prepared the corresponding hydrogen bromide derivative and obtained a material; this formula corresponded to $(C_5H_8.HBr)_x$.

In recent years, as the result of work carried out by Bradley [2a] and McGavack, commercial derivatives of some potential importance have been obtained from rubber hydrochloride.

If hydrogen chloride is passed into a solution of rubber at ordinary temperatures, a white solid product is obtained which can be easily separated. This is rubber hydrochloride. Calvert [7a] showed how, when suitably stabilized, it can be converted into films and sheets having wide commercial application.

This has been marketed by the Goodyear Company as *Pliofilm*. It is transparent, tasteless, and odourless. It is strong, can be stretched, is resistant to tear, is moisture proof, and resistant to oils and greases. Its thermoplastic character is illustrated by the fact that it can be heat sealed at 105° C., a fact of some importance for many applications.

Influence of Oxygen. Oxygen plays a dominating part in the behaviour of rubber. Many of the disadvantages of rubber are attributed to its vulnerability towards oxygen. Raw rubber tends to take

up oxygen ; it sometimes oxidizes during storage, becomes very tacky, and can change to an almost unrecognizable inelastic resinous mass. This is due to the presence of oxygen which promotes changes in its structure. The effect is assisted by the presence of substances which catalyse the oxidation process. It is also aided by increase in temperature and by exposure to ultra-violet light. Oxygen makes vulcanized rubber perish and lose its valuable mechanical properties.

In recent years it has been conclusively established that oxygen plays a vital rôle in rubber behaviour. It is thought to have a profound influence on such phenomena as tackiness,[7] mastication behaviour,[8] structural changes, etc. Many investigations have shown that rubber takes up oxygen during oxidation although the quantity is very small. It has always been a mystery why such small quantities of oxygen should be able to exert such a profound effect on solution properties and mechanical properties. The explanation put forward by Staudinger and Leopold [35] is the most plausible so far, based on the macromolecular theory. Assuming a rubber molecule to be very long, made up of, say, 1,000 isoprene units as a polymerization chain, then oxygen may affect it in this way—

$$(C_5H_8)_{1,000} + O_2 \rightarrow 2(C_5H_8)_{500}O$$

The molecules formed will be considerably shorter, and will thus tend to give lower viscosity and modified physical properties. Evidently, viewed in this manner, very minute amounts of oxygen will profoundly alter the rubber. This appears also to be the case with some synthetic products, notably Buna S.

The outstanding feature about other oxidizing agents in relation to rubber is the use of benzoyl peroxide. Ostromislensky [26] in 1915 found that this produced a vulcanizing or setting action on rubber without involving the customary use of sulphur. This work led up to the extended successful use of benzoyl peroxide and similar materials as polymerization agent for many synthetic elastics and ethenoid resins notably by Klatte and Rollett.[23] In contrast to this it has recently been found that small amounts of benzoyl peroxide have a profound depolymerizing action in masticating rubber ; this seems to be a function of temperature.

Harries [19] found that oxidizing agents such as alcoholic potassium permanganate solution converted rubber into a thick syrup, which was still $(C_5H_8)_x$. His inference was that the rubber had depolymerized.

The deliberate resinification of rubber by oxygen has resulted in the formation of interesting commercial materials known as *Rubbone.* ‡ Stevens [37] treated well-masticated rubber in solution in white

spirit, with small amounts of cobalt linoleate. When air was passed through this for eight hours at 80° C. a resin was obtained which has found application for paints and lacquers. As described by Stevens and Stevens,[38] it is a pure thermo-setting resin having the composition $(C_5H_8)_2O$. It has no elastic properties but is very resistant to corrosion.

Cyclo-Rubbers. The work so far described has been largely concerned to establish that rubber is an open-chain material. In recent years a great deal of work has been carried out to convert rubber into isomeric compounds. These, while still having the same empirical formula as rubber, nevertheless are much less unsaturated and differ considerably in properties. The lower unsaturation is attributed to cyclization within the molecule. For this reason they are often referred to as cyclo-rubbers. The behaviour described has a considerable bearing on the polymerization of butadiene and its derivatives, particularly in relation to the processing properties.

The iso-rubbers made by Harries have already been mentioned. Staudinger [33] has produced numerous cyclo-rubbers by reducing rubber or rubber hydrochloride in toluene with zinc dust. Staudinger and Geiger [36] heated rubber above 250° C., so that cracking was avoided. They found that the degree of unsaturation decreased. They considered that a cyclo-rubber had been formed. The cyclic product contained only one double bond for every five isoprene units, four of which had combined to form a ring. Its appearance had changed, for it was a light yellow powder without rubbery properties. Its density was greater. Staudinger's macromolecule or long-chain theory of the structure of rubber was largely based on this work. He thought rubber was made up of enormously long open chains of isoprene units. The tendency for cyclization among the repeating groups at different positions accounted for his different cyclo-rubbers.

Fisher [15] in 1927 showed that rubber behaves in a remarkable manner when treated with concentrated sulphuric acid. He was able to obtain a number of thermoplastic materials merely by milling rubber with sulphuric acid. Tough materials which could be rendered plastic with heat could be obtained when rubber was milled with 5 per cent. of concentrated sulphuric acid, and thereafter heated at 130° C., for about fifteen hours. Kirchhof [22] independently arrived at the same conclusions working on rubber solutions. When the method was developed by replacing sulphuric acid with sulphonic acids, a number of most useful materials became available. Fisher milled rubber together with organic sulphonic or chloro-sulphonic acid or sulphonyl chloride. The materials when subsequently heated were tough and thermoplastic, in some instances resembling shellac, and others resembling balata or

gutta-percha. These are the commercial *thermoprenes*, which are very extensively used as adhesives.

According to Fisher [16] the nature of the products varied with the temperature and the time of reaction. The products have characteristics which enable them to be grouped as—

(*a*) Somewhat resilient materials which resembled vulcanized rubber.

(*b*) Hard tough thermoplastics resembling balata and gutta-percha.

(*c*) Hard brittle materials resembling shellac.

The various products were all much less unsaturated than rubber, the value decreasing as low as one-third of the unsaturation of rubber. They could be vulcanized to give products somewhat similar to those obtained from raw rubber.

It is interesting to observe that these synthetic isomers of rubber in many respects resemble the natural isomers, balata and gutta-percha.

Rubber and Metal Halides. The behaviour of rubber towards reactive metal halides is very interesting. By treating anhydrous rubber solutions with materials such as stannic chloride, ferric chloride, antimony chloride, etc., Bruson, Sebrell and Calvert [3] obtained coloured products which broke up in alcoholic acetone to yield hydrocarbons in many respects similar to thermoprenes. The stannic chloride addition product had the composition $(C_5H_8)_{10}\ SnCl_4$. When decomposed, this gave a white powder which was $(C_5H_8)_r$.

Bruson [4] was able to obtain interesting commercial materials by adding about 10 per cent. of chloro-stannic acid, either direct to rubber on a mill or to a benzene solution of rubber. The products contain a certain amount of bound chlorine. These are the basis of the *Plioform* resins which have come into industrial use.

The members of this group are all thermoplastic. They are resistant to most acids, alkalies, and many solvents. They withstand water, and have excellent electrical properties.

According to Winkelman and Jones,[41] amphoteric metal halides seem particularly effective in producing thermoplastic materials from rubber. Thus 10 parts of ferric chloride milled into 100 parts of rubber and heated at 100° C. for fifteen hours gave a hard brittle thermoplastic material.

All these products are cyclo-rubbers. In the main they tend to be more plastic than elastic, and in this respect tend to resemble the ethenoid type of elastic materials.

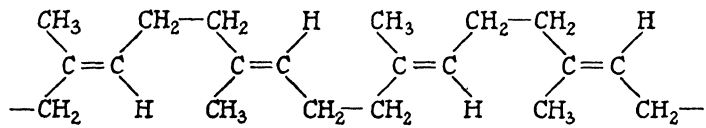
It has also been found that the halogen compounds of non-metals have a profound cyclizing effect on rubber. Boron and phosphorous compounds are outstanding in this respect. This is particularly inter-

esting in view of the influence of these materials on the polymerization of isobutylene for example. Bruson [5] found that boron trichloride converted rubber in benzene into a white powder. He also showed that boron fluoride and fluoboric acid reacted with rubber on the mill to give thermoplastic cyclo-rubber. Stevens found that 2 to 3 per cent. boron trifluoride or 8 per cent. fluoboric acid on the rubber gave hard flexible materials which were partly cyclized rubbers and could be vulcanized. Farmer, Rowe and Stevens [13] obtained various cyclo-rubbers by the use of fluorine compounds of boron and phosphorous. Reaney [30] prepared cyclo-rubbers by milling phosphorous pentachloride into rubber which contained aluminium sulphate; the mass was then heated at 160° C. for some hours.

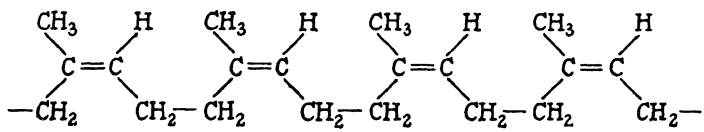
It is interesting to note that sulphur chloride has a profound effect on rubber, being the basis of the cold cure, or low-temperature vulcanization of rubber. This was discovered by Alexander Parkes [27] in 1846. The action is extremely rapid, but whereas other cyclizing agents give thermoplastic materials, sulphur chloride yields elastic products; so that sulphur chloride certainly only results on partial cyclization.

In passing it is interesting to observe that those concerns who have led in the production of cyclo-rubbers are also prominently concerned with the production of synthetic elastics.

Structure of Rubber. So far as the chemical structure of rubber is concerned, current opinion favours Staudinger's theory of macro-



Gutta-percha 'cis' form



Rubber 'trans' form

FIG. 9.

molecules or giant molecules. This has been supported by X-ray examination of rubber. Katz [21] showed that stretched rubber has an orderly structure. Thus he obtained a diagram from stretched rubber but not from rubber in the unstretched state. Meyer and Mark [24] by

X-ray measurement found that the results corresponded with an isoprene unit as being the chief constituent of the main valency chain.

It is singular that gutta-percha, which is a natural isomeric form of rubber, shows many chemical reactions similar to rubber, but lacks elasticity. Staudinger [32] has suggested that the difference may be due to a different space arrangement of the molecule, rubber being the *trans* form, and gutta-percha being the *cis* form. It is interesting to note, according to Ferri,[14] that gutta-percha, when heated with cyclizing agents, give the same products as are obtained from rubber.

Molecular Weight of Rubber. The molecular weight of rubber has so far not been conclusively determined. It would be extremely valuable information, for it would determine the length of the molecule, and would then explain much of its behaviour.

In his work on rubber ozonides, Harries found that the freezing-point depression in benzene solution corresponded to a formula $C_{25}H_{40}$. Pummerer [29] estimated the molecular weight of rubber to range between 1,400 and 2,000 on the basis of the lowering of the freezing-point in camphor. In this case the rubber molecule would contain from 15 to 30 isoprene units. Staudinger [34] found that hydrogenated rubbers had molecular weights from 3,000 to 5,000. This suggested that rubber would be much higher, as it would inevitably break up during hydrogenation. He estimated the length of the rubber macromolecule at 8,100 Ångstrom units. On the basis of osmotic pressure measurements of rubber in benzene, Meyer and Mark [25] considered the molecular weight to be as high as 250,000. Schade [31] has summarized the position by the comment that calculations indicate that from 200 to 4,400 C_5H_8 units for the rubber molecule according to the treatment to which it has been submitted.

Elastic Properties. So far as the structure of rubber in relation to its elastic properties are concerned, there has been the greatest confusion. A complete new orientation of ideas has come about in connection with the work on synthetic rubber. The clearest and most cogent exposition of the position has been made by Thomas, Lightbown, Sparks, Frölich and Murphree [39] as follows :

> The tradition that rubber properties were related to high unsaturation persisted and has led to numerous theories of elastic behaviour based on geometric structures resulting from unsaturated linkages. Whitby and Staudinger questioned the importance of unsaturation in determining rubber-like behaviour but encountered some difficulty in finding adequate support for this view, owing to the poor elastic properties of the practical examples available to them. Our studies on polymers of the simple mono-olefines, which have been in progress for the past ten years, have led to some interesting conclusions in regard to this point. It was shown that high-

molecular-weight linear polymers derived from simple olefines, such as the butylenes, possess a majority of the properties characteristic of rubber. Only the susceptibility to chemical action can definitely be attributed to the unsaturation of the natural rubber molecule. Physical properties which appear not to be intrinsically dependent upon the carbon-double bond-carbon configuration are: tensile strength, elasticity, rebound, elastic memory, X-ray structure, mechanical orientation, electrical properties, and fractional solubility. It was, however, conclusively demonstrated that the saturated polymers are not capable of vulcanization in conventional manner.

From these and other studies it is concluded that the chemical unsaturation, which is so important from the standpoint of permitting vulcanization to take place, is also the greatest weakness of the natural rubber molecule. The reason for this is that in the case of soft goods, which represent by far the major outlet for rubber, only a fraction of the available double bonds is utilized in the vulcanization with sulphur. The low but definite consumption of unsaturation during vulcanization of rubber was first pointed out in 1912 by Spence and Scott. Their conclusions were further confirmed by Boggs and Blake and by Brown and Hauser. The latter showed that there is evidence of overcuring after as little as 2 to 3 per cent. of the unsaturation has been used up. The large residual unsaturation is responsible for the pronounced chemical reactivity of soft rubber goods. It is this unsaturated character which makes natural rubber so susceptible to oxidation with consequent deterioration on ageing and disintegration when subjected to the action of ozone. It is also responsible for its lack of resistance to such chemical agents as strong mineral acids, and also to its lack of heat stability under oxidizing conditions.

As a result of this analysis, they have been able to develop new synthetic elastics—butyl rubbers—from which many of the undesirable properties of natural rubber are absent.

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CHAPTER 6

RAW MATERIALS: ALCOHOL AND ACETYLENE

Raw Materials. Many years ago the idea of using isoprene as the fundamental raw material was discarded owing to the apparently insuperable difficulties of obtaining it. Nor has any polymer been obtained from it with physical properties close to those of natural rubber. For years the quest for synthetic rubber hinged on discovering a cheap source of isoprene. Tapping pine trees for turpentine offered no advantage over tapping rubber trees for latex. Nearly all work has been founded on butadiene. It would be foolhardy to assume that this is conclusive. It is not. For isoprene is being made from turpentine on a very large scale by the Hercules Powder Co.[20] It is also being made by the Standard Oil Company from butyl alcohol in large quantities. The amounts involved are larger than the butyl rubber programme requires.

The great problem in the production of butadiene has been to obtain at low cost a molecule of some sort having four carbon atoms in a row. That is why the earlier efforts were based on materials such as butyl alcohol and isobutyl alcohol. For these alcohols, and indeed alcohols in general, can be easily and smoothly dehydrated to yield the respective olefines—butylene and isobutylene in the above cases. Simplifying this, it seems evident that the key material is actually ethylene.

As Dunstan [12] has put it, ethylene, propylene, butylenes and amylenes "are the authentic chemical bricks of our new synthetic chemistry—the chemistry of rubber, of plastics, and of polymers of various degrees of complexity . . . such chemical bricks are of outstanding importance and value".

As already stated, butyl alcohol was the chief starting-point used by the English workers on synthetic rubber.[32] It was obtained by the Fernbach [17] fermentation process. This fermentation of starches by means of enzymes was developed further by Weizmann,[3] who was a member of the research team led by W. H. Perkin, junior, and which included Matthews and Strange.

Thus secondary butyl alcohol, which is obtainable in fairly large quantities, can be converted into butadiene without untoward difficulty. It is dehydrated by passing over a catalyst—phosphoric acid—at

450° C., to yield an olefine—butylene. This may be easily brominated If followed by removing two molecules of hydrogen bromide, the resulting product is butadiene.

$$\underset{\text{Sec. Butyl Alcohol}}{CH_3.CH(OH).CH_2.CH_3} \xrightarrow{\text{dehydrate}} \underset{\text{Butylene}}{CH_3.CH{=}CH.CH_3} + H_2O$$

$$\xrightarrow{\text{bromine}} CH_3.CHBr.CHBr.CH_3$$

$$\xrightarrow{\text{remove 2HBr}} \underset{\text{Butadiene}}{CH_2{=}CH{-}CH\ \ CH_2}$$

FIG. 10. Butadiene from Secondary Butyl Alcohol.

The Use of Ethyl Alcohol. Ethyl alcohol has been one of the chief raw materials utilized for the production of butadiene. It has been the basis of many synthetic processes. In view of the importance of alcohol to other chemical industries and the plastic industry, it is worth while closely considering this angle. This use of alcohol to make butadiene had encountered great competition from cheaper raw materials. Latest activities in the United States have completely altered the picture. Alcohol from grain is one of the main planks in the current synthetic rubber production.

For many years alcohol derived from potatoes was the chief starting material used in the U.S.S.R. Since production of synthetic rubber has there been carried out on a large scale, no doubts can be entertained as to its practicability. Its use for making synthetic rubber had been strongly recommended in France, where large excesses of ethyl alcohol were available. It is also known that the projected production of synthetic rubber in Italy was also being partly based on alcohol (the remainder on acetylene, to fall in line with German practice).

The use of alcohol is no departure from the rule that the fundamental unit in these syntheses is ethylene, for the dehydration of ethyl alcohol gives ethylene:

$$CH_3.CH_2.OH \rightleftharpoons CH_2{=}CH_2 + H_2O$$

Although alcohol is a cheap industrial material, yet in view of the subsequent processing involved it is not cheap enough. Most alcohols are manufactured by fermentation processes based on sugars.

The principal sources are:

1. Starchy materials, such as potatoes, corn, barley, etc.
2. Cane-sugar, molasses, beet-sugar, etc.
3. Wines.

Seen in this light, the raw materials are essentially agricultural and, as such, dependent on the vagaries of nature and the food situation.

The processes involved in the production of alcohol are, briefly:

(*a*) The conversion of starchy raw materials into solutions containing sugar;

(*b*) The fermentation and decomposition of the sugars, and

(*c*) The distillation of the alcohols formed.

The position has changed somewhat with improved catalytic methods. The estimate of possible yields of alcohol from the various sources is of great interest.

TABLE 24. YIELD OF ALCOHOL FROM AGRICULTURAL PRODUCTS [23]

Raw Material	Alcohol—Gal./acre	Yield—Gal /ton
Sugar Beet	287 0	22 1
Sugar Cane	268 0	15 2
Jerusalem Artichokes	180 0	20 0
Potatoes, White	178 0	22 9
Potatoes, Sweet	141 0	34 2
Apples	140 0	14 4
Raisins	102 0	81 4
Grapes	90 4	15 1
Corn	88 8	84 0
Rice (rough)	65 6	79 5
Molasses (blackstrap)	45 0	70 4
Grain Sorghun	35 5	79 5
Wheat	33 0	85·0

Whenever agricultural surpluses have accrued, it has been suggested to utilize them for the production of synthetic rubber. It has been put forward as an outlet for the enormous over-production of sugar which has been the rule in recent years. The idea of obtaining rubber from potatoes excited great interest at the beginning of the century. Even in this country, when there has been a surplus of potatoes, suggestions have been made to utilize them for synthetic rubber. Until recently only the Russians had been bold enough to attempt the use of alcohol on a really large scale, starting from potatoes. Moreover they have made the process very efficient for they claim to obtain 600 gallons of alcohol per acre of potatoes. The occasional abundance of corn in some countries has also been a source of interest in this connection.

Activity in the United States has been such that the Baruch Committee recommended the immediate erection of plants to produce 100 million gallons a year on sites near the grain-producing areas. The actual programme far outstrips this. In 1943 in the United States, it is

intended to make 510 million gallons of alcohol chiefly from wheat and corn. Of this some 200 million gallons are scheduled for synthetic rubber. Improved accelerated methods of fermentation have latterly been developed which improve the production of alcohol. Thus the latest methods show a yield of 2·5 gallons per bushel of corn and 2·7 gallons per bushel of wheat.[39]

Much work has been carried out to explore the possibilities of producing synthetic rubber from corn, wheat and other surplus farm crops. Some controversy has arisen as to the merits of making butadiene from alcohol by a number of steps through the aldol process or by a shorter procedure. Thus Standard Oil Co. of N.J. working with aldol estimate to produce 2·2 lbs. butadient per gallon of alcohol.[36]

On the other hand Carbon and Carbide Union [5] have a two-step process for the production of butadiene from alcohol. Part of the alcohol for their large butadiene programme is to come from grain. The Szukiewicz process based on alcohol, which involves passing alcohol over a heated catalyst, results in a yield of 75 per cent. butadiene by a single pass (v.i.).[34]

Yet another alternative was the proposal to prepare alcohol from waste sulphite liquors from pulp mills, put forward by McCarthy.[27]

A new process has been announced from the United States recently, by Christensen,[7] whereby synthetic rubber can be made from agricultural products. It is claimed that 10 lbs. of synthetic rubber can be obtained from a bushel of wheat, corn, or other agricultural material containing starch or sugar.

The procedure takes the following course :

(i) Preparation of 2.3-butylene glycol by fermentation of sugar or farm crops.
(ii) Evaporation of solution to one-third original volume.
(iii) Glycol is removed by solvent extraction or distillation.
(iv) Conversion of glycol into butadiene by a vapour phase catalytic process.

The process would also yield vinyl compounds from glycol and alcohol, which can also be used to make synthetic rubber. The principal rubber ingredients can be made for 10 cents a pound. The rubber could be produced at 20 cents per lb., and 600,000 tons would involve about 5 per cent. of the U.S. corn crop, or 120 million bushels.

A pilot plant for the production of butadiene from grain by a fermentation process to make butane-diol as intermediate, is being built by the Seagram Company. Apparently the procedure is to

ferment grain with *Aerobacter aerogenes* for a period of about 40 hours, after which reaction is 90 per cent. complete in conversion to 2·3 butylene glycol. The greatest difficulty lies in separating this from the charge. Butyl alcohol appears to be the best selective solvent for the purpose. The final conversion into butadiene is carried out by forming butylene glycol diacetate which is heated at 500° C. giving a yield of 88 per cent.[15] Yields are between 6·8 and 7·5 lb. butadiene per bushel of corn.

By-products in the manufacture of ethyl alcohol from fermentation spirits include such materials as butyl alcohol, which, of course, can also be used to produce butadiene. Obviously the commercial factors are even greater against this being used as a major source.

Other Agricultural Products

According to Hecht and Reppe,[19] butadiene is produced by leading another agricultural derivative tetrahydrofurane in the gas phase at temperatures between about 250° and 450° C. over a phosphate catalyst having an acid reaction.

The United States Bureau of Agriculture at its Peoria Laboratory of the North-Western University, has made an outstanding development in the production of synthetic rubberlike material from agricultural sources. They have produced a synthetic elastic by the polymerisation of fatty acids obtained mainly from soya bean oil, together with ethylene glycol. The raw materials involved are soya beans, corn, and some vegetable oils. The generic name is Norepol.[30] One commercial type made by the Reichhold Company is known as Agripol.[35]

In general it may be handled just like rubber, the same range of compounding and vulcanizing ingredients being utilized. Similar vulcanizing conditions and times likewise apply. The products do not show such high tensile strength, nor is the resistance to abrasion as good as that of rubber. There appear to be many applications for this material and a production programme of about 20,000 tons is envisaged for 1943.

Articles in production include heels, fruit jar rings, tubing, and gaskets. The tensile strength is of the order of 500 lb. per square inch as against 3,000 lb. for rubber, while elongation at 200 per cent. is less than the 600 per cent. elongation of comparable rubber compounds.

Synthetic Alcohol as a Possible Source. Apart from new possibilities envisaged by the traditional production of alcohol based on agricultural materials, there appear to be possibilities in the synthetic

production of alcohol. The cheap production of ethyl alcohol is a matter of extremely great importance to chemical industries generally. It is estimated that in the United States there is adequate ethylene available to make 1,000 million gallons of alcohol a year.[13]

Ethylene is available in enormous quantities from coke-oven gas, and from petroleum products. Ethyl alcohol can be obtained synthetically from ethylene, reversing the procedure already outlined. Of late there has been a strong trend towards its synthetic production. This has been particularly the case in Great Britain, where activities started as early as 1919. In recent years it has made great strides and is already competitive with ethyl alcohol obtained by fermentation processes. The chief conversion process depends on the fact that ethylene reacts with sulphuric acid to give ethyl hydrogen sulphate, which, when hydrolized, yields ethyl alcohol.

Although this is still the leading synthetic process, new methods are well advanced which in due course may produce much cheaper material. The outstanding trend in this direction is the catalytic hydration of ethylene in the vapour phase under the influence of catalysts, such as sulphuric acid, sulphonated acids, etc., at temperatures of 150°–300° C.

There is a trend for carrying out continuous production of alcohol by treating ethylene with dilute sulphuric acid at high temperature and pressure, which avoids any necessity for reconcentration.

The Standard Oil Company of New Jersey,[36] when recently expanding their plant at Baton Rouge, La., to produce 10,000 tons of Buna S from petroleum and 5,000 tons of butyl rubber, included as part of the programme the production of 20 million gallons of alcohol.

Synthesis of Butadiene from Alcohol. Once alcohol was available the general method employed was to oxidize this to acetaldehyde. Thereafter this was subjected to aldol condensation. That is to say, under the influence of a small amount of alkali two molecules of acetaldehyde combined to form a new molecule of aldol. This was one of the earliest known examples of polymerization. The production of butadiene via acetaldehyde is an indirect process requiring a number of stages. Yet it is the basis of German production. The strangest feature of this is that it provides an outstanding example of history repeating itself. The process was first developed by W. H. Perkin, junior, and his associates in 1912. Yet synthetic rubber had the identical frigid reception in Great Britain accorded to synthetic dyestuffs prior to the last war, and which were also subsequently developed by the Germans.

The Russians appear to have achieved some considerable measure

of success by a direct method with ethyl alcohol. The production of the chief Soviet type of synthetic rubber, S.K.B., was a direct process based on alcohol obtained from potatoes. The process was developed by Lebedev,[25] and utilized ethyl alcohol, or propyl, or isopropyl alcohols. The method was comparatively simple. The alcohol obtained from potatoes was passed over a mixed dehydration and dehydrogenation catalyst such as alumina and zinc oxide, at a temperature of 400° C. The reaction product was strongly cooled. The uncondensed gas containing most of the butadiene was washed with turpentine or petrol, which removed the butadiene. This was separated and rectified by distillation. The yield of butadiene was said to be 34 per cent. According to Petrenko [33] there have been considerable improvements in recent years. During 1939 the yield of butadiene from alcohol rose to 36·25 per cent. compared with 32·5 per cent. in the previous year. At the end of 1939 the yield was at 41 per cent., representing 70 per cent. of the theoretical. Thus the consumption of alcohol per ton of synthetic rubber decreased from 3·288 tons in 1938 to 2·806 tons in 1939.

Ostromislensky [31] discovered that a mixture of alcohol and acetaldehyde could be made to condense when heated in the presence of a catalyst such as kaolin, with the formation of butadiene. Incidentally, Ostromislensky, in the course of his researches for synthetic rubber, carried out much of the fundamental work which has led up to the commercial application of polyvinyl resins, notably with vinyl chloride.

Bearing in mind these Russian developments it is interesting to consider the United States activities in closer detail. The leading method practised by the Carbide and Carbon Union makes butadiene on the largest possible scale from alcohol and acetaldehyde, i.e. from alcohol. The Publicker (Szukiewicz) process is also well under way. Most of the alcohol used comes from grain, etc., by improved fermentation processes.

At the present time, 240,000 tons of synthetic rubber per year is scheduled for production based on butadiene from alcohol. The major portion of this is being made by the Carbon and Carbide Union, based on alcohol, chiefly derived from corn and wheat. This company is also using synthetic alcohol. They have a very successful process, and have led the way in getting into production.

The other alcohol process of interest in the United States is known as the Publicker Process, developed by Szukiewicz. He had built plants in Poland and in Italy before the war. At first the value of his process was underestimated. Investigation proved it to be at least as

effective as any other. Superficially it appeared to have a number of features in common with the Carbon and Carbide process; closer examination shows this is not the case.

The Carbon and Carbide Process.[5] Alcohol and acetaldehyde are catalytically converted into butadiene. This is separated from the by-products and unchanged alcohol and acetaldehyde, which are re-used. The converters consist of 753 steel tubes, 20 ft. long by 3 in. diameter, containing catalyst. The tubes are surrounded by a temperature regulating bath of "Dowtherm" liquid. A 20,000-ton unit possesses 12 such converters, 4 converting alcohol to acetaldehyde by means of one catalyst, and 8 making the butadiene with another catalyst. So that it is a two-stage process. The yield is about 2·3 lb. of butadiene per gallon of 95 per cent. alcohol. The catalyst becomes foul after a time, and is cleaned by passing air over to burn off the carbon. During a single passage, about 10 lb. of the alcohol mixture has to be vaporized to give 1 lb. of butadiene, the remainder being re-cycled and used again. The butadiene is obtained 97 per cent. pure.

The Publicker Process.[41] In this case alcohol alone is employed. It is vaporized and passed over a catalyst at about 400° C., being converted substantially into butadiene. The butadiene has to be separated from the other reaction products. The set-up resembles that for the previous process, i.e. many tubes, this time 10 feet long by $1\frac{1}{2}$ inches diameter. They are heated by molten salt. The catalyst is in due course poisoned by the deposit of carbon which is then burnt off with a stream of air and the catalyst regenerated. The catalyst is a uranium salt.

Advantage of the process is that alcohol is converted into butadiene in a single stage, the conversion reaching 75 per cent. The yield of butadiene is 2 3 lb. per gallon of 95 per cent. ethyl alcohol with the prospect of reaching 2 5 lb. per gallon.

The by-products, apart from butadiene, contain mainly ethylene, butylene and water. The butadiene is obtained at 80 per cent. purity, and is comparatively easily purified up to the specified 99 5 per cent. It is of interest that the ethylene produced is more than adequate for use in the production of the requisite amount of ethyl benzene for the styrene involved in the conversion of the butadiene to Buna S. The comparison of the two processes is outlined in Table 25.

Considering both these processes from the engineering point of view on a large scale, it is clear that the vaporization of alcohol is not a difficult operation, nor is the passage over a catalyst. This contrasts with the complex high pressure arrangements involved in the case of the petroleum derivatives, and also the somewhat involved chemical

syntheses working from carbide. Of course, the butadiene in all the processes must be collected, separated and purified. Butadiene for making G-R-S (Buna S) must be 98·5 per cent pure.

TABLE 25. COMPARISON OF ALCOHOL PROCESSES [39]

	Carbide and Carbon	Publicker
(*a*) Alcohol converted to acetaldehyde	50 per cent.	None
(*b*) Pounds vaporisation of charge per lb. —butadiene	10	5
(*c*) Pounds condensation for re-use per lb.—butadiene	8	1½
CONVERTER		
(*d*) Tube Material	Steel	Steel
(*e*) Inside diameter of tube	3 inches	1½ inches
(*f*) Heating method	" Dowtherm "	Molten Salt
(*g*) Reaction Temperature	315 deg. C.	405 deg. C.
CYCLE		
(*h*) On Stream	6 days	4 hours
(*i*) Regeneration of Catalyst	1 day	2 hours
(*j*) Per cent. time on Stream	85 5 per cent.	66 7 per cent.
PRODUCTION		
(*k*) Lbs. butadiene per hour per lb. Catalyst	On Stream 1 5 Average hour 1 3	3 6 2 4
(*l*) Yield—lbs. pure butadiene per gallon alcohol (100 per cent. at 20 deg. C.)	2 3–2 4	2·1–2 2
(*m*) Purity of crude butadiene	97 per cent.	80 per cent.

It is interesting to compare the American experience from the point of view of critical materials. The following Table summarizes the known facts.

TABLE 26. CRITICAL MATERIALS, ETC., INVOLVED PER 1,000 TONS BUTADIENE [39]

Process	Steel	Copper	Chrome	Nickel	Compressor Capacity Horse Power
	Tons	Tons	Tons	Tons	
Petroleum (Butane)	165	9 0	5·0	2	
Petroleum (other Processes)	194	—	—	—	312–490 H.P.
Alcohol (Carbon and Carbide)	140	50·6	2 2	1	180 H.P.
Alcohol (Publicker)	100	10	0·1	—	100 H.P.

Acetylene—An Established Source of Synthetic Rubber.—At the present time one of the chief sources of butadiene, chloroprene, ethenoid resins, etc., is undoubtedly acetylene obtained from calcium carbide. Acetylene is also obtained in large quantities from coal hydrogenation, petroleum wastes, etc. Acetylene can be obtained by the pyrolysis of methane, of which, throughout the world something like 10 million tons a year is available.

Carbide is one of the most important industrial chemical raw materials; which seems to be a very satisfactory reason for neglecting it in this country. For many years the Germans have concentrated on the use of carbide as a source of numerous chemicals, notably acetaldehyde, acetic acid, and numerous other derivatives. It is one of the mainstays of their chemical industry. It is certainly the backbone of their synthetic rubber industry and their plastics industry. Prior to the war they were consuming 600,000 tons per year. With present synthetic rubber capacity, the figures must be far in excess of this. We normally import about 60,000 tons per year.

Among leading important industrial materials obtained from acetylene are:

Acetic acid, which is important for so many chemical industries including rayon, plastics, dyestuffs, explosives, etc.;

Ethyl alcohol, which is necessary as a solvent for dyestuffs, chemicals, explosives, motor fuel, etc.;

Acetone, which is essential for explosives, for lacquers, and innumerable chemical processes;

Ethyl acetate, which is a leading solvent;

Trichlorethylene; and a host of other synthetic chemicals, plasticizes, solvents, etc.

It is the parent material of numerous plastics, including the leading ethenoid resins such as polyvinyl chloride, polyvinyl acetate, etc. It is a source of vinylacetylene from which chloroprene is made, and other polymers which have attained commercial significance. It is also the source of acetylene black, one of the leading filling materials in a number of industries, including rubber.

The importance of the carbide industry to plastics and industry in general has often been stressed. Unfortunately, all efforts to start carbide manufacture in this country have so far proved abortive. The importance of carbide and therefore coal as a source material has never been fully appreciated in Great Britain. Some indication of the significance may be gained from Fig. 10A.

The Manufacture of Calcium Carbide. The commercial manufacture of calcium carbide was started towards the end of the last

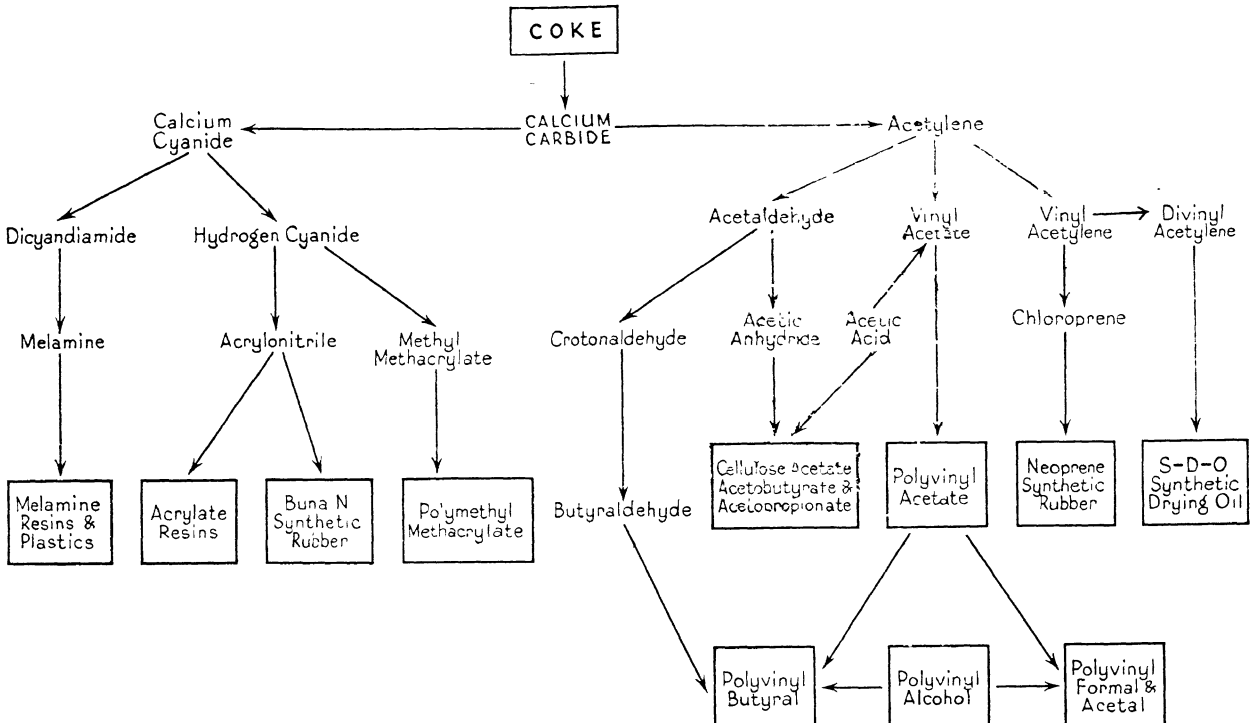
COKE
CALCIUM CARBIDE
Calcium Cyanide
Acetylene
Dicyandiamide
Hydrogen Cyanide
Acetaldehyde
Vinyl Acetate
Vinyl Acetylene
Divinyl Acetylene
Melamine
Acrylonitrile
Methyl Methacrylate
Crotonaldehyde
Acetic Anhydride
Acetic Acid
Chloroprene
Melamine Resins & Plastics
Acrylate Resins
Buna N Synthetic Rubber
Polymethyl Methacrylate
Butyraldehyde
Cellulose Acetate Acetobutyrate & Acetopropionate
Polyvinyl Acetate
Neoprene Synthetic Rubber
S-D-O Synthetic Drying Oil
Polyvinyl Butyral
Polyvinyl Alcohol
Polyvinyl Formal & Acetal

FIG. 11.

century, and is now the largest consumer of energy in the electric-furnace industry. The chief considerations in establishing a carbide factory are supplies of raw material which consist of limestone and coke or anthracite, and an abundant supply of cheap electric power. The latter item contributes the chief cost factor. It is found that many large carbide factories have been set up on sites where cheap hydro-electric power is available. The preparation of raw materials is a matter of some importance owing to the high temperatures involved. The limestone, which is calcium carbonate, is heated at a very high temperature in lime-kilns to drive off carbon dioxide. The present-day practice employs lumps of lime reduced to pieces from 1 to 2 inches in size, while coal is reduced to pieces between $\frac{1}{4}$ and $\frac{1}{2}$ inch mesh. The ingredients are mixed in proportions of about 100 parts of lime to 65 parts of coal. The electric furnaces used are of special construction and have to withstand temperatures up to 3,000° C. Enormous electrodes are employed, ranging up to sizes of about 22 inches square. It is said that the progress in the design of electric furnaces for high temperatures follows developments in carbide manufacture.

As a result, manufacturing plants are chiefly located where there is unlimited water power. Norway and Sweden have been the chief European producers, although requiring to import the coal. Great Britain has been almost the only industrial country without carbide industry. The United States and Canada are very large producers of carbide, possessing all the conditions necessary. The advances in the production of thermoplastics have largely come about because of this extensive manufacture.

The actual production of carbide involves heating a mixture of lime and coal in electric furnaces by means of the electric arc. Extremely high currents are passed through built-up electrodes, one typical modern plant, for example, using 10,000 kilowatts on a single three-phase supply. The temperature reaches 3,000° C., when a fluid melt of carbide is formed and may be tapped off. The batch size is of the order of four tons in the most efficient plant, the furnace being continually fed with fresh materials. The largest commercial units produce about 200 tons per day. According to Bingham,[3] one ton of carbide requires 4,250 units of current for its manufacture, including the amount required for crushing, grinding and all other processes. It is quite certain that the power consumption is now much less than this figure.

Large capacity carbide plants are features of the enormous German synthetic rubber-manufacturing units.

The following account by Ambros [2] of the process carried out at the

enormous Schkopau Buna Works gives some idea of the principles adopted.

The synthesis of rubber depends upon the solution of two fundamental problems—

1. A smooth commercial process for the synthesis of the parent material, butadiene, is required.
2. A method for polymerizing this fundamental material into a product which will behave for all practical purposes as if it were natural rubber.

There are various ways for obtaining butadiene. At Schkopau a four-stage process is carried out; in the first, acetylene is formed into acetaldehyde, which in the second stage undergoes the aldol condensation. In the third stage the aldol is dehydrated to 1.3-butylene glycol, and in the final stage by removing water, butadiene is obtained.

Starting from coal which is converted into carbide, acetylene is obtained. From this material containing two carbon atoms the four-carbon compound butadiene is formed via acetaldehyde. A difficult process, but one which has been technically mastered.

Acetylene Production. Carbide is manufactured at a large carbide works. The notable things about this factory, which has the most modern carbide furnace in the world, includes the amazing freedom from dust, which is carried away by very comprehensive and efficient equipment. Another noticeable feature is the great extent to which mechanising and automatic control of the various furnace processes has been carried. The furnaces are fitted with external instruments which control all measuring, mixing, and regulating equipment, all of which are simultaneously co-ordinated, being supervised by specially skilled operatives. For example, the movement of the electrodes, the addition of coke and lime, etc., are all adjusted by these external controls. The mighty furnaces work continuously, the power being obtained from mid-German brown coal; the resulting carbide comes to the ovens as a molten white fluid, and enters a sealed water-cooled inclined conveyer, on which it cools down, and in so doing breaks into small pieces, so that at the end of the run cooled and crushed carbide is obtained.

This carbide is ground to powder in a separate mill, and then goes to the gassing chamber, which works so that gassing is carried out without the formation of sludge, as a result of which dry finely powdered lime remains. This gassing chamber is also fully mechanized, being operated by a few skilled men with the help of centralised controls. The remaining spent lime is partly used for agricultural purposes, while part is regenerated by burning and is used once again in the furnace. In this manner it has become possible to utilise a considerable portion of reclaimed lime in the manufacturing process.

Preparation of the Chief Product. Acetylene is now converted into butadiene in a row of various installations. These installations are spaced well apart in the extensive grounds of the works, not only so that there should be room for further development, but also to facilitate the co-ordination of other manufacturing operations, including synthetic resins. There is another leading consideration to account for this spacious layout. The user of the greatest bulk of raw material, in this case the carbide oven, is located in the

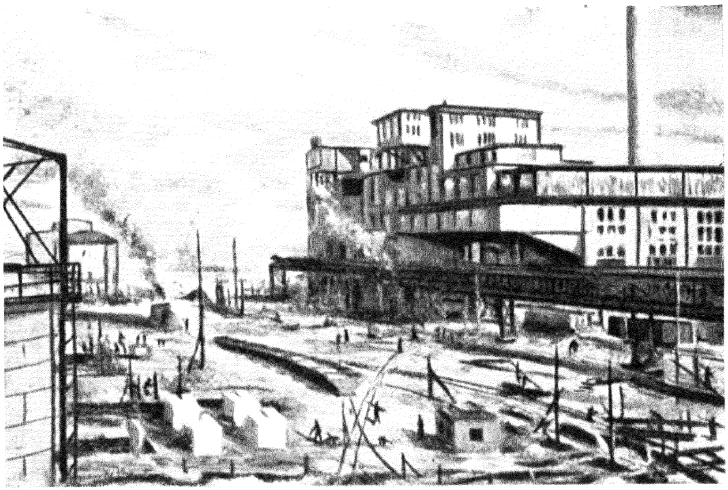

FIG. 12.—The carbide plant at Schkopau.

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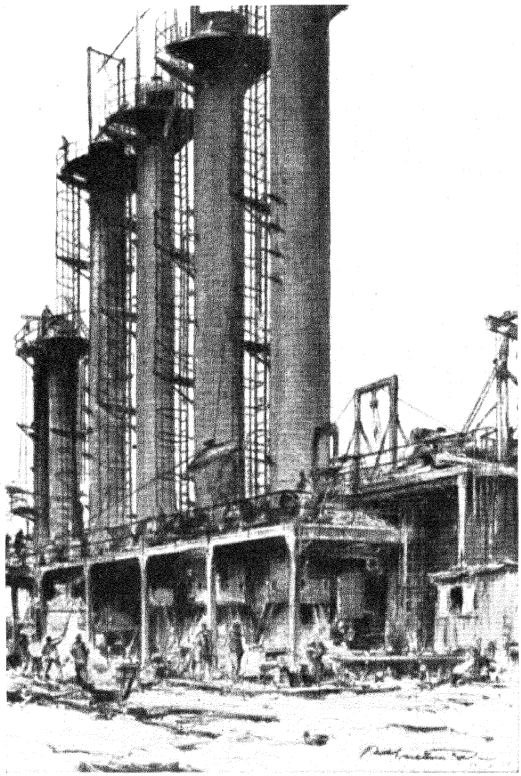

FIG. 13.—Fractionating columns at the Buna works.

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chief communication route and also the navigation route, whereas the remaining operations are further away, so that the further the product progresses in the chemical operations, and the more valuable it becomes, so the less important become the transport costs. There is another consideration in the planning, for by laying out the main conveyance in an East-West direction, advantage is taken of the predominating wind for thorough ventilation of the works, those works giving off dust, being grouped together and arranged to take advantage of the predominating wind, so as generally to achieve elimination of dust, soot and undesirable gases.

The various operations for the production of the chief material, to which must also be added the plant for making styrene, which is used in copolymerisation with butadiene, are likewise extensively mechanised. To a great extent they are exposed to the atmosphere with just a roof over the top, some being completely exposed. A typical example, are the rectifying columns which, suitably insulated, stand in the open, whereas the other parts of the equipment such as pumps, and so on, are half-covered, while the control rooms which supervise the installations lay back.

It has been stated by the Deutsche Bank that the production of a ton of Buna synthetic rubber requires 40,000 kilowatt hours. According to the *Electrical Times*,[14] electrical energy is dearer in Germany than it is here. They assumed a figure of 0·25*d.* per unit, on which basis the cost of electricity alone would be about 4·3*d.* per lb. of Buna rubber. Presumably most of this electricity would be used in the carbide production.

Butadiene from Acetylene. Acetylene is obtained from carbide by addition of water. For the manufacture of butadiene the next step is to produce acetaldehyde. The manufacture of acetaldehyde from acetylene is carried out by passing acetylene into a dilute sulphuric acid solution containing a catalyst generally composed of mercury salts. This is one of the fundamental reactions of industrial chemistry. It appears that this is the basis of the major portion of Germany's large-scale production of Buna synthetic rubbers.

Acetaldehyde is polymerized to aldol by means of dilute alkali. Aldol is hydrogenated by passing hydrogen under pressure at a temperature of 100° C. in the presence of a nickel-alumina catalyst; it is converted almost quantitatively into butylene glycol. This has to be dehydrated in order to yield butadiene. The most popular method adopted by the I.G. was to pass the vapour at a temperature of about 200° C. over a catalyst comprising salts such as calcium or sodium phosphate, and thereafter freezing out the butadiene. Satisfactory commercial yields were claimed for this method. The yield is claimed to be quite high.

When starting either from alcohol or from acetylene it is quite evident that acetaldehyde is the real starting point in the production of

butadiene. There seems little doubt that in the weighing up of the respective merits of these raw materials, carbide is far cheaper. In fact acetylene has been seriously considered as a source of alcohol. At any rate, the use of carbide has expanded even in the U.S.S.R.

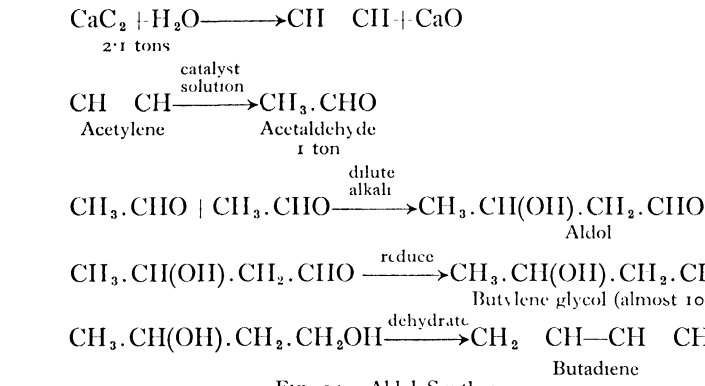


FIG. 14. Aldol Synthesis.

Another method for making butadiene involves the direct union of acetylene and ethylene at 50 atmospheres pressure and 500° C. in tubes containing alkali metal oxides.

The United States is a large producer of calcium carbide. As a result, the firms concerned have played a leading part in developing thermo-plastics of the vinyl type, for example, the Carbide and Carbon Corporation, specializing in carbide production was responsible for the first large-scale commercial production of polyvinyl chloride and its copolymers in the form of Vinylite products. In a similar manner Shawinigan Corporation in Canada has been largely responsible for the development of products such as vinyl acetates, alcohols, formals, acetals, etc.

B. F. Goodrich Co. have a very large plant at Niagara where the raw material for Koroseal (polyvinyl chloride) is prepared.

It is interesting to note that the United States firms would not launch out into synthetic rubber production on an acetylene basis. With all their resources of lime and coal and unlimited cheap electrical power, they held back. There is much evidence to show that they were nevertheless extremely interested in the possibility, being cautious merely because of the developments with petroleum products which they knew lay ahead.

Many other methods have been devised for making butadiene from acetylene. When acetylene is passed into dilute solution of cuprous chloride monovinylacetylene is formed. Thus Leuhdeman, Reppe and

Rothhaas [25] continuously converted monovinylacetylene into butadiene by bringing it into contact with an aqueous solution of an alkali metal by dioxide and zinc dust, these being added continuously as they are used up. The butadiene formed is continuously removed. Acheman, Lehrer and Stadler [1] treated vinyl acetylene with amalgams of alkali metals in the presence of water or an alcohol which develops hydrogen.

According to Hurukawa,[21] acetylene bubbled into aqueous copper chloride-ammonium chloride mixture gave about 20 per cent. conversion of acetylene, and production of 73 per cent. by weight of monovinylacetylene. Ethyl acetate or acetone solution of monovinylacetylene hydrogenated with palladium black or palladium-kieselguhr gave about 60 per cent. yield of butadiene. Zinc and alkali as reducing agent gave over 95 per cent. yield of pure butadiene. The small amount of monovinylacetylene remaining in the butadiene can be completely removed by sodium or sodamide.

Another German method for obtaining butadiene from butylene glycol is as follows: [9]

Water is split off from 1 : 3-butylene glycol by means of dehydrating catalysts such as sulphuric acid, acid salts of sulphuric acid, sulphonic acids, phosphoric acid, and so on, in the presence of a large amount of water. For example, 80 parts of the glycol dissolved in 20 parts of water was passed at a rate of about 800 parts per hour into 2,000 parts of 1 per cent. sulphuric acid boiling at about 200° C. in an autoclave, the butadiene formed being withdrawn as fast as it is formed. The water produced by the splitting is drawn off with the help of a separator, and the process can proceed for indefinitely lengthy periods.

According to the I.G.[22] butadiene can be obtained in good yields from normal butylenes by leading them in admixture with at least an equal volume of inert gas (nitrogen, carbon dioxide, steam) at preferably 680°–710° C. over graphite or lustrous carbon at such high speed that the butylene is not in contact with the carbon for more than one second. The carbon is desirably free from iron and alkali, and may be supported on a carrier (silica gel, aluminium or magnesium oxide). In the second application, it is claimed that butadiene is obtained when the dilution with inert gas is very low or zero, but the speed through the carbon has to be increased still further when the butylene is undiluted.

Butadiene has also been obtained by heating such things as naphthenes, terpenes, cyclohexene, cyclohexane, etc., usually at temperatures of 550° C. to 700° C. in the presence of catalysts such as aluminium silicate, calcium alumniate, oxides, phosphates, and chromates on silica gel, platinum, quartz, and strontium uranate.

Chloroprene. The statement about American reluctance to pro-

ceed from acetylene must be qualified to cover only straight butadienes, as a basis for synthetic rubber. For the first commercial elastomer—neoprene—was developed by Du Pont de Nemours, and was derived from acetylene.

Actually, of course, acetylene was the raw material employed in the production of chloroprene, the monomer used for making neoprene. Chloroprene is a substituted butadiene. This production was almost entirely due to the fundamental work of Nieuwland [28] on the polymerization of acetylene.

According to Bridgewater,[4] "In 1925 Du Ponts were engaged in research towards the production from acetylene of a synthetic rubber that would excel natural rubber in certain respects, but our results had been most disappointing."

At that time they became aware that Nieuwland had obtained good results for the polymerization of acetylene by using copper catalysts. He was able to provide the essential first step towards the direct manufacture of a butadiene derivative from acetylene that could be polymerized. By means of his methods two acetylene molecules could be made to form a four-carbon chain. By passing acetylene through a highly concentrated solution of cuprous chloride and ammonium chloride catalysts, he was able to produce monovinylacetylene and divinylacetylene. The method was subsequently outlined by Nieuwland, Calcott, Downing, and Carter.[29] In due course Downing, Carter and Hutton [8] were able to make this a continuous process. Monovinylacetylene is a colourless liquid, b.p. 5° C. having a density of 0·7095.

In a recent patent Du Pont de Nemours [11] obtained vinylacetylene from acetylene by polymerization in presence of a liquid mass of catalyst comprising water saturated with ammonium chloride and cuprous chloride in proportion 1·7 to 2·2 mols. to 1 mol. cuprous chloride, and not containing more than 0·6 per cent. of HCl, the catalyst being in contact with solid phase components including metallic copper. A temperature of 75° C. is appropriate.

In themselves these derivatives could not supply a satisfactory synthetic rubber; actually they are the basis of satisfactory synthetic resins, finding use for coatings. But the Du Pont team of research workers had the starting point and soon overcame existing difficulties. Carothers, Williams, Collins, and Kirby [6] discovered that monovinylacetylene could be quickly and smoothly converted into 2-chloro-1.3-butadiene. They called this chloroprene. The monovinylacetylene merely required to be treated with hydrochloric acid in the presence of cuprous chloride as catalyst. This was the basis of the first commercial synthetic rubber.

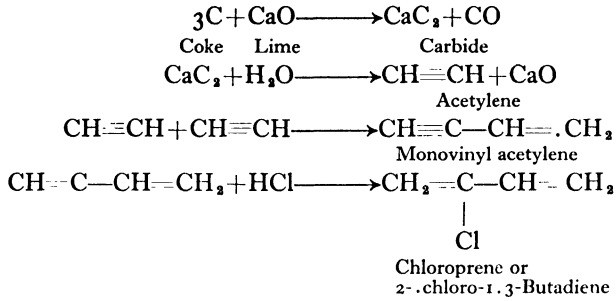


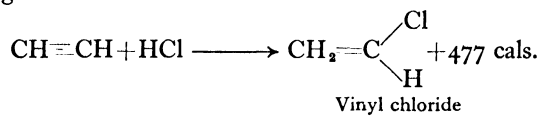
FIG. 15. Production of Chloroprene

Chloroprene is a pungent colourless liquid, boiling at 59·4° C., with a density at 20° C. of 0·9583, and refractive index 1·4583. It is notable for the speed with which it polymerizes spontaneously to form a rubbery polymer.

Production of Vinyl Chloride from Acetylene. The process of manufacture of vinyl chloride from acetylene actually consists of effecting the union of hydrogen chloride with acetylene in the presence of a catalyst.

The patent literature relating to synthesizing vinyl chloride from acetylene may be summed up in a fundamental formula of passing acetylene and hydrogen chloride, compressed up to 1–1·5 atmospheres, over a contact catalyst. The main points of difference among the many variations of this process being the definition of the temperature range, the selection of catalyst and the plant required for the procedure.

The synthesis of vinyl chloride by this method is carried through according to reaction :



The temperature level, with liquid catalysts, in the majority of cases is maintained between 60° and 80° C. The hydrochloric acid solutions of metal chlorides are the most popular catalysts used in the process.

The following reagents are recommended for application as dry catalysts : (*a*) mercuric chloride precipitated on silica gel ; in this case the process of obtaining vinyl chloride may be performed at reduced temperatures from 20° to 30° C. ; (*b*) activated carbon ; here the reaction is conducted at higher temperatures up to 200° C.

The yield of vinyl chloride on the basis of acetylene is usually of

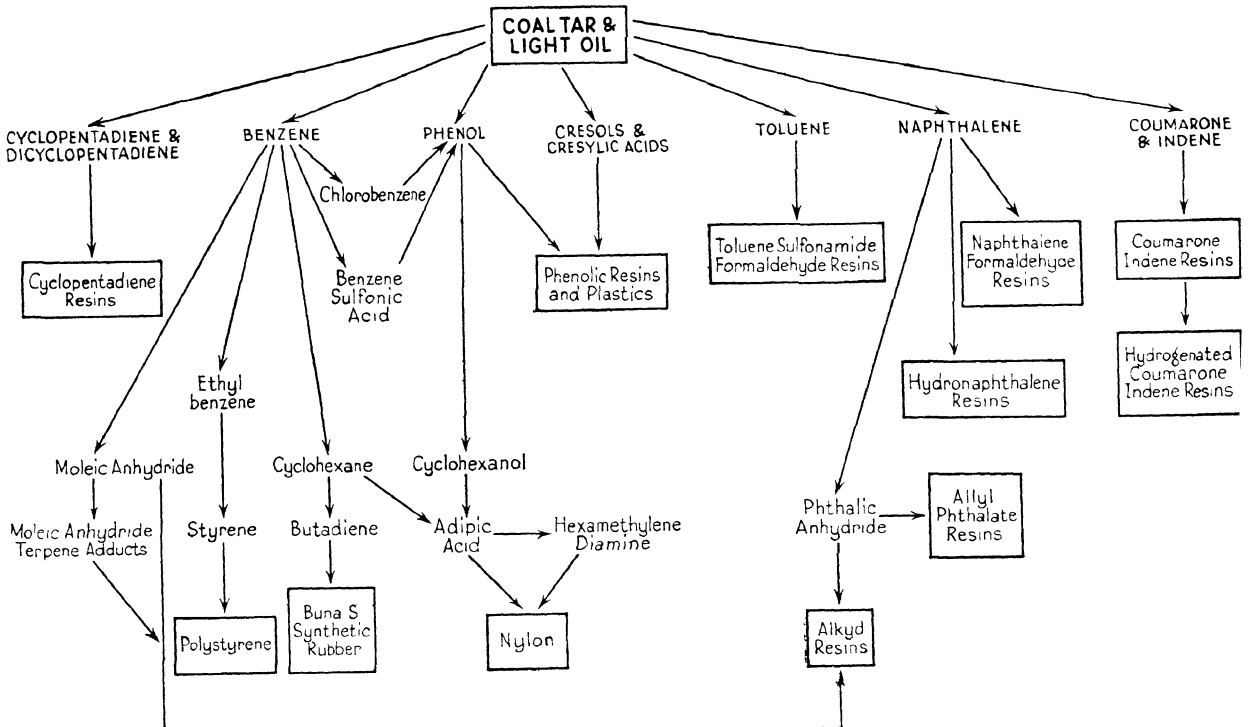

COAL TAR & LIGHT OIL
CYCLOPENTADIENE & DICYCLOPENTADIENE
BENZENE
PHENOL
CRESOLS & CRESYLIC ACIDS
TOLUENE
NAPHTHALENE
COUMARONE & INDENE
Chlorobenzene
Cyclopentadiene Resins
Benzene Sulfonic Acid
Phenolic Resins and Plastics
Toluene Sulfonamide Formaldehyde Resins
Naphthalene Formaldehyde Resins
Coumarone Indene Resins
Ethyl benzene
Hydronaphthalene Resins
Hydrogenated Coumarone Indene Resins
Moleic Anhydride
Cyclohexane
Cyclohexanol
Moleic Anhydride Terpene Adducts
Styrene
Butadiene
Adipic Acid
Hexamethylene Diamine
Phthalic Anhydride
Allyl Phthalate Resins
Polystyrene
Buna S Synthetic Rubber
Nylon
Alkyd Resins

FIG. 16.

the order of 55–70 per cent., and an additional heat economy in the process can be effected by re-circulating exhaust gases.

Judging by the numerous American patent specifications for deriving vinyl chloride from acetylene, it is evident that this method is definitely favoured in the U.S.A.

It is also worth while noting that the rapidly expanding use of the acetylene process for vinyl chloride synthesis in America is paralleled by a similar tendency in Germany. In that country the great reactivity of vinyl chloride, yielding derivatives of far-reaching technical and strategic importance, has been assiduously exploited and manufacture is carried out on a large scale.

Vinyl chloride is a commodity quite amenable to transportation, and may be conveniently carried in steel bottles or in tank-cars.

Some Further Aspects of the Importance of Coal. It is abundantly clear that coal through carbide plays a great part in the production of synthetic elastic materials. This is, however, only part of the story. For the interlocking of plastics with synthetic elastics greatly emphasizes the importance of coal as a source of raw materials. In the preparation of synthetic materials generally, including synthetic elastics, considerable quantities of chemical intermediates are involved. Coal has been the chief source of these intermediates, although in many cases they are now also derived from petroleum products, and on an increasing scale. These include such things as acetic anhydride, acetone, butyraldehyde, ethyl alcohol, ethyl chloride, formaldehyde, hydrogen chloride, methyl methacrylate, methyl alcohol, styrene, vinyl chloride and vinylidene chloride.

Thus synthetic elastics of one sort or another may be derived from the light oil and coal tar obtained by treatment of coal. These will include polystyrene, and the butadiene rubbers. For one method of making butadiene is by cracking cyclohexanes obtained from benzene.

Water gas is of course produced on an enormous scale from coke. This is of the greatest possible importance in connection with such synthetic elastics, which are also, of course, base materials for plastics, as acrylic esters, methacrylic esters, polyvinyl alcohol, etc.

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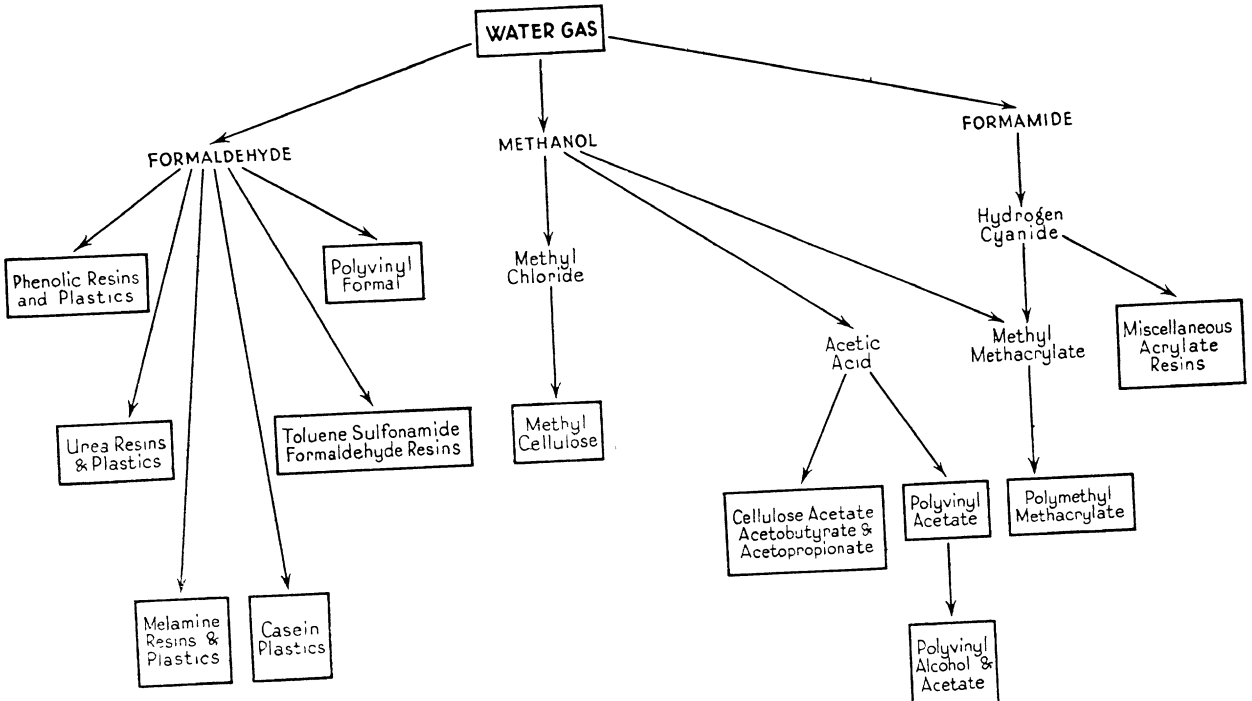
WATER GAS
FORMALDEHYDE
METHANOL
FORMAMIDE
Phenolic Resins and Plastics
Polyvinyl Formal
Methyl Chloride
Hydrogen Cyanide
Urea Resins & Plastics
Toluene Sulfonamide Formaldehyde Resins
Methyl Cellulose
Acetic Acid
Methyl Methacrylate
Miscellaneous Acrylate Resins
Melamine Resins & Plastics
Casein Plastics
Cellulose Acetate Acetobutyrate & Acetopropionate
Polyvinyl Acetate
Polymethyl Methacrylate
Polyvinyl Alcohol & Acetate

FIG. 17.

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CHAPTER 7

RAW MATERIALS—PETROLEUM

Oil as a Source of Synthetics. The immediate future of synthetic rubbers is closely connected with petroleum. This is due to the fact that the necessary raw materials may be obtained from this source at a remarkably low cost. The United States, as the world's greatest oil producer, is obviously favourably placed in this respect. As the greatest rubber consumer the question has added importance. It is interesting to note that the next largest oil producer is the U.S.S.R., which is also very actively interested in synthetic rubber production.

It is unnecessary to stress the general importance of oil. As in the case of coal, its primary function is as a source of power. But, while for many years an ever-growing number of commercial materials have been obtained from coal via coal tar, only in recent years has a similar trend set in for petroleum derivatives. The potentialities as a source for synthetic rubber and synthetic resins, etc., add further to its importance.

As petroleum is a major source of olefines, notably ethylene, it is not surprising that the industry should become interested in the growing field of synthetic resins. But as Frölich [14] has pointed out, " Because of its general set-up, the petroleum industry is, as a rule, dependent upon a relatively large scale of operation to obtain the full advantage of its low potential manufacturing costs." So that unless some great industry is affected, progress cannot be very rapid. Obviously, rubber is a major field offering scope for such large-scale operations. Thus the activity with synthetic rubber is likely to bring in its trail the other profound developments with synthetic resins. Without it their progress would be greatly retarded.

Frölich has drawn up the following list of products connected with the general aspect of synthetic rubber which are either now being manufactured wholly or in part from petroleum products, or for which the petroleum industry would be able to supply raw materials.

1. Natural petroleum resins by light hydrocarbon precipitation.
2. Cracking-coil tar resins by condensation of highly condensed petroleum hydrocarbons, such as those which are present in the tar bottoms from the cracking operation, with formaldehyde or ethylene chloride.

3. " Santoresin " by reaction of olefines and diolefines in the presence of aluminium chloride.
4. Polystyrene by polymerization of styrene, which may be produced from ethylbenzene made by alkylation of benzene with ethylene.
5. Polybutylene by polymerization of unsaturated gaseous hydrocarbons to give substantially linear polymers ranging in consistency from that of a viscous oil to rubbery materials with molecular weights as high as 300,000.
6. " Buna " rubber and similar products by polymerization of butadiene made from acetylene or from *n*-butylenes.
7. Neoprene rubber by polymerization of chloroprene derived from acetylene.
8. " Thiokol " by condensation of sodium polysulphide with ethylene dichloride or other chlorine-containing derivatives.
9. Polysulphones by reaction of olefines with sulphur dioxide.
10. Vinyl resins by polymerization of vinyl chloride and vinyl acetate derived from acetylene or ethylene.
11. Phenol-formaldehyde resins by condensation of formaldehyde with phenols.
12. Alkyd resins by reaction of dibasic acids with polyhydric alcohols—e.g. ethylene glycol and diethylene glycol, from ethylene; and glycerol which may be prepared from propylene.
13. Ethylcellulose by reaction of cellulose with ethyl chloride or diethyl sulphate produced from ethylene
14. Cellulose acetate by reaction of cellulose with acetic anhydride, which may be derived from ketene obtained by thermal decomposition of acetone produced by dehydrogenation of isopropyl alcohol.
15. Acrylate and methacrylate resins derived in various ways from olefinic compounds.

But particularly in regard to all these activities it has been shown time and time again that so many factors are changed when small-scale results are transferred to commercial unit operations that it is not safe to base commercial operations on small-scale results. This is another reason why full-scale operations with synthetic rubbers will profoundly influence plastics.

Waste in the Oil Industry. The history of oil is probably the most outstanding example of waste. And nowadays whenever there are wastes there is an almost automatic implication of plastics and synthetic rubber. From the time of its discovery in the United States in 1859, oil was prized most highly because of its kerosene content, becoming the fuel for oil lamps. All the low boiling fractions were regarded as a dangerous nuisance and were dumped. The high boiling fractions were equally useless. The arrival of the internal combustion engine in due course completely changed this situation, so that kerosene became very much a secondary material. The once embarrassing fluid now acquired paramount importance as motor fuel.

To bring the matter into its right perspective it is estimated that manufacturing cost of petrol in the United States is about 3 to 4 cents per gallon, while to produce it from coal costs about four times this amount.[2]

As the number of motor-driven vehicles expanded at a terrific rate, petrol production could not keep pace (incidentally, nor could rubber production). The direct distillation method of production was terribly wasteful and inefficient. A shortage appeared imminent. The first step forward came in 1912, when the Burton [6] process of cracking was introduced. Not only was this epoch-making as regards motor spirit production, but it also marked the beginning of synthetic processes based on oil. Since that time there have been numerous effective methods developed for treating oils, including cracking processes, hydrogenation processes, catalytic methods, etc. With each improvement the amount of waste has been decreased, and all sorts of by-products have appeared.

Composition of Petroleum. Petroleum consists of a mixture of hydrocarbons whose composition varies with place of origin. It may contain members of the paraffins, together with cyclo-paraffins and also aromatic hydrocarbons. Nearly always associated with petroleum are gaseous paraffins known generically as " natural gas ".

Straightforward rectification of petroleum yields :

Petrol or gasolene or motor spirit, up to 60° C., consisting chiefly of pentane and hexane.
Benzine distilling up to 90° C., made up largely of hexane and heptane.
Ligroïn distilling up to 120° C.
Kerosene boiling between 150° C. to 300° C.
Heavy oil distilling above 300° C. used for lubricating oils and petroleum jelly.
Tars, asphalts, etc.

Natural Gas. A great deal has been heard about " natural gas ". Natural gas consists of a mixture of gaseous paraffins, chiefly methane, ethane, propane, butane and isopentane. Wherever petroleum is found there is generally a certain amount of natural gas about. However, the gas does occur frequently alone without any associated petroleum. According to Dunstan,[12] the composition of a typical example is as shown in Table 27. There are many seemingly unlimited subterranean reservoirs which when tapped blow off in a spectacular manner. Enormous amounts are available in the United States and

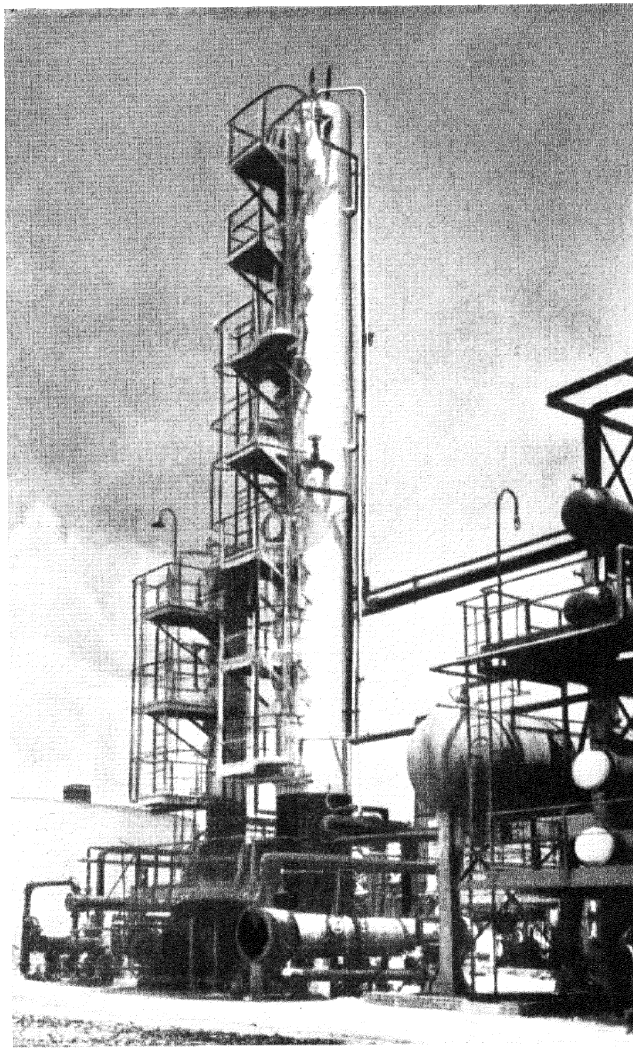

FIG. 18.—Fractionating Tower with re-boiler.

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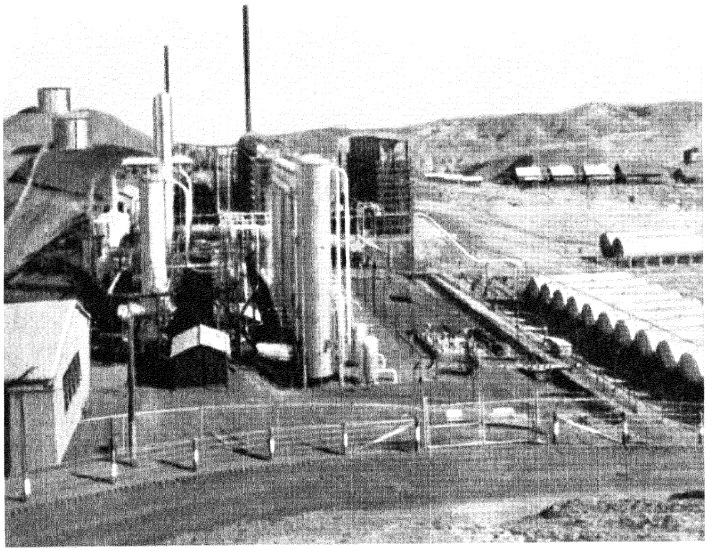

FIG. 19.—Plant for stripping Petrol from Natural Gas.

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in the U.S.S.R. In the United States about 45 per cent. comes from oil wells. For many years all natural gas was allowed to blow off to waste into the air.

TABLE 27. THE MAIN CONSTITUENTS OF NATURAL GAS

	M.p. °C.	B.p. °C.
Methane	−182	−161
Ethane	−172	− 89
Propane	−187	− 42
n-Butane	−135	− 0·6
iso-Butane	−145	− 10
n-Pentane	—	+ 37

This natural gas is expected to be the primary source of raw materials for synthetic rubbers and synthetic resins. In recent years a certain amount has been stripped for petrol. In the United States, for a number of years, a large proportion of natural gas has been used to perform the functions carried out by coal gas, which it does more efficiently. There is a network of natural-gas pipe-lines spreading all over the American Continent. In other countries this activity is more localized.

Another great industry based on natural gas is the manufacture of channel black, made by burning the gas under special conditions. Thus the production of carbon black in the United States, according to the Bureau of Mines, in 1941 was 504 million lbs. In this connection we come across a very ironical situation. The rubber industry has expanded to its present volume mainly on the merits of one product—the tyre. Tyres owe their remarkable wearing and service properties almost entirely to the presence of large amounts of carbon black, which reinforce the rubber to a remarkable degree. No satisfactory explanation of this phenomenon has yet been put forward. The vast bulk of carbon black produced goes into tyres. It can fairly be claimed that rubber owes much of its importance to carbon black, and through this, to the "natural gas" from which carbon black is made. Now there is every prospect of the same "natural gas" producing potentially serious competitors for rubber. It should be made clear that carbon black is of equally fundamental importance to the performance of every synthetic rubber.

In spite of these applications of natural gas, the major portion of available gas is still being wasted into the atmosphere. As raw material for any products it is there for the asking It is not to be wondered that the petroleum concerns are interested in the possibilities which may lead to major uses. According to Grosse and Ipatieff,[15] there is available in the United States annually from all sources 300 billion

cubic feet of ethane, 120 billion of propane, and 70 billion cubic feet of butanes.

Some of the Leading Processes. The processes which lead to those products, which may form the basis for synthetic rubbers and synthetic resins, are briefly as follows :

Cracking Processes with Oils. Cracking is a heat treatment which converts hydrocarbons of relatively high boiling points and high molecular weights into materials of lower boiling points and low molecular weights, suitable for use as motor spirit. Cracking divides large molecules into smaller units. It results in an increase in the amount of total motor spirit obtained from crude oils. These oils may be cracked under high pressure in the liquid form, or at higher temperatures as gases. Invariably large quantities of gaseous products are obtained, mainly of olefines and some diolefines.

In effect cracking is the thermal decomposition of heavier hydro-carbon molecules into simpler molecules. According to Dunstan [12] 100 gallons of cracking stock will yield something like 60 gallons of petrol. The residue will be heavier oil together with gas and coke.

Cracking Processes with Gaseous Hydrocarbons (i.e. natural gas). Gaseous hydrocarbons are submitted to high temperatures when dehydrogenation occurs with the formation of olefines. The paraffins tend to produce simpler molecules of the corresponding olefine, sometimes lower paraffins and often hydrogen. Thus, with the exception of methane, the paraffins such as ethane, propane, *n*-butane, and isobutane, yield olefines such as ethylene, propylene, and four isomeric butylenes.

The decomposition takes hours at 400° C., but only seconds at 800° C. It is very profoundly influenced by catalysts, such as chromium oxide, molybdenum oxide, vanadium oxide, together with aluminia or magnesia, activated charcoal, zinc-chromium alloy, etc., all of which facilitate dehydrogenation at lower temperatures, about 350° C.

The following account by Grosse, Morrell and Mavity [16] clearly explains the position :

The dehydrogenation of the paraffin gases to the corresponding olefines is the problen of fundamental importance to the oil industry. The technical problem of efficiency converting gaseous olefines into liquid motor fuel has been solved within recent years by both catalytic and purely thermal pro-

cesses. Therefore a process for the conversion of paraffins into olefines would put to good use all the paraffin gases except methane. These gases are available in enormous quantities from such sources as natural gas, and gasolene, petroleum, petroleum gas, gas from the cracking processes, coke-oven gas, and refinery gasolene.

TABLE 28. FORMATION OF CONJUGATED DIOLEFINES BY DEHYDROGENATION

Compounds Dehydrogenated	Temp	Contact Time	Diolefin		Unreacted Charge	Carbon
			Name	Yield		
	°C.	Sec.		Wt. % of charge	Wt. %	Wt % of charge
n-Butenes . . .	600	0·75	1,3-Butadiene	18	50	11·2
n-Butenes . . .	600	0·34	1,3-Butadiene	20·6	59	4·8
3-Methyl-1-butene .	600	0·5	Isoprene	21·4	34	12 8
2-Methyl-1-butene +2-methyl-2-butene	600	0·39	Isoprene	22·3	44	6·2
2-Pentene . . .	600	0·40	Piperylene	30·3	44	7·6
Cyclopentane . .	500	1·85	Cyclopentadiene	8·9	62	8·8

A catalytic dehydrogenation process has been developed for converting normal and isobutane, propane, butane and ethane to the corresponding olefines. The process briefly consists in passing the pre-heated gases over a suitable catalyst. The outgoing gases contain olefine and hydrogen besides the unreacted original paraffins. The olefines are polymerized or used in alkylation. The hydrogen is separated and the unreacted original paraffins are recycled.

The plant consists essentially of a furnace, banks of catalyst reactors, and hydrogen separation units. Automatic controls alternate the flow of paraffin gases first through the furnace and one section of reactors, and then through another, while the catalyst is being regenerated in the first section. The regeneration consists in passing automatic control amounts to air mixed with composition gases or steam to burn off the carbon on the catalyst at a moderate composition temperature, usually below 900° C. A feature of the process is that the length of operating cycle is short, usually of the order of one hour. The advantages of the catalytic process over purely thermal cracking are the much larger over-all yields of the corresponding olefines and a much higher reaction velocity.

According to Frey and Hepp [13] the reactions which occur and the yields which are obtained under different conditions are illustrated in Table 29.

TABLE 29. CONVERSION OF PARAFFINS TO OLEFINES

Reaction		Yield of Olefine
$CH_3.CH_3$ (ethane)	$\longrightarrow CH_2{=}CH_2$ (ethylene) $+H_2$	100%
$CH_3.CH_2.CH_3$ (propane)	$\longrightarrow CH_3.CH{=}CH_2$ (propylene) $+H_2$	45%
	$\longrightarrow CH_2{=}CH_2 + CH_4$ (methane)	55%
$CH_3.CH_2.CH_2.CH_3$ (*n*-butane)	$\longrightarrow CH_3.CH_2.CH{=}CH_2$ (1-butene) $+H_2$	12%
	$\longrightarrow CH_3CH{=}CH.CH_3$ (2-butene) $+H_2$	12%
	$\longrightarrow CH_3.CH{=}CH_2 + CH_4$	50%
	$\longrightarrow CH_2{=}CH_2 + CH_3.CH_3$	
	high temperature $\longrightarrow 2CH_2{=}CH_2 + H_2$	38%
$(CH_3)_2CH.CH_3$ (iso-butane)	$\longrightarrow (CH_3)_2C{=}CH_2$ (iso-butylene) $+H_2$	60%
	$\longrightarrow CH_3.CH{=}CH_2 + CH_4$	40%
$(CH_3)_4C$ (neo-pentane)	$\longrightarrow (CH_3)_2C{=}CH_2 + CH_4$	100%

In fact, the paraffins, with the exception of methane, can be catalytically dehydrogenated to the corresponding olefines according to the general reaction:

$$C_nH_{2n+2} \longrightarrow C_nH_{2n} + H_2$$

In this manner, and in almost every treatment of petroleum fractions, vast quantities of a whole range of olefines can be obtained. There are other processes such as alkylation, isomerization, etc., but these have not such a pronounced bearing on synthetic rubbers and plastics.

To maintain the sense of proportion it should be added that hitherto the main urge has all the time been to produce more motor spirit. Indeed, during the last twenty years, the amount of petrol obtained from a given amount of crude oil has doubled. The olefines lend themselves very readily to conversion into such products, since they polymerize quite easily under heat and pressure to yield liquid hydrocarbons in the petrol range.

On the other hand, chemical manufacturers have concentrated on developing cracking conditions which give maximum production of simple olefines and a minimum production of motor spirit. While this applies to ethylene and propylene without qualification, the butylenes are not quite so amenable, and other uses have been sought for them. The influence of various catalyzed treatments of isobutylene,

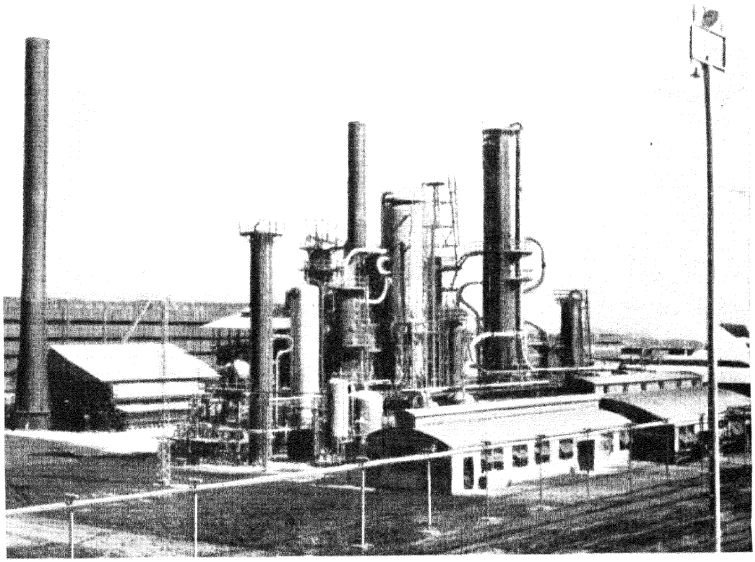

FIG. 20.—A modern Cracking Unit.

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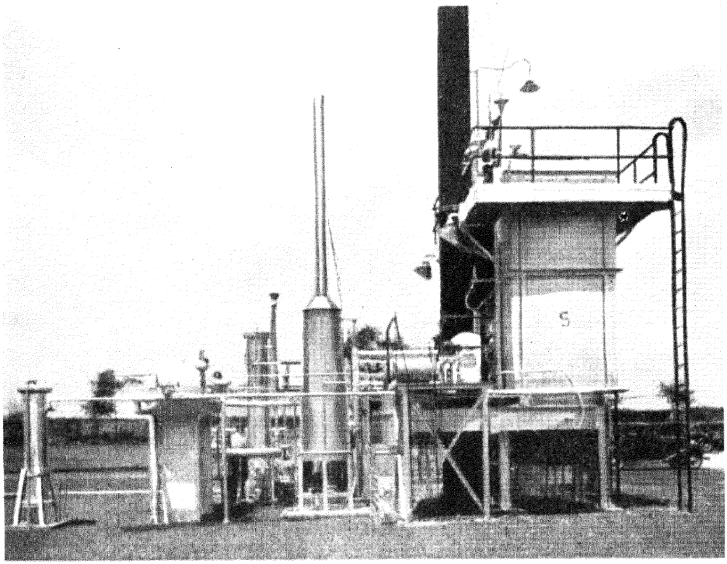

FIG. 21.—Pilot Plant converting Butane into Butadiene.

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for example, has led to the production of the polyisobutylene range of materials—ranging from very viscous liquids up to extremely rubbery products.

One of the chief conditions required for a reasonably economic production of synthetic rubbers is evidently satisfied. A cheap unlimited source of compounds having four carbon atoms in a row is available. Since these compounds are already unsaturated the conditions are even more favourable.

The Houdry Process. One of the most interesting and important methods for the production of butadiene in the United States is the Houdry process based on petroleum products. This is a development of the hydrogenation process evolved by Houdry.[17] The process depends on the use of butane. This is employed because it is available in large quantities in a relatively pure form.

Thayer, Lassiat and Lederer [27] state that butane is obtained as a by-product of (*a*) alkylation processes for aviation fuel, (*b*) in natural gas, (*c*) in recycle plants in refining operations. There is no question of the use of this material affecting the requirements for the production of aviation fuels. This is a great consideration, particularly where butylene is employed as the starting material for butadiene. At the present time the demand for butylene for aviation fuel is so great that there is little available for the manufacture of butadiene. By contrast butane is freely available in very large quantity. They have described that in 1941 there were available about 175,000 barrels of butane per day being made up of 92,000 from natural gas, 36,700 from cracking processes at refineries, 50,400 being obtained from crude oils used at refineries.

The principle of the process is to dehydrogenate butane in two stages. The products from the first reactor system are butane, butylene, and lighter gas. The butane and butylene portion is concentrated in a vapour recovery system. This constitutes the charge for the second dehydrogenating stage. It is at this point that butadiene is made. The materials are passed over the specially heated catalysts which are the characteristic features of the Houdry process.

Carbon is formed on the catalyst during the dehydrogenating stages. The catalyst is regenerated by burning the carbon deposit by passing air through. The same carbon deposit on the catalyst provides the heat necessary to convert the butane to butylene and then to butadiene. The separation and purification of the butadiene is conveniently carried out by any available purification process. It is stated that a yield of 66·9 per cent. butadiene is obtained by the Houdry method. This is far higher than the yield from any other known

method based on petroleum derivatives. It has been stated that the cost of butadiene obtained in this manner is 6·421 cents per lb., an extraordinarily low cost. Figures have been provided to explain the cost of installation and the working cost of a Houdry unit. The unit favoured is one capable of producing 15,000 tons per annum. This size can conveniently be fed by the output of butane at almost any refining centre. Costs for the unit:

TABLE 30. COSTS OF THE HOUDRY PROCESS

	(Dollars)
1. *Process Plant*	
(*a*) Dehydrogenation plant	1,902,825
(*b*) Purification plant	955,000
(*c*) Auxiliaries	559,100
	3,416,925
2. General Administration, purchasing, engineering and development expenses	225,000
Making a grand total of	$3,641,925

Utilities Required for a Houdry Plant

Electric power	33,600 units per day.
Fuel oil or gas	309 barrels per day.
Steam	2,000,000 lbs. per day.
Cooling water	10,000 g.p.m.
Make up water	300 g.p.m.

Ethylene again a Leading Product. For the moment let us refer back to ethylene. Its importance to the plastics industry cannot be over-stressed. Something has already been described about its potentialities for the production of alcohol. This is being energetically pursued. It is estimated that the potential capacity of the oil industry in the United States is more than 1,000 million gallons of alcohols per year from cracked gases alone. This includes ethyl alcohol, propyl alcohols, butyl alcohols, etc., all of great importance to plastics, lacquers, and many other industries. At the present time these olefines are being used for the manufacture of numerous glycols and related compounds. And indeed quite recently it has been stated that a commercial plant for the production of glycerol has begun to operate. The implications of this activity in relation to alkyd resins are obvious.

While most emphasis has been laid upon the use of butadiene elastomers, because most types are derived from it, yet we must remember there are others. Their raw materials have not yet been discussed, because these products are anomalous (or appear to be so at present). For example, Thiokol is based upon ethylene dichloride and various inorganic polysulphides.

Ethylene dichloride, in itself a very valuable and widely used solvent, is made by direct combination of ethylene and chlorine.

$$Cl_2 + CH_2 \quad CH_2 \longrightarrow CH_2Cl—CH_2Cl.$$

Thus another synthetic rubber-like material has a direct tie-up with the petroleum industry.

Recently ethylene dichloride has acquired a greater significance from the plastics angle as a source for vinyl chloride. By virtue of its rubbery properties polyvinyl chloride comes into consideration as a leading member of the group of elastoplasts. Brous,[5] of the Goodrich Company, has produced vinyl chloride by heating ethylene dichloride in the presence of methyl alcohol and adding aqueous sodium hydroxide.

Ethyl chloride may be synthesized via ethylene or hydrogen chloride. Interacting with benzene under the influence of aluminium chloride it gives ethyl benzene, from which styrene is derived—essential for Buna-S rubbers.

The Production of Synthetic Rubber Raw Materials. Reviewing this position, it is evident that, so far, it has only been shown that the petroleum industry is on level terms with coal, acetylene, etc., which have previously been described, possibly with raw materials somewhat cheaper. If this were so then there would be no overwhelming advantage, as against the other raw material sources. The same lengthy series of synthetic processes would be necessary to produce the synthetic rubber monomers. Clearly the olefines are available cheaply and in unlimited quantity. This is not enough.

It is axiomatic that the development of the synthetic rubber industry depends upon the production of cheap butadiene and isoprene.

For the oil industry to be well and truly leading in this field, the ultimate raw material—butadiene (or possibly isoprene) was, therefore, necessary.

Butadiene is found in petroleum in small quantities. As far back as 1933 large-scale work was being carried out in the U.S.S.R. to recover butadiene from petroleum. In the aggregate the amount would be very large, but the difficulties of separating it are considerable.

Butadiene is extremely difficult to separate from other constituents. One method is to prepare the yellow solid compound with cuprous chloride or hydrogen chloride. When heated at 30–100° C. pure butadiene in high yield is obtained. Many materials enhance the effect of the cuprous chloride solution, including ammonium chloride, stannous chloride, sodium chloride, and ethylene glycol. A certain amount is available in the butene fraction separated from the gas

produced industrially by the vapour phase (high-temperature) cracking of oils. According to Brooks and Ellis,[4] such a fraction contained:

	Per cent.
Butenes	10–12
Isobutene	20–24
n-Butenes	50–55
Butadiene	12–14
C_2 and C_5	2

According to Grosse, Morrel and Mavity,[16] the fundamental requirement was to find " the connecting link between the billions of cubic feet of butanes present in natural and cracked gases, and of butenes present in the latter, and the billions of gallons of pentanes available in natural gasolene and crude oil on the one hand, and the production of synthetic rubber from these raw materials on the other ". This has been found, in the catalytic dehydrogenation of olefines to diolefines (or dienes).

Olefines can be further dehydrogenated with the same catalysts (chromium, molybdenum, or vanadium oxide on aluminia) to diolefines. The diolefines formed are of the conjugated type and have the same carbon framework as the parent olefine. Other catalysts used include tungsten, titanium, zirconium, cerium, and thorium oxides, notably for dehydration of butylene.

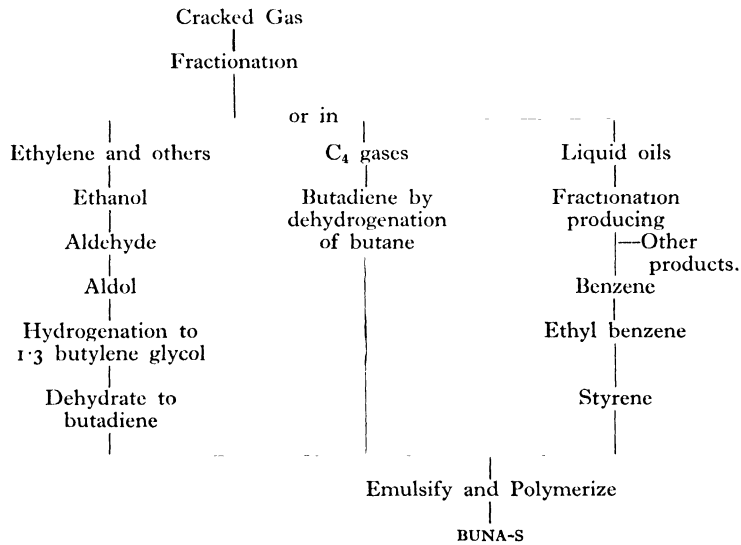


FIG. 22. Buna Rubber from Cracked Gas.[12]

Thus from 1- or 2-butylene, 1,3-butadiene is formed; from straight-chain pentenes, piperylene (1,3-pentadiene); and from branched-chain pentenes, isoprene (2-methyl-1,3-butadiene). The original position of the double bond in the framework of the olefine is probably of no consequence since, especially in the presence of the aluminia base catalyst, it is freely shifted. Thus isoprene was obtained in approximately equal yields from either 3-methyl-1-butene or from a mixture of 2-methyl-1-butene and 2-methyl-2-butene.

According to Brooks [3] diolefines, such as butadiene, isoprene, cyclopentadiene, etc., could be separated from mixtures containing olefines by passing through finely divided cuprous chloride in water. These diolefines are produced by pyrolytic methods which are less drastic than those required for the conversion of olefines into motor fuel.

According to the Dow Chemical Co.,[10] butadiene is separated from mixtures with other hydrocarbons having four carbon atoms, such as the butylenes and butanes by fractionally distilling the liquefied hydrocarbons in the presence of liquid ammonia.

Work along somewhat similar lines in Germany has been described by Schulze and Schulze.[20]

Grosse, Morrell and Mavity (loc. cit.) have described some very successful processes. The charge of gas was passed at a definite rate over granular catalyst at reduced pressure (0·25 atm.) and at temperatures between 600 and 650° C. The catalysts were oxides of chromium, molybdenum, or vanadium on aluminia.

Single pass yields were of the order of 20–30 per cent. diolefine, while recycled yields were up to 79 per cent.

The crux of the whole matter is that processes, which resemble the ordinary everyday processes being carried out in the refineries in existing plant, produce butadiene, etc., ready for conversion into synthetic rubber.

Cramer [9] has summarized the various methods for producing butadiene practised in the United States at the present time.

TABLE 31

1. Petroleum $\xrightarrow[\text{cracking}]{\text{normal}}$ $CH_2{=}CH{-}CH{=}CH_2$ ($\frac{1}{2}$ to $\frac{3}{4}$%)

2. Petroleum $\xrightarrow[\text{cracking}]{\text{special}}$ $CH_2{=}CH{-}CH{=}CH_2$ (5 to 12%)

3. $CH_3.CH{=}CH.CH_3 + Cl_2 \longrightarrow CH_3.CHCl{-}CHCl.CH_3$

$\xrightarrow[BaCl_2]{\text{Heat with}}$ $CH_2{=}CH{-}CH{=}CH_2 + 2HCl$

4. $CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_3 \xrightarrow[\text{at } 600^\circ \text{ C.}]{Al_2O_3 + Cr_2O_3} CH_3{-}CH{=}CH{-}CH_3$

$$\xrightarrow[\text{at } 650^\circ \text{ C.}]{Al_2O_3 + Cr_2O_3} CH_2{-}CH{=}CH{-}CH_2 + H_2$$

5. Acetylene $\xrightarrow[NH_4Cl]{Cu_2Cl_2 \text{ and}} CH_2{-}CH{-}C{\equiv}CH$

$$\xrightarrow[\text{hydrogenation}]{\text{selective}} CH_2{-}CH{=}CH{-}CH_2$$

These processes have been developed to a very high pitch of efficiency.

As a result the petroleum industry bears the main brunt of producing butadiene for the American synthetic programme. So much

TABLE 32. VAPOUR PRESSURE OF 1·3-BUTADIENE [7]

	lb./in.²
− 130° F.	0 08145
− 94	0 4364
− 68	1 6290
− 22	4 7900
− 4	7 623
+ 14	11 8300
24	14 7500
50	25 6100
86	51 400
104	70 090
140	124·200
176	203 7

so that a number of adjustments have been found necessary in the industry. The Baruch Committee has even recommended that there should be a reduction of petrol output in favour of butadiene, while cracking plants should be converted to the production of butadiene.

The preparation of enormous quantities of butadiene has introduced a variety of storage problems. Since butadiene is a gas at ordinary temperatures, the problem is not altogether simple. A great deal of work has been carried out on it. Another complication is the fact that butadiene tends to polymerize under the influence of active oxygen, whether as air, or as oxygen, or as inorganic or organic peroxides. Moreover, the rate of high molecular polymerization has been shown to be directly proportional to the square root of the concentration of peroxide or active oxygen.

It has been established that the best type of storage container is a

vapour-tight air-free vessel. It has been suggested that it should be an insulated and refrigerated double-walled cylindrical container with a suspended bottom and a dome roof. In the United States these have been designed for a working pressure of 3 lb. per square inch and are kept at 32° F.

There is another extensively interesting development which brings petroleum and agricultural activities closer. This is the enormous demand for furfural which is to be used as a selective solvent in the various stages of manufacture of butadiene. The richest sources of furfural are oat hulls, cotton-seed hulls, and corn cobs. About 10 lbs. of these raw materials yield 1 lb. furfural. Here is yet another example of how synthetic rubber production will affect plastics, for this particular activity will have reprecussions on the manufacture and use of furfural resins.

Direct Processes from Petroleum. Petroleum chemists have not been content to leave the matter here. It has been maintained by one leading group that synthetic rubber should be obtainable from refinery gases by even more direct methods than have existed. These members of the Esso laboratory of the Standard Oil Development Co. are familiar with every aspect of synthetic rubber production. They understand all the implications of butadiene rubbers, for eleven years ago Standard Oil entered into a working arrangement with I.G. Farbenindustrie to exchange and share research developments.[21] Arising from this it becomes clear why polyisobutylene, for example, has only been available from these two sources—as Oppanol made by the I.G., and as Vistanex made by Standard Oil. Just before the war, Standard Oil traded some of its oil technology patents for exclusive United States' rights to manufacture Buna.

The first notable success of petroleum chemists in the synthetic rubber field was with polyisobutylene. There are a number of polyisobutylenes based upon isobutylene. As already described isobutylene is one of the chief olefines obtained by cracking processes. This is the material used in the United States. In Germany isobutylene is obtained by passing gaseous hydrocarbons through the electric arc. It must also be remembered that the Germans have had large sources of petroleum derivatives available to them in recent years, chiefly from Rumania, but also from Austria.

According to Standard Oil Development Co.,[26] mono-olefines of 2, 3, and 4 carbon atoms form additional compounds with solid cuprous chloride and other cuprous halides, and it is shown that the dissociation temperature/pressure properties of these compounds quite sharply separate ethylene, propylene, and isobutylene from one another.

Direct Processes from Petroleum. Petroleum chemists have not

Advantage of these properties is taken to separate the olefines from saturated hydrocarbons by forming the copper compounds at suitable temperature and pressure, isolating the mixture of copper compounds and dissociating it in stages at suitable temperatures and pressures to obtain each olefine in turn. If the cuprous halide is suspended in a saturated hydrocarbon of high boiling point, the speed of reaction is greatly increased, e.g. ethylene in contact with cuprous chloride at 25° C. and 17 atmospheres requires 24 hours for complete reaction, but in the presence of kerosene only 15 minutes.

Isobutylene may be polymerized by heating in the presence of catalysts such as aluminium chloride, boron chloride, stannic chloride, etc. Although it was found in 1873 by Butlerov and Gorianov [8] that isobutylene could be polymerized to a liquid product by means of sulphuric acid and/or boron fluoride as catalyst, it is only recently that rubbery products have been obtained, first by Otto and Mueller-Conradi.[19] Standard Oil Development Co. and I.G. Farbenindustrie [24] purified light cracked oil to give a mixture containing at least 95 per cent. isobutylene. Crude oil containing butanes and butylene was then added to produce a mixture containing from 20 to 40 per cent. of isobutylene, and 10 to 20 per cent. of other olefines. The mixture was then polymerized with boron fluoride at a temperature below — 40° C. to yield plastic solid or semi-solid rubbery materials. In another patent Standard Oil Development Co.[25] produced high molecular weight polymers of olefines, notably polyisobutylene, by passing the olefine into a bath of hydrocarbon diluent, such as ethane, propane, or butane, having an active catalyst, such as boron fluoride, and keeping the temperature below — 10° C. Isoprene, styrene, and butadiene could also be polymerized by this method. Polymerization occurred with the formation of substantially straight-line polymers. The nature of these varied with the molecular weight, ranging from oily viscous fluids up to strong rubbery materials with molecular weights as high as 500,000.

Jessup [18] has described how either or both of the straight chain chlorides or bromides of butane is heated in the presence of aluminium chloride, ferric chloride, or beryllium chloride at 300–500° C., when isobutylene is obtained.

The polyisobutylenes have already attained importance as commercial materials, being available as Oppanol made by I.G. Farbenindustrie, and as Vistanex made by Standard Oil Company.

Production of Styrene. Styrene is second in importance only to butadiene, for enormous quantities are used as secondary component in the formation of elastomers such as Buna S. This is not only the

predominant German type, but has been adopted as standard for United States production.

It is prepared by a process first discovered by Berthelot,[1] namely the dehydrogenation of ethyl benzene. Ethyl benzene is obtained in small quantities as a by-product from petroleum refining and this source is being exploited in the United States. It is generally prepared by direct synthesis from benzene and ethyl chloride. Under the action of aluminium chloride as catalyst benzene and ethylene also combine to form ethyl benzene. This is catalytically dehydrogenated or cracked at high temperature, from 800–950° C. According to one process, when carried out betweeen 500–600° C. over suitable catalyst, a yield of 35 per cent. is obtained.

Dow [10] has made an interesting comparison of existing methods of production of styrene, illustrating the advantages of the processes used by his company. He stated that in one method benzene and 95 per cent. alcohol were the starting materials being reacted at temperatures of about 600° F., and pressures of 250 lbs. per sq. in. over a phosphoric acid catalyst. In another method ethylene is used instead of alcohol. In both these cases very pure benzene is required. The benzene and ethylene must be recycled several times.

The Dow process can use impure ethylene containing as little as 38 per cent. of ethylene. Their operating pressure is only 190° F. at the low pressure of 15 lbs. per sq. in. The catalyst is aluminium chloride, giving a yield of up to 100 lbs. of ethyl benzene per lb. of catalyst. A much lower grade of benzene could be used in this case. The reaction is carred out continuously, and gives almost theoretical yields of ethyl benzene. They can also recover about 80 per cent. of the spent aluminium chloride catalyst.

Benzene is, of course, obtained from coal tar, while ethyl chloride may be prepared via alcohol, or by the direct catalytic interaction of ethylene and hydrogen chloride.

Styrene is a colourless liquid with a characteristic pungent odour. It boils at 143° C., and has a density $d = 0.904$.

In the United States it is proposed to make 845,000 tons Buna-S per annum. This will involve something like 250,000 tons of styrene per annum. The fact of having large amounts of styrene available at low cost must have tremendous repercussions upon the use of styrene in other industries, notably in the plastics industry and in the electrical industry.

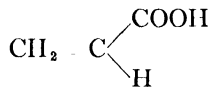
Wakeman and Weil [28] have summarized the position.

With the current development of synthetic rubber, styrene as one of the components of Buna-S, will become a large-tonnage chemical, a fact

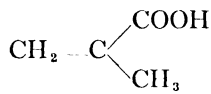
which will be reflected in increased production of polystyrene plastics in moulded, extruded and film form. In Germany it is to-day one of the most available plastics and is utilized for many applications where cellulose acetate is used in the United States. It has been freely predicted that because of the increased production of styrene caused by the rubber industry, polystyrene will be one of the most available and least expensive plastics in this country after the present war.

Acrylic Acid Monomers. These are the secondary ingredients in such important products as Perbunan (containing acrylic nitrile), Hycar, Chemigum, and so on.

The group includes acrylic and methacrylic acids, their esters, halides, nitriles, etc. Polymers of many of these have already achieved considerable commercial importance as synthetic resins, notably methyl methacrylate (Lucite, Perspex, Plexiglas, etc.) and ethyl acrylate (Diakon, Plexiglas moulding powders).

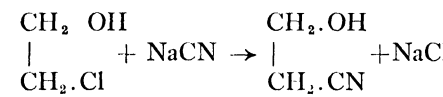


acrylic acid

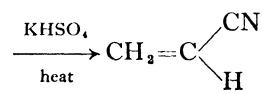


methacrylic acid

The formation of acrylic acid esters conveniently starts from ethylene chlorohydrin. This is treated with sodium cyanide and yields ethylene cyanhydrin. When this is heated in the presence of sodium hydrogen sulphate, acrylic nitrile is formed, the most important derivative from the synthetic rubber angle.

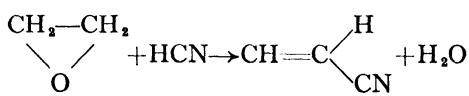


Ethylene chlorohydrin



Acrylic nitrile

Another method is the direct catalyzed combination between ethylene oxide and hydrogen cyanide.



Another process employed in the United States proceeds according to the following reaction:

$$CH_3.COOCH_2.CH_2CN \xrightarrow{\text{heat}} CH_2=C(H)(CN) + CH_3.COOH$$

Methyl methacrylate is derived from acetone, which, of course, can be obtained from acetylene. Acetone reacts with hydrogen cyanide to give acetone cyanhydrin. This is treated with sulphuric acid and methyl alcohol.

$$\underset{\text{Acetone cyanhydrin}}{(CH_3)_2C(OH)CN} + H_2SO_4 + CH_3OH \rightarrow \underset{\text{Methyl methacrylate}}{CH_2=C(COOCH_3)CH_3} + NH_4HSO_4$$

Methyl methacrylate is a colourless liquid with a specific gravity at 16° C. of 0·9497 and refractive index n^{16}_{D} 1·4168. It boils at 100·3° C. It is soluble in most organic solvents, but is insoluble in water.

Acrylic nitrile is a colourless liquid boiling at 77° C. and possessing a mild, pleasant odour.

Some Costs. It is fascinating to consider the potential costs of many of these materials. Fortunately sufficient data is available.

The Standard Oil Company [22] investigated the costs of producing butyl rubber and Buna-S on a large scale. They considered four possible cases: the production of 100 tons per day, and 300 tons per day, of butyl rubber and Buna-S respectively. They selected their best possible location of establishing such a project. The results of their study are summarized in the accompanying tables. One outstanding conclusion was that the costs of butyl rubber were extremely attractive, and that it was potentially the cheapest synthetic rubber. The production costs of Buna-S were found to be something of the order of twice as great as those of butyl rubber. In connection with the estimate regarding butadiene, they selected a non-catalytic dehydrogenation method for making their estimate. They considered that in connection with the production of styrene for Buna-S it would not be a difficult matter to prepare ethyl benzene by the alkylation of benzene, although the subsequent steps would present some difficulty. Of unusual interest is the fact that they also included information obtained from the I.G. in 1938 for their production of 73 tons of Buna-S per day. The particulars given are of considerable interest as having a degree of authenticity which has hitherto been lacking.

TABLE 33. ESTIMATED COST OF BUTYL RUBBER—BAYTOWN [22]

(Plant of the Standard Oil Co.)

	Case I			Case II		
Quantities :						
Butyl rubber production, T/D		100			300	
Isobutylene consumed, lbs./D		212,000			636,000	
Butadiene ,, , lbs./D		10,000			30,000	
Normal Butane ,, , B.P.D.		1,550			4,650	
Investments :						
Isobutylene		$4,400,000			$10,500,000	
Butadiene		750,000			2,200,000	
Butyl rubber		4,650,000			11,100,000	
Total incl 25% for offsite		$9,800,000			$23,800,000	
Production cost, $/day :						
Isobutylene	at 3·1 c.	$6,500	3·3 c.	at 2·7 c.	$17,300	2·9 c.
Butadiene	at 12·2 c.	1,200	9·6 c.	at 9·2 c.	2,800	0·5
Butyl rubber		7,300	3·6		19,300	3·2
Total		$15,000			$29,400	
c./lb. butyl rubber			7·5 c.			6·6 c.
Increase in c /lb. butyl rubber for a $1/bbl. increase in normal butane			0·78 c.			0·78 c.

TABLE 34. ESTIMATED COST OF BUNA-S MANUFACTURE—BAYTOWN [22]

	Case III			Case IV		
Quantities :						
Buna-S production, T/D		100			300	
Butadiene consumed, lbs /D		165,000			495,000	
Styrene ,, , lbs./D		50,000			150,000	
Stabilizer gas ,, , MCFD		0·48			1·45	
Normal butane ,, , BPD		2,400			7,200	
Benzol, gals./D		7,000			21,000	
Investments :						
Butadiene		$9,600,000			$23,300,000	
Styrene		3,550,000			8,300,000	
Buna-S plant		7,500,000			18,000,000	
Total, incl. offsite at 25%		$20,650,000			$49,600,000	
Production cost, $/day :						
Butadiene	at 8·6 c.	$14,200	7·1 c.	at 7·9 c.	$39,200	6·5 c.
Styrene	at 11·4 c.	5,700	2·9	at 9·5 c.	14,300	2·4
Buna processing cost, ex chemicals		6,000	3·0		15,000	2·5
Chemicals for Buna processing		6,000	3·0		18,000	3·0
Total		$31,900			$86,500	
c./lb. Buna			16·0 c.			14·4 c.
Increase in c /lb. Buna-S for a $1/bbl. increase in normal butane			1·20 c.			1·20 c.

TABLE 35. ESTIMATED COST OF ISOBUTYLENE FOR BUTYL RUBBER MANUFACTURE—BAYTOWN [22]

	Case I		Case II	
Quantities :				
Butyl rubber produced, T/D	100		300	
Pure isobutylene ,, , lbs./D	212,000		636,000	
Isobutane ,, ,,	—		—	
N-butane consumed, BPD	1,550		4,650	
Investments :				
Fractionation of field butane	$ 0		$ 0	
Isomerization and fractionation	750,000		1,800,000	
Catalytic dehydrogenation	1,700,000		4,100,000	
Isobutylene concentration (H_2SO_4 process)	1,050,000		2,500,000	
Total	3,500,000		8,400,000	
Offsite at 25%	900,000		2,100,000	
Total	$4,400,000		$10,500,000	
Processing costs, $/day :				
Fractionation of field butane	$ 0	0 c.	$ 0	0 c.
Isomerization and fractionation	1,500	0·71	3,600	0·57
Catalytic dehydrogenation	2,200	1·04	6,000	0·94
Isobutylene concentration	1,700	0·80	4,400	0·69
Total	5,400	2·55	14,000	2·20
N-butane cut at 70 c./B	1,100	0·52	3,300	0·52
Total	6,500		17,300	
Isobutylene cost, c./lb. with *n*-butane at 70 c./bbl		3·1 c		2·7 c.
,, ,, ,, ,, ,, ,, $1.70/bbl.		3·8 c.		3·4 c.

TABLE 36. ESTIMATED COST OF BUTADIENE FOR BUTYL RUBBER—BAYTOWN [22]

	Case I	Case II
Quantities :		
Butyl rubber produced, T/D	100	300
Butadiene ,, , T/D	5	15
Concentrated butylenes, lbs./D	22,000 [a]	65,500 [b]
Investments :		
Butylene concentration	$ 0	$ 450,000
Butylene cracking and butadiene concentration	600,000	1,300,000
	600,000	1,750,000
Offsite	150,000	450,000
	$750,000	$2,200,000
Processing Costs :	(cents)	(cents)
Butylene concentration	0	1·4
Butylene cracking and butadiene concentration	10	5·6
	10	7·0
Butylene raw material at 1·0 c./lb. (value for U. O. P. polymer + frt.)	2·2	at 1·0 c.[c] 2·2
c./lb. Butadiene	12·2	9·2

[a] From Baton Rouge V. P. cracking plant.
[b] ½ from B.R. cracking plant (34,200 lb./CD N. C_4H_8 in C_4 cut) and ½ from Baytown spent C_4 from codimer plant.
[c] Value for alkylation.

TABLE 37. ESTIMATED COST OF BUTADIENE FOR BUNA-S MANUFACTURE—BAYTOWN [22]

	Case III		Case IV	
Quantities:				
Buna-S produced, T/D	100		300	
Pure butadiene produced, lbs./D	165,000		495,000	
N-butane consumed, BPD	2,400		7,200	
Investments:				
Fractionation of field butane	$ 0		$ 0	
Catalytic dehydrogenation	2,600,000		6,300,000	
Butylene concentration (H_2SO_4 process)	1,700,000		4,100,000	
Butylene cracking (non-catalytic)	1,800,000		4,300,000	
Butadiene concentration (Cu process)	1,600,000		3,900,000	
	7,700,000		18,600,000	
Offsite at 25%	1,900,000		4,700,000	
Total	9,600,000		23,300,000	
Processing costs, $/day:				
Fractionation of field butane	$ 0	oc.	$ 0	oc.
Catalytic dehydrogenation	3,800	2·3	10,300	2·1
Butylene concentration	2,900	1·8	7,500	1·5
Butylene cracking	3,000	1·8	8,400	1·7
Butadiene concentration	2,800	1·7	7,900	1·6
Total	12,500	7·6	34,100	6·9
N-butane at 70 c./bbl.	1,700	1·0	5,100	1·0
	14,200		39,200	
Butadiene cost, c/lb. with *n*-butane at 70 c./bbl.		8·6 c.		7·9 c.
Butadiene cost, c./lb. with *n*-butane at $1.70/bbl.		10·1 c.		9·4 c

TABLE 38. ESTIMATED COST OF STYRENE FOR BUNA-S MANUFACTURE—BAYTOWN [22]

	Case III		Case IV	
Quantities:				
Buna-S production, T/D	100		300	
Styrene production, lbs /D	50,000		150,000	
Benzene consumed, gals./D	7,000		21,000	
Ethylene consumed, lbs./D	18,700		56,100	
Stabilizer gas consumed, MCF	0·48		1·45	
Investments:				
Propane cracking and Ethylene fractionation	$ 700,000		$1,500,000	
Ethyl benzene manufacture	650,000		1,500,000	
Styrene manufacture	1,500,000		3,600,000	
	2,850,000		6,600,000	
Offsite at 25%	700,000		1,700,000	
	3,550,000		8,300,000	
Processing costs, $/day:				
Ethylene manufacture	at 4·3 c./lb. $ 800	1·6 c.	at 2·9 c./lb. $1,600	1·1 c.
Ethyl benzene manufacture	1,300	2·6	2,600	1·7
Styrene manufacture	2,500	5·0	6,800	4·5
	4,600	9·2	11,000	7·3
Benzene raw material at 16 c./gal.	1,100	2·2	3,300	2·2
	$5,700		$14,300	
c./lb. styrene				9·5 c.

TABLE 39. ESTIMATED YIELDS [22]

Butyl rubber:

1. 98% normal butane to 98% isobutane by alkylation, incl. fractionation . . . . . 95% of theory
2. 98% isobutane to *net* dilute isobutylene, by catalytic dehydrogenation . . . . . 80% of theory
3. Net dilute isobutylene to pure isobutylene, by regeneration from H_2SO_4 . . . . . 95% of theory
4. 1·06 lbs. pure isobutylene/lb. butyl rubber
   0·05 lb. „ butadiene / „ „ „

$$\frac{1{\cdot}06 \times 58}{4{\cdot}86 \times 56 \times 0{\cdot}95 \times 0{\cdot}80 \times 0\ 95 \times 0{\cdot}98} = 0{\cdot}320 \text{ gals. 98\% normal butane cut/lb. butyl rubber}$$

Buna-S:

1. 98% normal butane to net dilute *n*-butylenes, by catalytic dehydrogenation . . . . . 80% of theory
2. Net dilute *n*-butylenes to pure *n*-butylenes, by regeneration from H_2SO_4 . . . . . 95% of theory
3. Pure *n*-butylenes to net dilute butadiene, by thermal cracking . . . . . 50% of theory
4. Net dilute butadiene to pure butadiene, by cuprous salt extraction . . . . . 95% of theory
5. 0·825 lb. butadiene/lb. Buna-S
   0·250 lb. styrene /lb. „ „
   (0·035 gal. benzol /lb. „ „)
   (0·0935 lb. ethylene/lb. „ „)
   (2·4 CF stabilizer gas/lb. Buna-S)

$$\frac{0{\cdot}825 \times 58}{4{\cdot}86 \times 54 \times 0{\cdot}80 \times 0{\cdot}95 \times 0\ 50 \times 0\ 95 \times 0{\cdot}98} = 0{\cdot}516 \text{ gals. 98\% normal butane cut/lb. Buna-S}$$

TABLE 40. I.G. COST ESTIMATE (DEC. 1938) FOR 73 TONS BUNA-S/DAY (2,000 MT/MO) [22]

	(dollars)
Investment:	
Butadiene (chlorination process)	6,500,000
Styrene	900,000
Polymerization	5,000,000
Other, in battery limits	2,600,000
	15,000,000
Offsite	5,000,000
	20,000,000
	(cents)
Production Cost:	
Butadiene at 10·5 cents	8·4
Styrene at 13·4 cents	3·5
Buna processing cost, ex chemicals . . .	3·7
Chemicals for Buna processing	2·9
cents per lb. Buna-S	18·5

An estimate of butyl rubber costs for a production of 20 tons per day at their Baton Rouge plant has been made by Standard Oil Development Co.

TABLE 41. BUTYL RUBBER COSTS (20 TONS PER DAY)

	c./lb. of butyl rubber
Raw material :	
Isobutylene, at 7·76 c./gal.	1·70
Isoprene, at 30 c./oz.	1·20
Operating costs :	
Operating labour and supervision (approximately 26 men per shift)	2·17
Maintenance :	
Normal	2·01
Changes and additions	1·55
Utilities :	
Fuel-free	0·46
Fuel, at 12 c./MM B.T.U.	0·86
Chemicals :	
Methyl chloride	0·35
Aluminium chloride	0·30
Other chemicals	0·49
Total	1·25
Other supplies	0·12
Burden and administrative and general expenses	3·18
Containers	0·71
Total, excluding royalty, depreciation, profit	15·21
Say	15·00

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CHAPTER 8

POLYMERIZATION

Polymerization a Major Problem in the Production of Synthetic Rubber. The production of the primary materials for making synthetic rubbers appears to be streamlining to a cheap and simple procedure. Vast quantities of olefines, diolefines, and their derivatives are being obtained from plentiful cheap raw materials such as coal, petroleum, lime, salt, and so on. It is equally important that conversion of these materials into the final synthetic rubbers should also be smooth and easy, and should yield regular homogeneous products. The process of polymerization has proved just as difficult a problem as the production of raw materials.

Examples of the polymerization process described in the historical introduction make it evident that the procedure was invariably laborious, lengthy, and usually resulted in unsatisfactory materials. Synthetic rubber production has run the whole gamut of polymerization processes. One of the major fields for polymerization, it has greatly contributed to its development in other directions, in many other industries. For example, there has been a very notable contact between activities to produce synthetic rubbers and those directed at making synthetic resins. That is why producers interested in the one are almost invariably equally interested in the other form of production.

The academic work on raw rubber has all along provided the background for the production of synthetic resins; but even the work on rubber was merely a continuation of still earlier work. For example, polymerization action has been known for a very long time, certainly for 100 years. Thus Regnault[32] described the production of vinylidene chloride as long ago as 1838, although the first commercial materials known as Saran have only recently made their appearance. There was a considerable amount of similar empirical work prior to the first systematic efforts with natural rubber. The profound contributions of Harries, and his contemporaries, as a preliminary to the production of synthetic rubber has already been discussed.

The Polymerization Process. A monomer is a chemical entity such as styrene, vinyl chloride, vinyl acetate, methyl methacrylate, and so on, in the vinyl series, or such as butadiene, isoprene, chloroprene, etc., in the diolefine (or divinyl) series.

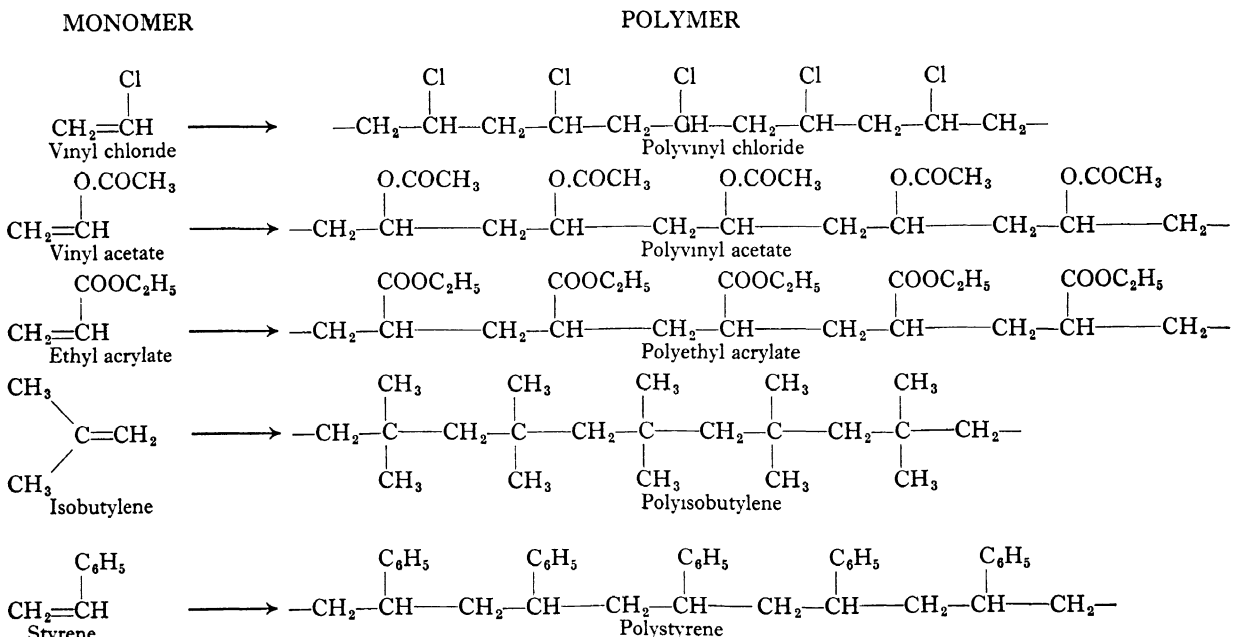


FIG. 23.—Monofunctional Monomers and their Polymers.

Polymerization is generally regarded as the linking up of a number of these monomeric units into long open chains or macro-molecules. This is the Staudinger conception, which is widely accepted. Each monomer unit forms a link in a straight uninterrupted chain. According to the treatment and the conditions, it is thought that chains of various lengths are formed. The properties of the product depend upon the extent to which polymerization is carried out, or, in other words, to the length of the chain. The molecular weight (generally determined by the viscosity) of the product gives the measure of the degree of polymerization. As the length of the polymer increases so the valuable mechanical properties become more apparent.

The character of the material changes, generally from the liquid state, since most monomers are liquids. These become more viscous, and then perceptibly change over towards the solid state. The various monomeric butadiene derivatives change to rubbery solids, and so on. Liquid styrene ultimately changes to the solid, glassy polystyrene, having remarkable electrical properties. Gaseous vinyl chloride which actually boils at $-14°$ C. forms the tough, strong polyvinyl chloride. Ethyl acrylate becomes a somewhat soft glassy solid, flexible, but having exceptional mechanical strength. Methyl methacrylate polymerizes to much harder transparent solids, which have remarkable light transmission. The straight chains initially formed by polymerization may tend to become cyclized by linking along the chain.

During the last twenty years, a vast amount of work has been carried out on polymerization notably by Staudinger,[37] Carothers,[5] Mark,[24] Whitby,[42] Marvel,[26] and their [illegible].

Structure of Polymers. All the work carried out by these authorities almost unanimously leads to the conclusion that high polymers generally, whether natural or synthetic, are made up of enormous molecules containing hundreds of thousands of atoms bound together. There seems general agreement that many naturally high polymers such as rubber, cellulose, silk, etc., have a long molecule in the form of a long chain or thread. It seems likely also that in these materials the number of cross linkings between adjacent long molecules is very small. The term cross linking refers to straight chains or branch chains which have more than one main valency bridge between them. There is a great weight of evidence also that many other polymers which come into the study of synthetic rubbers such as polyisobutylene, polyacrylic esters, polystyrene, polyvinyl acetate, etc., also have these long-chain threadlike molecules, especially when they have been produced at low temperatures. Branching refers to long-chain molecules which branch as one proceeds along the molecule. So that

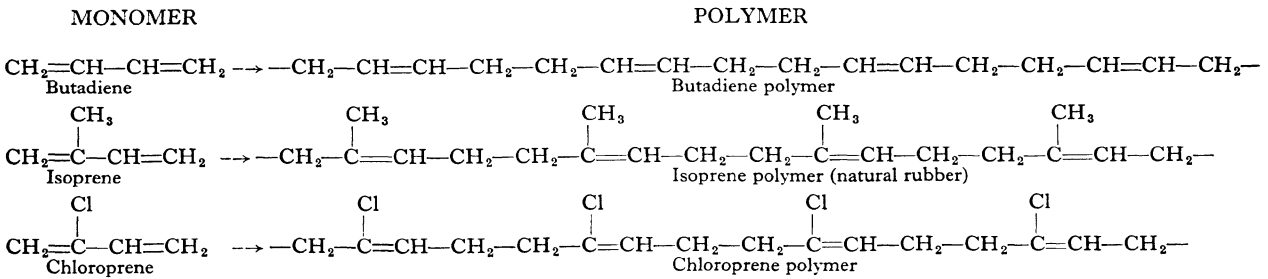
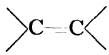
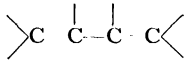
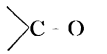
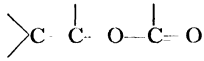
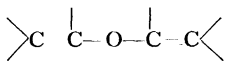
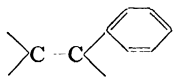
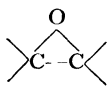
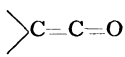


FIG. 24.—Bifunctional Monomers and their Polymers.

starting off with a single linear structure, this branches into two or more straight chains each of which in turn may branch, and so on. This type is more frequently encountered with multi-functional polymers.

TABLE 42. ATOMIC GROUPS WHICH PARTICULARLY FAVOUR POLYMERIZATION (Thompson) [39]

Group	Compound
	Ethylene, vinyl chloride
	Butadiene, chloroprene
	Aldehydes
	Vinylacetate
	Divinylether
	Styrene
	Ethylene oxide
	Ketene

In addition to these types of polymers, there are also those known as net and space polymers, which are 2 or 3 dimensional.

The general behaviour of these types of materials show very clearly defined differences. These have been summarized by Mark and Rath.[25] Thus the 2- or 3-dimensional polymers usually swell to a limited extent and do not go into solution. Examples of these are vulcanized rubber, Perbunan, neoprene, etc. They have no definite softening zone of temperatures. They tend to become plastic only at relatively high temperature, and then decompose slowly; a breakdown which is accompanied by increasing plasticity. They exhibit much greater resistance to abrasion and impact and heat than do the long-chain polymers. If there are many cross linkages, they become brittle and

lose their elasticity. They are also found to give very indistinct ring amorphous X-ray diagrams.

In the actual polymerization there are two main directions for the process. One can either produce straight-chain polymers, or alternatively, cyclized polymers, while combinations of these are also possible. It is generally accepted that straight-chain products will process easily, and if subsequent vulcanization or setting is not impeded, then probably such products are most desirable. Cyclized materials are much less readily processed, possibly owing to steric hindrance. In any event, the great problem is to make the polymerization process steer a regular well-defined course.

It is generally considered that in the production of synthetic high polymers the straightforward chain polymers are predominantly formed in those cases where the monomeric material contains only one polymerizable group, i.e. a double or triple bond. Outstanding examples of such monomers are vinyl chloride, vinyl acetate, acrylic acid ester, isobutylene, etc. These are the materials which Carothers called *mono-functional* (see Fig. 23).

In the case of most synthetic rubbers the reacting monomer is one which contains two or more reactive groups, such as butadiene, isoprene, chloroprene, etc. In these cases the formation of 2- or 3-dimension polymers is not only possible, but usually takes place. These are the monomeric materials which Carothers called *bi-functional*, or *multi-functional* (see Fig. 24).

It is interesting to observe that these modern conceptions of the formation of polymers no longer find it necessary to use the idea of partial valencies which was the essential feature of Thiele's theory,[41]

TABLE 43. COMPARISON OF THE RATES OF POLYMERIZATION OF HYDROCARBONS DIFFERING ONLY IN THE AMOUNT OF UNSATURATION.[36]

Compound	Percentage conversion under given conditions
Butene-1 CH_2 - CH—CH_2CH_3	39·6% in 52·5 seconds at 750° C. Stable at 200° C.
Butadiene-1,3 CH_2=CH- CH=CH_2	10 days at 150° C. in sealed tube, all polymerized. 70% polymerized in one hour at 350° C.
Vinylacetylene CH≡C- CH=CH_2	Explosive polymerization on contact with sulphuric acid or upon heating. Under pressure readily polymerized to a solid. Homologues form viscous syrups upon standing for two or three months.
Diacetylene or Butadyn CH≡C—C≡CH	Explodes at 35°. Definite polymerization in 5 minutes at 0° C.

and on which many of the earlier ideas were based. Particularly in connection with rubber-like polymers it is important to notice the part played by a conjugated system of double bonds.

In the case of butadiene and its homologues on which most synthetic rubber work has been based, it soon became evident that substitution in the butadiene molecule had a profound effect on the rate of polymerization, and on the nature of the product formed. Lebedev [23] first showed that 1-phenyl-1.3-butadiene polymerized much more rapidly at 150° C. than did isoprene, which in turn polymerized much faster than 1-methyl-1.3-butadiene. Whitby and Gallay [44] showed that the

TABLE 44. INFLUENCE OF CONJUGATION ON POLYMERIZATION [36]

Substance	Formula	Polymerization
Diacetylene	CH C C CH	Polymerizes extremely rapidly
Divinylacetylene	CH_2 CH—C C—CH CH_2	Polymerizes rapidly
Vinylacetylene	CH C—CH CH_2	Polymerizes very readily
Butadiene-1.3	CH_2 CH—CH CH_2	Polymerizes readily
Pentadiene-1,4	CH_2 CH—CH_2—CH CH_2	Rearranges into the conjugated system and polymerizes readily
Hexadiene-1,5	CH_2 CH—CH_2—CH_2—CH CH_2	Polymerizes slowly

ability of a conjugated diolefine to form synthetic rubber required the presence of three hydrogen atoms on the end carbons of the molecule. Their extensive investigations showed that terminal substitution and increase in the degree of substitution both retard polymerization.

Carothers has carried out comprehensive investigations of the influence of substituting halogens in butadiene.[6, 7, 8] His results are summarized in Table 45.

Methods of Polymerization. Polymerization is generally achieved by four main methods, namely:

1. Direct polymerization of the monomer without a solvent.
2. Polymerization of the monomer in some solvent.
3. Polymerization of the monomer dispersed in some immiscible solvent.
4. Polymerization in the gaseous phase.

The medium plays a very important rôle in the polymerization.

The first two types are both single phase, the systems being homogeneous liquids. The first method is still widely used in the production

TABLE 45. RELATIVE SPEEDS OF POLYMERIZATION OF VARIOUS DIENES COMPARED WITH ISOPRENE

(According to Carothers)
Temperature 25° C.

Compound	Position and nature of substituent				Estimated speed	Character of polymer
	C 1	C 2	C 3	C 4		
1	—	Cl	Cl	—	2000	Hard, not extensible
2	—	I	—	—	1500	Rubber-like under certain conditions
3	—	Br	—	—	1000	Good rubber
4	—	Cl	—	—	700	Excellent rubber
5	—	Cl	CH_3	—	500	Fair rubber, but low extensibility
6	Cl	Cl	Cl	—	120	Soft, elastic
7	—	C_6H_5	—	—	90	Soft
8	CH_3	Cl	—	—	30	Soft
9	C_2H_5	Cl	—	—	30	Soft
10	C_4H_9	Cl	—	—	10	Soft
11	C_7H_{15}	Cl	—	—	10	Soft
12	—	C_7H_{15}	—	—	9	Soft
13	Cl	—	—	—	7	Soft, sticky
14	—	CH_3	CH_3	—	3	Fair rubber, but low extensibility
15	CH_3	CH_3	Cl	—	1·5	Soft
16	—	CH_3	—	—	1·0	Fair rubber
17	—	—	—	—	0·8	Fair rubber

of synthetic resins, for example, in the polymerization of styrene and methacrylic ester. The second method involving solvents is employed with vinyl chloride, styrene, and so on. Normally these processes are carried out at moderate temperatures up to 150° C., and at ordinary pressure. With isobutylene very low temperatures are customary. In some cases, notably ethylene, high pressures are employed.

For many years the first two methods were predominant, but recently the third type of procedure has overshadowed the others and seems destined to supersede them. It is usually referred to as emulsion polymerization, because the immiscible solvent is generally water, and consequently since most monomers are liquids, emulsions are formed. Moreover, with adequate precautions such as the presence of a protective colloid, the final product remains in the dispersed form, either as an emulsion, or dispersion, according to whether the polymer is liquid or solid.

In some instances as, for example, vinyl acetate, the monomer is soluble in water, and thus represents the second type of polymerization. As polymerization proceeds, the product may be insoluble in water, in which case this forms a dispersion, and the subsequent action is once again that of emulsion polymerization.

The method adopted to carry out polymerization has a profound effect on the properties of the ultimate product. Staudinger and Frost[37] have effectively demonstrated this by the work on the polymers obtained from styrene. They found that polymerization in emulsion was much more rapid than polymerization of pure styrene. The variations in molecular weights of the polymers were considerable, as shown in Table 46.

TABLE 46. VARIATIONS IN MOLECULAR WEIGHT OF POLYMERS PRODUCED BY DIFFERENT POLYMERIZATION METHODS

Temperature of polymerization of Styrene °C.	Molecular weights of polymers	
	From pure styrene	From styrene in emulsion
30	600,000	750,000
60	350,000	400,000
100	120,000	175,000

When the commercial materials are considered, namely, the synthetic elastomers and the ethenoid plastics, it becomes quite evident that the most important method of production at the present time is that of emulsion polymerization. Most large manufacture is based on this process. It also represents the most outstanding trend in plastics production at the present time. It brings in its train another very important trend, namely, the production of synthetic rubbers by continuous process. It heralds the transition from batch production to continuous production.

The other leading method for the production of synthetic rubber involves the use of sodium as promoting agent. This was the process developed before the last war, and the one which the Germans worked for some time until comparatively recently. It appears that they have now abandoned this method of polymerization in favour of emulsion polymerization.

According to Ziegler [19] the particular advantage of polymerization with sodium is the use of a concentrated system while the disadvantage is the difficulty of dissipating the considerable heat of polymerization.

'he properties of the polymers, using the viscosity of a solution as ıe criterion, can be controlled by addition of specific reagents during olymerization and various products can thus be made. The out-tanding user of the sodium process has always been the U.S.S.R. 'hich has specialized in it. They still carry out very large-scale ıanufacture using the sodium method, although they also have an ıcreasing production based on the emulsion process. The advantages f emulsions are the complete control over heat of polymerization, vailability of the product as a latex, and the facilities to form copoly-ıers. Another advantage is the enormous increase in scope afforded.

Heat Polymerization. It was observed quite early that isoprene nd dimethylbutadiene underwent spontaneous polymerization to ubber-like products when kept for a long period at room temperature. 'rom this it was only a short step to the discovery that the polymeriza-on of the dienes could be brought about more quickly by the applica-on of heat. The polymerization of isoprene by heat was patented y Hoffman and Coutelle [15] in 1909. Harries [11] examined the product btained by the heat polymerization of isoprene and in 1910 reported . to be similar in chemical and physical properties to natural rubber. n the same year, Lebedev [22] published the results of an investigation on ıe heat polymerization of conjugated dienes in which he stated that oth butadiene and dimethylbutadiene gave rubber-like products in ddition to various oily dimers. Subsequently he measured the

TABLE 47. HEAT POLYMERIZATION OF ISOPRENE AND DIMETHYLBUTADIENE [43]

TIME Hours	ISOPRENE				DIMETHYLBUTADIENE			
	Oil %	Rubber %	Mol. wt.	Relative viscosity [a]	Oil %	Rubber %	Mol. wt.	Relative viscosity [a]
	At 85° *C.*							
97·5	9·07	17·05	4589	4·62	—	—	—	—
101	7·9	16·25	—	—	0·9	10·5	2318	3·69
154	—	—	—	—	1·5	13·8	3345	3·83
250	—	—	—	—	2·7	19·6	3524	4·55
900	—	35·3	5715	8·20	—	49·7	3483	9·21
	At 145° *C.*							
5·25	38·2	10·03	3291	3·14	—	—	—	—
12·5	54·7	15·56	3936	4·69	11·1	15·6	2138	2·3

[a] Relative viscosity at 30·1° C. of a sol containing approximately 0·68 gram er 20 c.c. of benzene.

amount of polymerization produced by heating various diolefines at 150° C.

Heat polymerization of the pure dienes is attended by serious limitations, as was shown by Lebedev, and more fully by Whitby and Crozier.[43] The chief limitations are that at elevated temperatures : (1) the diolefines form oily, dimeric by-products as well as rubber, and the proportion of the former is the greater the higher the temperature, i.e. the more rapid the polymerization ; (2) the degree of polymerization of the rubber is not high, and the molecular weight of the product is lower the higher the temperature applied.

Isoprene at elevated temperatures has a much greater tendency than dimethylbutadiene to form oily, dimeric by-products instead of rubber. At 145° C. the oil formed is more than three times the amount of rubber. In great measure these conclusions hold generally for the polymerization of the other diolefines.

Catalysts. As a consequence the use of catalysts is general in almost every form of production of rubber-like materials. In each instance a catalyst of polymerization is usually present. This is generally an oxidizing agent, such as benzoyl peroxide, hydrogen peroxide, and so forth. A specific catalyst is sodium. In the case of olefines, the best catalysts are halides of boron, aluminium, titanium, etc. The process of polymerization is promoted by heat, light, irradiation, or occurs spontaneously, and in some instances is further aided by pressure, notably when carried out in the gas phase.

Difficulty of Control. Diolefines are extremely reactive materials. They tend to polymerize with some ease, in some instances spontaneously. But with different conditions, the progress of polymerization very easily takes wrong turnings. Instead of straight-chain polymerization there may be cyclization, with formation of two- or three-dimension polymers. Too often the process may get out of hand. The lack of control inevitably results in poor products. It is consequently essential to establish a satisfactory routine which must be adhered to. It is no use obtaining at each cycle a rubber having very different properties.

According to Koch [19] it is certain that when butadiene is polymerized not only does the normal 1.4 addition occur to form long chains, but also 1.3 and 3.4 additions take place. Through this abnormal process cyclization results. These molecular structural differences between natural rubber and Buna rubber may account for the poor processing properties of the latter, but may also explain such advantages as superior heat resistance and better abrasion resistance.

Sebrell and Dinsmore [33] have carried out extensive work on the

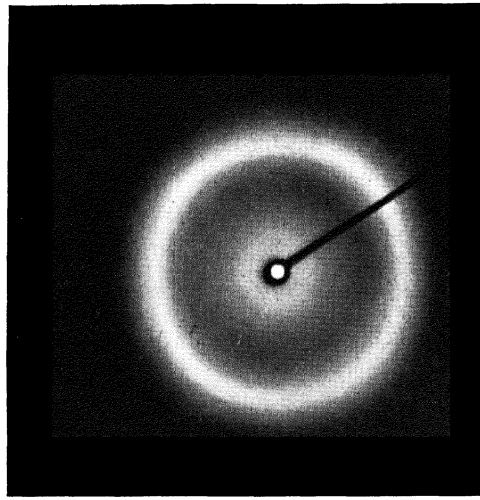


FIG. 25.—X-ray photograph of Unstretched Rubber.

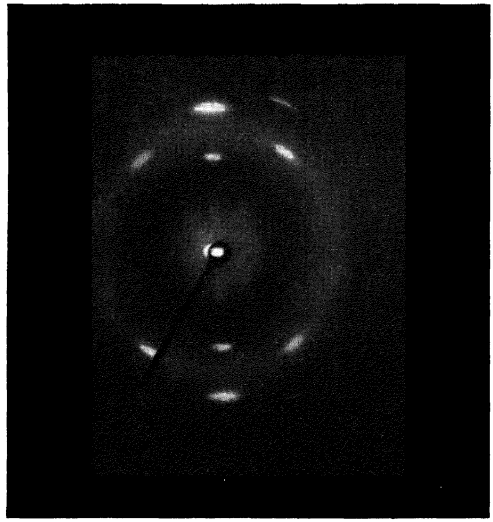


FIG. 26.—X-ray photograph of Stretched Rubber (Sebrell and Dinsmore).

[*To face page* 133.

structure of synthetic rubber-like materials, particularly in relation to their X-ray diagrams. They failed to get any characteristic pattern comparable with that obtained from natural rubber, in the case of Buna S, Perbunan, Thiokol, Chemigum and Vistanex. They considered therefore that the structure of these synthetic elastics is quite different from that of rubber and that they may owe their elastic properties to the operation of some completely different mechanism. They considered that there was probably considerable cross-linking of the chains.

Polymerization of diolefines to elastomers is complicated and not

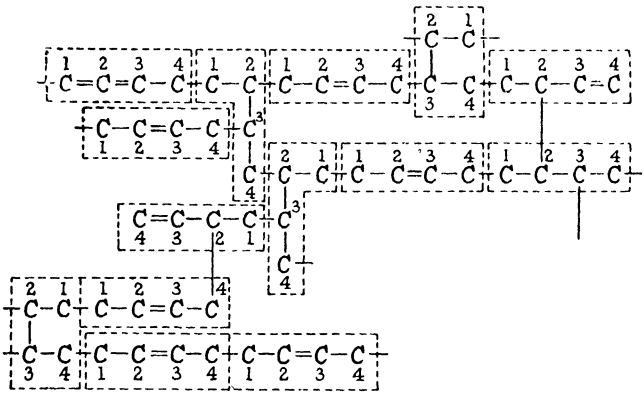


FIG. 27.—Butadiene Polymer according to Staudinger.

easily controlled. According to Williams [45] trouble begins as soon as the first molecule of diene is activated and polymerizes with a second molecule. This polymerization of two molecules with rearrangement of valency bonds leaves a new activated molecule, and a chain of reaction starts, which proceeds until terminated in some way. The reaction may terminate immediately, with production of cyclic products or it can proceed to build up into high molecular weight products. The final products may be rubbery materials of varying quality or balata-like thermoplastics. Plastic bodies may be formed which will change spontaneously into elastic products of a vulcanized nature.

Williams [46] stressed the importance of the presence of foreign matter in the case of butadiene, which profoundly affected the direction of polymerization. The latest methods for production of butadiene reduce the significance of this factor.

Summarizing the earlier work, it was observed that diolefines were

polymerized chiefly by heat processes, in the presence of one of an ever growing number of catalysts. But the time factor was considerable and the quality of the rubber poor. Other methods were mere curiosities. The laboured procedure used by the Germans in the last war perfectly illustrated the disadvantages of all these methods.

Two major forms of procedure have gradually evolved. Until comparatively recently (about 1936) the methods based on the use of sodium as catalyst predominated. Inaugurated by Matthew and Strange,[27] and by Harries, the sodium polymerization process passed through all the various stages of development, and has been the basis of large-scale production, notably in U.S.S.R. and Germany. The I.G. has an almost interminable string of patents dealing with different aspects of the subject. It is to be noted that the German generic term " buna " is derived from *bu*tadiene and *na*trium.

Sodium Polymerization. The use of sodium as catalyst at first gave most unsatisfactory results. The products were extremely tough, and could not be brought to a reasonably plastic stage. They were also very difficult to vulcanize. For one thing sodium tends to react with butadiene. Polymerization proceeds irregularly and is difficult to control.

According to Abkin and Medvedev,[1] polymerization occurs heterogeneously with butadiene in the liquid phase; both in liquid and gas phases the rate of polymerization increases to a definite value and then remains constant. The first stage marks the formation of primary sodium butadiene compounds and lasts as long as metallic sodium remains in the system. Oxygen has a strong inhibiting effect on the reaction.

In the early days sodium was almost invariably used as wire. Many of the most recent processes have depended for their success upon variations of the form in which sodium is present. For example, it has been utilized as powder or as very fine spherical particles. Thus Tschajanov [40] described how butadiene was polymerized in a steel bottle using as catalyst a sodium dispersion in paraffin. A 99 per cent. yield was obtained after 63 hours. Zelmanov and Shalnikov [48] utilized colloidal sodium and obtained a rubber from butadiene in less than 36 hours at 10–15° C. using less than 0·3 per cent. sodium. Many of the most successful methods have used it in the form of surface films on formers of every conceivable shape.

The most powerful controlling factor in the sodium polymerization process has been the use of inert solvents. Stable, non-reactive, low-boiling hydrocarbons such as cyclohexane, petroleum ether, benzene, etc., were used in proportions of 10–20 per cent. Being

swelling agents for the rubber which was produced they reduced the viscosity and increased the plasticity, moreover they facilitated the production of reasonable products from relatively impure dienes.

Bock and Tschunkur [3] polymerized isoprene with sodium in the presence of materials such as starch or ethyl cellulose in an inert atmosphere. For example, 100 parts of isoprene, 2 parts of sodium pieces, 1 part ethyl cellulose were introduced in hydrogen in an autoclave at 40° C. for 12 hours, yielding a soft elastic rubber.

Numerous other materials have been claimed to regulate the polymerization, including many vinyl derivatives. For example, 100 parts of butadiene with 0·3 per cent. of sodium and 1 per cent. of vinyl chloride at 60° C. was converted into polymerized butadiene in 30 hours.[16]

Cyclic diethers are also very effective.[17] Thus butadiene with 0·4 per cent. of sodium and 5 per cent. dioxane heated in an autoclave at 40° C. gave a solid product after 36 hours which could be vulcanized.

Ammonia and amines [18] have a similar effect, slowing the rate of reaction and keeping the temperature down, thus 0·5 per cent. of sodium and 0·05 to 0·10 per cent. aniline at 80° C. quantitatively polymerized butadiene in 30 hours.

Zavalkov [47] has described the method used at the Yaroslav plant in the U.S.S.R. to make S.K.B. rubber. Impure butadiene was used containing not less than 75 per cent. butadiene.

The batch was 1700 litres, the reaction vessel being lined with paste of clay and glycerine. The sodium was present as a coating on 72 iron combs. The charge was heated at 30° C., the temperature being raised by 0·5° to 0·8° C. per hour for 8 hours. Cooling was necessary, the polymerization being exothermic, giving 349 cals. per kilogram of rubber formed. The maximum temperature was 65° C. at 8 atmosphere pressure, the reaction being finished after 120 hours.

According to Nebidovsky [29] butadiene is polymerized in nitrogen in an autoclave containing 5 per cent. of sodium deposited on zinc rods. After two hours the temperatureis raised to 30° C. and 8 atmospheres pressure. Polymerization is complete in 36 hours and 90 per cent. yield is claimed. The resulting rubber is said to be more resistant to friction, sunlight, oxygen, solvents and alkalies, than the natural rubber.

According to Ebert and Orth,[11] butadiene is continuously polymerized in the presence of an alkali metal as the polymerization catalyst, by introducing the material to be polymerized and the catalyst into a tube provided with a conveyor worm. The material is polymerized while thoroughly mixing it with the catalyst during forward movement

through the conveyor. The finished product is withdrawn at the end of the tube.

The use of sodium as polymerizing agent now appears to be practised only in the U.S.S.R. According to Koch the I.G. still make a small amount of Buna 85 by the sodium method, this being used mainly for hard rubber. In 1937 Konrad [20] still referred to the effective use of sodium as catalyst for making Buna 85 and Buna 115. The trend is strongly in the direction of polymerization in aqueous emulsion, utilizing less stringent catalytic agents. This is a trend which applies equally well to the plastics industry.

Polymerization of Olefines. — The first notable success of petroleum chemists in the synthetic rubber field was with polyisobutylene. There are a number of polyisobutylenes based upon isobutylene. As already described isobutylene is one of the chief olefines obtained by cracking processes. This is the material used in the United States. In Germany isobutylene is obtained by passing gaseous hydrocarbons through the electric arc.

Isobutylene may be polymerized by heating in the presence of catalysts such as aluminium chloride, boron chloride, stannic chloride, etc. Although it was found in 1873 by Butlerov and Gorianov [4] that isobutylene could be polymerized to a liquid product by means of sulphuric acid and/or boron fluoride as catalyst, it is only recently that rubbery products have been obtained. Standard Oil Development Co. and I.G. Farbenindustrie [34] purified light cracked oil to give a mixture containing at least 95 per cent. isobutylene. Crude oil containing butanes and butylenes was then added to produce a mixture containing from 20 to 40 per cent. of isobutylene, and 10 to 20 per cent. of other olefines. The mixture was then polymerized with boron fluoride at a temperature below 40° C., to yield plastic solid, or semi-solid rubbery materials. In another patent Standard Oil Development Co.[35] produced high molecular weight polymers of olefines, notably polyisobutylene, by passing the olefine into a bath of hydrocarbon diluent, such as ethane, propane, or butane, having an active catalyst, such as boron fluoride, keeping the temperature below −10° C. Isoprene, styrene, and butadiene could also be polymerized by this method. Polymerization occurs with the formation of substantially straight-line polymers. The nature of these varies with the molecular weight, ranging from oily viscous fluids up to strong rubbery materials with molecular weights as high as 500,000.

The Use of High Pressure. There has been a certain amount of interest in the influence of very high pressures on the polymerization of diolefines, for polymerization of conjugated diolefines occurs with

a great decrease in volume, which would therefore be aided by pressure. Conant and Tongberg [9] used pressures up to 1,800 atmospheres for the polymerization of isoprene. They found 10 per cent. was polymerized in 20 minutes at 23° C., while after 3 hours 76 per cent. was polymerized. The results obtained varied considerably in successive batches. According to Williams, the high-pressure polymer resembled vulcanized rubber in being both insoluble and non-plastic. He considered that the commercial application of pressure to polymerization would present many difficulties.

Starkweather [36] found that chloroprene polymerized eight times as fast at 6,000 atmospheres as at 3,000 atmospheres pressure.

There has been an enormous amount of work on high-pressure polymerization of ethylene. The main objective was to convert it into suitable fuels. But at least one outstanding commercial material with rubbery properties has emerged. This is the solid polymerized ethylene obtained by Imperial Chemical Industries, Ltd., and known as polythene.[12] It is prepared by heating ethylene at 100°–300° C. under a pressure of at least 1,200 atmospheres, when solid or semi-solid polymers are formed.

Although most polymerizing processes on isobutylene have been carried out at very low temperature, yet according to Kuentzel and Webb [21] interesting resinous products are obtained by submitting it to pressures of 300 atmospheres at temperatures as high as 100° C.

Polymerization by Light. The effect of photochemical action on monomers is best brought out by its use in the case of polyvinyl chloride.

Regnault,[32] Bauman,[2] and Ostromislensky [30] used sunlight and ultra-violet rays to polymerize vinyl chloride.

According to Ostromislensky, the polymerization was effected by irradiation from a mercury quartz lamp for 12 hours at 20° C.

Ostromislensky classified the resultant polymers as alpha-, beta-, gamma- and delta-, polyvinyl chlorides, according to solubility in acetone or chlorbenzol; α-polymer is soluble in acetone; β-polymer is soluble in chlorbenzol; γ- and δ- polymers are insoluble in chlorbenzol.

In the opinion of Ostromislensky, in the photopolymerization the process progresses with formation at first of α-polymer, which, under the continued action of ultra-violet rays, is converted into the β-form; the transformation of vinyl chloride into γ- and δ-polymers is conditioned by a further prolonged action of the ultra-violet radiation.

In order to ensure a high degree of dispersion of polyvinyl chloride molecules the photochemical process, like the thermo-polymerization

may be conducted either in a solvent (e.g. alcohol, acetone, dichlorethane, etc.), or in emulsions.[10]

The problem of the photopolymerization of vinyl chloride in various solvents has been investigated by Plotnikoff,[31] and the colloidal properties of vinyl chloride polymers derived in different solutions were examined by Flumiani.[13]

The results of these researches showed that the speed of polymerization of vinyl chloride in solution, at constant concentration, depends on the nature of a solvent; for example, the comparative values of polymerization velocities in toluene is 1, in ethyl alcohol 25, and in carbon tetrachloride 68.

The effect of the ultra-violet rays upon the liquid vinyl chloride is so intense that the formation of polymers occurs almost spontaneously. It would seem, therefore, that out of numerous methods the photopolymerization of vinyl chloride has the most favourable chances of application, since it allows a continuous rapid procedure. There are certain difficulties of control which impede progress.

The Mechanism of Polymerization. Melville[28] has summarized the information available about the mechanism of the combination of substances of high molecular weight. Considerable progress has been made in this branch of chemical kinetics. In general, high polymers are formed by polycondensation reactions or by the union of ethylene derivatives into chain-like molecules. The latter is the interesting type for consideration in the study of synthetic rubbers. In the case of ethylene derivatives considerable progress has been made because the reaction can be followed in the liquid and in the gaseous phase. According to Melville these reactions are substantially chain reactions. He stated that the derivatives most susceptible to polymerization are the vinyl compounds of the general type CH_2:CXY; the substituent groups have a great influence on the course of the reaction. In general the more highly polar X or Y is, the more readily is the polymer formed. The evidence that the reactions are of the chain type depends on the fact that small amounts of catalyst or of radiation will produce large amounts of the polymer. Yet these reactions are easily stopped by anti-oxidants. According to Melville the chain carrier is the growing polymer which is in a very reactive state. So that when it collides with a monomer molecule the latter adds on quite easily involving a small amount of activating energy. When reactions are induced by addition of free radicals it seems clear that the growing polymer is simply a large free radical with a terminal free valency. It is, however, difficult to explain by this mechanism alone such reactions as photopolymerization of chloroprene and of methyl methacrylate. Melville

pointed out the striking property that these materials continue to polymerize in the dark, showing that the molecules exist for a long period. Another interesting feature is that these active molecules enable the development of heterogeneous polymers, so that it is possible to grow chloroprene on an active centre of polymethyl methacrylate. Since the action is subject to specific chemical inhibition it is probably chemical in nature. Melville stated that the structure of vinyl polymers has been established in several ways. By analogy with the behaviour of quite small molecules it seems that the predominating structure is of the head to tail type. X-ray evidence too, in general, supports this opinion. Also the way atoms or groups may be removed, for example, chlorine from polyvinyl chloride, also tends to confirm this.

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CHAPTER 9

COPOLYMERIZATION

IN spite of all the advances made in the polymerization of the butadienes etc., it became increasingly apparent that the materials obtained although good in themselves, were not good enough. While sharing many of the good properties of rubber, they also had the disadvantages It was also evident that while no single monomer had all the desirable characteristics, yet considered together with available vinyl monomers it became clear that the properties of any one were often complementary to those of another. The introduction of copolymerization provided a solution to this problem of bringing suitable polymers together.

In this manner many synthetic elastic materials have been obtained having some property, or properties, far superior to natural rubber An enormous amount of work has been carried out along these lines Although at first it was thought that admixture of different diolefines would give beneficial results, this has been abandoned in favour of the copolymerization of a diolefine with a synthetic resin. All the variations of this theme are now being worked out. Each new synthetic resin is tried out as it appears.

Copolymerization. In recent years the new technique of copolymerization has been evolved which not only goes far toward solving the problem, but has opened up further new fields for material capable of polymerization. For example, a fairly good synthetic rubber can be made by polymerizing isoprene or butadiene alone either in a single-phase system or in an aqueous emulsion. Better products can be made by copolymerizing these hydrocarbons with other compounds containing active vinyl groups such as styrene (vinylbenzene) acrylonitrile (vinylcyanide), vinylidene chloride, methyl vinyl ketone, methyl methacrylate, or any of a hundred other vinyl substituted hydrocarbons, chlorinated hydrocarbons, alcohols, ethers aldehydes, ketones, acids, esters, nitriles, etc. Another interesting group of synthetic rubbers comprises the copolymers of a diene, such as butadiene, with an olefine, such as isobutylene. Then, too, there are the polymers of chloroprene and, like butadiene, chloroprene can be interpolymerized with a wide range of vinyl compounds to give commercially valuable products. Moreover, diolefines may be poly

merized with other diolefines, e.g. butadiene with chloroprene—and there are many three-way copolymers which possess unique and interesting properties. There is almost no limit to the range of synthetic elastics which can be made. Instead of mixing the polymers, the original monomeric substances are brought together and are then polymerized to the desired degree.

This is the process known as copolymerization, interpolymerization, or mixed polymerization. Copolymerization is probably the best term, and should be recognized as a standard description. The process may be carried out upon mixtures of the monomers as they are, in solution or as emulsions. The method adopted has, however, a profound influence on the properties of the product.

At first sight it would appear that a mixture of the two separate polymer types would be formed. Actually this is not the case. Entirely new materials result, in which both monomeric groupings are found in the same polymerized molecule.

The properties of the materials are different from what might be anticipated. They are not intermediate between the two types. Generally they are much improved, while there are certain new characteristics that are of great value. Whereas with mechanically mixed polymers the individual ingredients may be separated, for example, by the use of solvents, yet in the case of copolymers such a separation is not possible. The solubility of a copolymer may be very different from those of the components. For example, while vinyl acetate and vinyl chloracetate each polymerize to give soluble products, the copolymer is virtually insoluble in the same solvents.

The Outstanding Copolymer. Consideration of the products obtained from vinyl chloride and vinyl acetate admirably illustrates the effects of copolymerization.

Vinyl acetate polymerizes to give polyvinyl acetate. This is quite useful commercially, and is widely employed as an adhesive; it is brittle although it softens between 30° C. and 40° C. It is exceptionally resistant to heat and light. Owing to the low softening temperature it cannot be processed and moulded with any ease. It also has a relatively high water absorption. A typical ester, it is fairly active chemically; for example, undergoing saponification in the presence of alkalis. It is soluble in alcohols, ketones, esters, chlorinated hydrocarbons and aromatic hydrocarbons.

Polyvinyl chloride is quite different. It has a very high softening point and is not very thermoplastic. It is chemically inert, virtually non-inflammable, tasteless and odourless. It has great resistance to corrosion, not being attacked even by acids such as sulphuric, nitric

and hydrochloric, nor is it affected by alkalis. It has extremely lo water absorption.

Furthermore it is almost insoluble in all solvents in the cold, althoug it dissolves fairly readily in hot chlorinated hydrocarbons such a ethylene dichloride. It is not particularly stable to light and hea This material is unusually strong and water and chemical-resistan but it softens so slowly with rise in temperature that decompositio begins before it can be properly moulded. For this reason the resi is always plasticized by mixing on a hot roll mill or in a jacketed doug mixer with a plasticizer, usually a compatible high-boiling liquid suc as tricresyl phosphate. Upon cooling, a resilient rubber-like mass i formed which has been used successfully in numerous application requiring greater resistance to sunlight, oxidation, oils, and grease than is exhibited by rubber. Such uses include wire insulation, tubing impregnated cloth for raincoats and shower curtains, and linings fo acid-resistant containers. The poor solubility of polyvinyl chloride i most organic solvents limits its use in the surface coatings field.

Consideration of the properties of these two vinyl compound showed that if they could be combined a useful material should b obtained. Mechanical admixture of polyvinyl acetate and polyviny chloride was tried from every conceivable angle, but they were incom patible and the resulting mixtures were invariably too weak and brittle It was then found that when the monomeric vinyl compounds wer polymerized together, a resin was formed that retained the strengt and water resistance of polyvinyl chloride but that had been sufficientl plasticized internally by the combined polyvinyl acetate to make i mouldable at temperatures within the range of its heat stability an soluble in many organic solvents. Thus a resin molecule was forme that consisted of a linear chain in which monomeric vinyl chlorid and vinyl acetate had reacted with themselves and with one anothe at the double bond to form a copolymer. The relative proportion of vinyl chloride and vinyl acetate in the chain depend upon the com position of the reaction mixture; and the length of the molecule, a in the case of other vinyl polymerizations, is governed by reactio conditions at the instant of formation. Average molecular weight ma also be controlled by fractionation and extraction. Extraction i accomplished by partial precipitation or by treating the finely divide dry resin with an appropriate solvent-nonsolvent mixture that dissolve out the lower polymers and leaves the higher bands intact as a granula powder.

The copolymerization of these compounds makes possible th synthesis of a wide range of resins suitable for a variety of industri

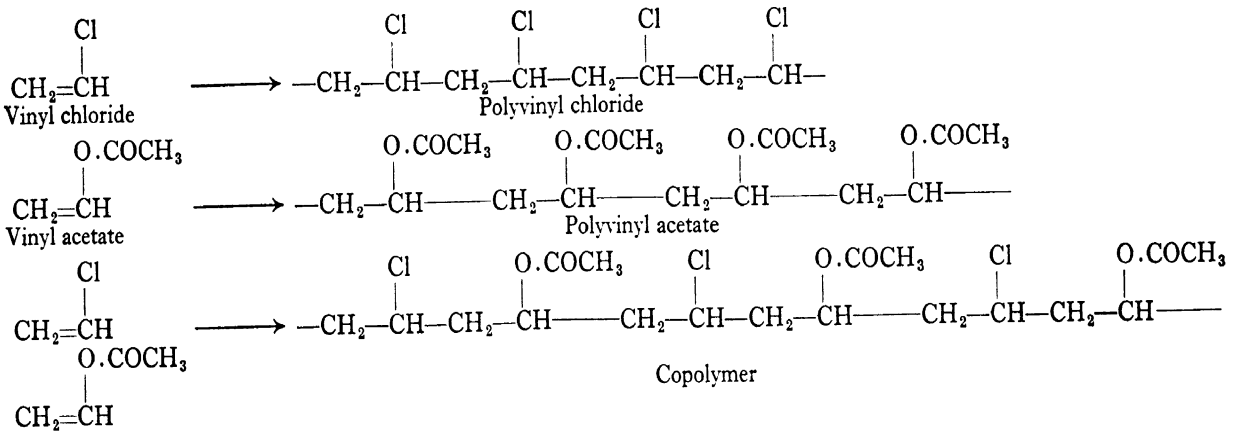

FIG. 28. Copolymerization of Vinyl Chloride and Vinyl Acetate.

applications. Not only is it possible to vary the average molecular weight as in the case of other vinyl resins to suit the application involved but to alter the vinyl chloride-vinyl acetate ratio as well.

Thus, in common with other vinyl resins, increase in the average molecular weight or degree of polymerization of these copolymers results in greater strength and toughness but makes the resin more difficult to mould or to put into solution. Electrical properties, specific gravity, refractive index, and water resistance remain constant. On the other hand, increase in vinyl chloride content improves water resistance and raises the softening temperature, but yields a less soluble and less easily moulded product.

The copolymers formed in this way are found to be thermoplastic, odourless, tasteless, and non-inflammable. The mechanical properties are considerably higher than could have been visualized. Not only is the tensile strength very high, but the products are extremely tough and have a measure of resilience. The electrical properties are very good. The resistance to moisture is extremely high. The resistance to corrosion and chemical attack is exceptionally good, while the products are unaffected by soaps, acids, alkalis, oils and alcohol.

The scope of the copolymer is extremely wide, for it is extremely versatile and can be worked or moulded without difficulty on rubber or plastics machinery.

The properties of any particular copolymer depend upon the molecular weight or, in other words, the degree of polymerization, upon the ratio of the two polymers, and upon their distribution. The latter factor in turn depends upon the method of production.

The actual distribution of the respective components along the copolymer chain is a matter of some uncertainty. It can be controlled within reasonable limits only by maintaining rigid control of the conditions under which the polymerization is carried out. Any deviations may lead to the production of products having different properties. Since the molecular chains may contain some hundreds of the monomer units joined together, there is evidently some scope for variation in the positions. It is these factors which make the reproduction of successive batches to have absolutely identical properties rather difficult.

In general, it has been found that the mechanical properties improve with a rise in the degree of polymerization, while the other properties are more or less independent of this, being rather a function of the chemical composition. In deciding upon a copolymer for any specific application, a type is naturally chosen that combines as many desirable properties as possible with a minimum of undesirable ones.

Copolymerization and Synthetic Elastics. There has been

great activity in the production of synthetic rubbers and similar materials by copolymerization of butadiene and other compounds. It is now the principal method used.

Synthetic rubbers made by straightforward polymerization have been found to have very marked limitations. By forming copolymers, each product possesses the general rubbery properties, but some additional specialized characteristic in addition. The formation of copolymers enables the production of materials which can be described as having " rubber-synthetic resin " characteristics, or " synthetic resin-rubber " characteristics according to whether the rubber component (butadiene, chloroprene, etc.) predominates, or the synthetic resin component (styrene, methyl methacrylate, etc.) predominates.

These are well illustrated by the different types of Buna rubber,

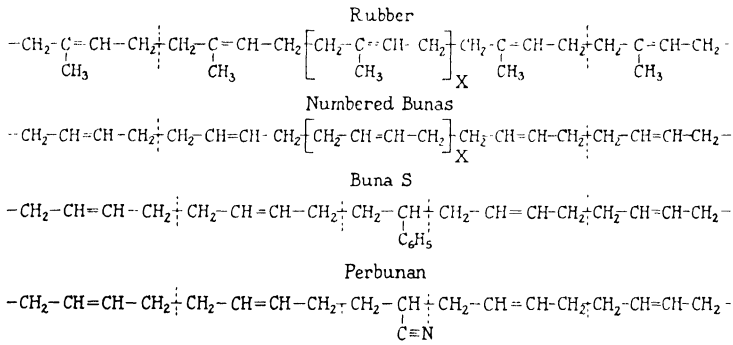

FIG. 29.—Chain Molecules of Rubber and some of the Buna Elastomers.

the German elastomers. The early types were based on experience obtained during the last war, and were found to be unsatisfactory in many respects. The copolymerization process has facilitated the production of successful materials, having properties which are specially suited for definite applications.

The production of these copolymer synthetic rubbers proceeds apace ; new types are being developed daily, although naturally many are found not to be suitable for commercial purposes.

Considering the various leading types of synthetic rubber-like materials the importance of copolymerization becomes quite unmistakable.

Perbunan is a copolymer of butadiene and acrylic nitrile ; so are Hycar and Chemigum. Thiokol RD is also a copolymer. Buna-S is a copolymer of butadiene and styrene. Some of the newest types of

neoprene are copolymers of chloroprene and other monomers. Butyl rubber is a copolymer of isobutylene and butadiene. And the same trend is equally marked in plastics production.

According to Mueller,[12] both copolymers S and N can be considerably changed in quality by changing the ratio of butadiene ; styrene or butadiene ; acrylonitrile, respectively resulting in softer or harder, tougher products. When one gram-mol of butadiene, 54 grams and one gram-mol of acrylonitrile, 53 grams, are used for the reaction, which is equal to a 1 : 1 ratio, a good grade of Buna-N is obtained. In the case of Buna-S the molecular ratio is approximately 1 : 2 as the molecular weight of butadiene is 54 and that of styrene 104.

The following selection of some recent rubber-like copolymers shows how actively this angle is being studied. Moreover, work is being carried out employing more than two monomers.

The I.G. made copolymers of butadiene with 2-vinyl furane,[8] the products being capable of vulcanization. In another patent [10] it was vinyl ethenyl carbinols which were copolymerized together with butadiene products to give synthetic rubbers. Other examples of copolymer synthetic rubbers include the following :

In one patent,[9] the I.G. polymerized butadiene and an ethylene dicarboxylic acid in aqueous emulsions using an oxidate catalyst. An example described the copolymerization of 75 parts fumaric acid ester and 25 parts butadiene. Konrad and Bock [11] polymerized an aqueous emulsion of a butadiene hydrocarbon with 40 per cent. of an acrylic, methacrylic, etc., derivative.

Müller-Conradi [13] and Daniel polymerized a butadiene emulsion in the presence of emulsions of highly polymerized isobutylene with the aid of peroxides. The products were claimed to be far superior to those obtained from butadiene alone.

Another rather good example is the following recent patent of the Wingfoot Corporation : [15]

> Butadiene is co-polymerized with vinylidene chloride to give vulcanizable rubber-like polymers. The 1.3-butadiene is preferred, but its homologues may also be used. From 50 to 65 per cent. of the butadiene component should be present to obtain products most nearly resembling rubber. Polymerization is best effected by heating aqueous emulsions containing sodium oleate or similar emulsifying agents, catalysts such as benzoyl peroxide or sodium perborate, and promoters such as carbon tetrachloride or trichloropropionitriles.

In this country too, there has been some activity along these lines. In one patent Habgood, Hill and Morgan [6] copolymerized butadiene with half its weight of specified methacrylic acid esters in the presence

of 5 to 30 parts carbon tetrachloride. In another [6] they copolymerized a chloroester of methacrylic acid with butadiene, while in yet another patent they showed how to copolymerize methyl methacrylate with butadiene.

Extremely interesting copolymers have been made from butadiene and methacrylates by Du Pont de Nemours.[5] They prepared the following table to show the effects of different proportions of the ingredients.

TABLE 48

Butadiene %	Methyl methacrylate %	Properties
4	96	Soluble resin more flexible than polymerized methyl methacrylate
6	94	More flexible than preceding resin
8	92	Fairly tough soluble resin
10	90	Fairly tough soluble resin
12	88	Tough soluble resin
16	84	Somewhat softer more pliable resin
20	80	Insoluble rather soft pliable material
30	70	Insoluble soft rubber-like copolymer

The laboratories of the world are working overtime to produce the various copolymers, trying out the whole range of diolefines and vinyl compounds one after the other.

The Process in Specific. The process of copolymerization is specific. That is to say, that it does not follow that admixture of any two vinyl monomers or a diolefine and a vinyl monomer will inevitably produce a copolymer. For example, styrene and vinyl acetate will not polymerize together. All that happens is that the styrene polymerizes in the normal way to yield polystyrene, while the vinyl acetate remains unchanged. The nature of the radical attached to the parent nucleus has a profound bearing on this ability to yield copolymers.

Another important point is that the presence of minute quantities of certain materials act as very effective poisons, inhibiting the reaction. One example is the case of the copolymerization of butadiene and acrylic nitrile, normally presenting no difficulty, which is completely stopped by the presence of minute traces of copper or certain amines.

Addition of Small Amounts of Secondary Ingredients. Yet another important aspect of copolymerization has yet to be considered.

It has recently been shown that by utilizing small quantities of specially selected secondary materials that it is possible completely to

modify characteristic properties of the polymers. Thus the introduction of small amounts of divinyl compounds to ordinary vinyl materials is found to give insoluble polymers by contrast to the polymerized vinyl compound which is soluble in the solvent in question. It is considered that these additions give the long-chain molecules a very pronounced three-dimensional character.

Staudinger and Heuer [14] showed that additions of small amounts of divinyl-benzene to styrene yielded, after polymerization, an insoluble polymer which would only swell to a limited extent in solvents in which polystyrene is freely soluble.

This was thought to operate because the divinyl benzene caused the normally unbroken straight chain of polystyrene to branch when one of these molecules joined in. Each branch would proceed from a certain length, would again pick up a divinyl-benzene molecule and would then branch again. In this way a three-dimensional structure is rapidly built up, a fact which is considered to modify profoundly the behaviour of materials in solvents. It only needs comparatively few molecules of the divinyl compound to exert a very marked effect.

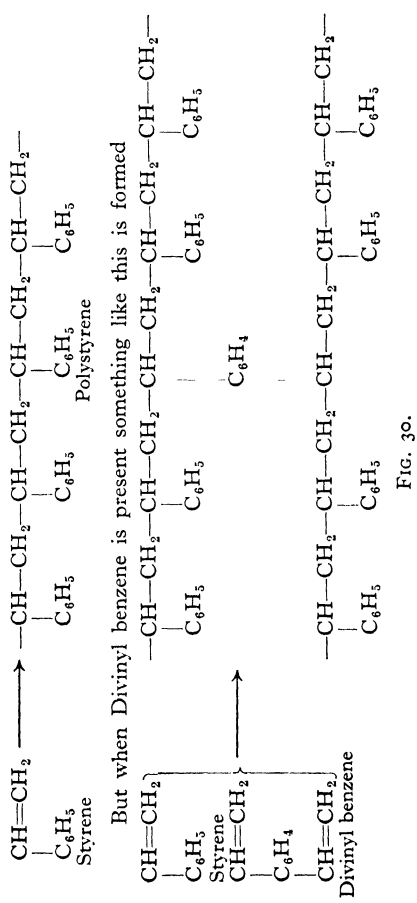

FIG. 30.

In the synthetic elastic field the outstanding example of this type of copolymerization is butyl rubber. In this instance, addition of a small amount of a diolefine butadiene is able completely to change the properties of the predominating ingredient—isobutylene. Less than 2 per cent. of

butadiene is present, yet the polymerized product can be vulcanized, in complete contrast to the polymerization of isobutylene which results in the thermoplastic polyisobutylene which cannot be vulcanized.

How Monomers Link Up in the Copolymer Chain. A certain amount of work has been done on the elastomers to determine how the respective polymers link up, whether they alternate in a regular manner or whether there is haphazard linking. Alekseeva [1] investigated the structure of butadiene and acrylic nitrile made by polymerizing an equimolecular mixture in emulsion at 60° C. for 116 hours. She subjected a solution to ozone treatment and then hydrogen peroxide, along the lines laid down by Harries. The resulting mixture of acids was analysed. It was found that one-half of the product was formed by an alternate succession of butadiene and acrylic nitrile in the molecule. About one-third consisted of molecules where one butadiene unit corresponded with two or three molecules of acrylic nitrile.

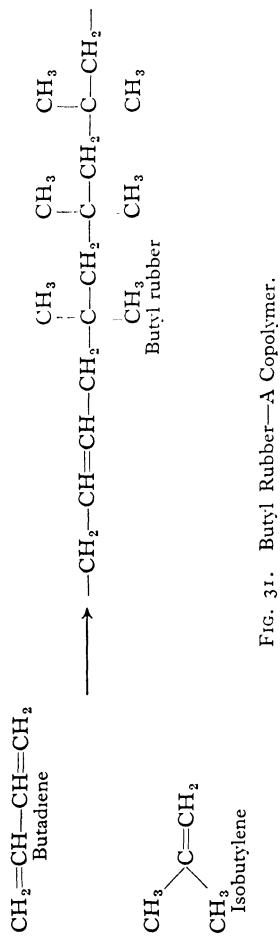

FIG. 31. Butyl Rubber—A Copolymer.

She [2] also examined the copolymer of butadiene and methacrylic acid nitrile by a similar technique, obtaining a mixture of acids which were separated as methyl esters. This yielded 62 per cent. by weight of 2-methyl- 1, 2, 4-butane tri-carboxylic acid and 8 per cent. succinic acid. It showed that the copolymer was mostly built up of alternate units of each monomer with 1.4 addition to the butadiene molecule.

Alekseeva and Belitsraya [3] applied to a Buna-S material the same process of ozonolysis, followed by hydrogen peroxide oxidation. This gave a mixture of formic, succinic, phenyladipic, and diphenyl-suberic acids, as well as a high molecular weight acid of undetermined structure. From the amounts of these acids it was calculated that the polymer consisted of mixed products, in which

31·2 per cent. of the styrene was joined by 1-4 addition alternately to butadiene units, 40 per cent. of styrene was in a union in which two units of styrene were joined in 1-4 positions to one or several units of butadiene, and 29 per cent. of styrene was united to butadiene in the 1-2 and 1-4 positions. Of the butadiene 23·3 per cent. was polymerized through 1-2 positions and the rest through 1–4 positions.

Cheney and Kelly [4] have investigated the degree of unsaturation of elastomers. They used the Wijs method on sodium butadiene polymer, and on copolymers of butadiene-styrene and butadiene-acrylic nitrile. Reaction was much slower than with rubber, taking 24 hours at 30° C. to complete the additional reaction. After this substitution occurs in the butadiene polymer and cyclization in the copolymers. They found the iodine values to show 4 per cent. cross linkage in the styrene copolymer and 10 per cent in the sodium polymer.

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CHAPTER 10

EMULSION POLYMERIZATION

The Growing Use of Emulsions. The current trend with synthetic elastics, and indeed with most synthetic materials, is to polymerize in emulsion. The evident intention is to simulate the simple processing of nature. And the time factor has been much reduced, so that in 1933 Whitby and Katz [30] could comment " most of the newly patented processes are claimed to produce a synthetic rubber after only a few days of polymerization, as compared with the period of several months required by methods used in Germany during the war ". It is now possible to carry out the process in a few hours. More important still, the process has been brought on to a continuous basis and it is only a matter of time before the conversion will be completed in minutes and not hours. According to Dinsmore [7] polymerization in emulsion without catalysts takes six months at 50° C.

It is interesting to note how the production of synthetic rubber begins to approximate to the production of natural rubber, where nature, using air, carbon dioxide, and water, with the aid of solar energy produces presumably isoprene which is then converted catalytically and continuously into rubber in the form of an aqueous dispersion-rubber latex. Synthetic rubber production begins to follow the pattern. As in many other aspects of synthetic work this seems to be the right line. It is interesting to observe that this remarkable change in the perspective of those engaged in making synthetic materials corresponds with the real arrival of the synthetic materials on a commercial scale.

Synthetic elastics have had very chequered careers. There have always been many disadvantages associated with them. These should be regarded as teething troubles, for from the commercial standpoint synthetic rubbers are still in their infancy. For many years it has been accepted that these materials must inevitably possess extremely unpleasant odours and poor colour. Other unsatisfactory features were associated with the difficulty of processing them. As events have shown these disadvantages are not inherent, but are merely the results of unsatisfactory methods of production.

The procedure adopted at the Buna works at Schkopau admirably

illustrated the practical application of this method, for according to Ambros [1]:

> As the best method for polymerization of butadiene, for example, in making copolymers of the two components, butadiene and styrene, the technique of emulsion polymerization was evolved. It was important to know that materials such as butadiene and other chemical compounds such as styrene could be polymerized together because with this there came the possibility of making new technically valuable types of Buna. The most important type of Buna is of course Buna-S, but Perbunan which is the oil-resisting quality of Buna, is also a copolymer (of butadiene and acrylic nitrile). It was a fortunate coincidence that the synthesis of styrene was developed in recent years at the I.G. Works at Ludwigshafen, so that it could easily be transferred to the adjacent Buna works.

It must be quite evident to those familiar with synthetic rubbers that they have undergone remarkable improvement in recent years. This is almost entirely due to the benefits derived by the use of emulsion polymerization methods in their production. It has been found that in every case far superior products have been obtained by avoiding the production of massive polymerization products.

These emulsion processes, begun before the last war, were based almost entirely on analogy with rubber latex. With the sudden growth of interest in rubber latex in the 1920's, it was natural that there should be a recrudescence of interest in synthetic latices. As the knowledge and experience with emulsions has developed and grown side by side with the knowledge of rubber latex, so the emulsion method for polymerizing synthetic rubbers, has been developed to the stage when it has become commercially practicable. By 1930, for example, the Germans were already polymerizing butadiene in emulsion. Thus Heuck [13] described how this was achieved by heating the emulsion with hydrogen peroxide as catalyst for three days at 40° C., after which time a synthetic latex had been produced.

The position is roughly analogous to the change-over from wild uncultivated natural rubber to the carefully graded pleasant plantation rubber of to-day. Indeed, the availability of synthetic rubbers as latices enables the solid materials to be produced in a similar manner to that practised in the production of the commercial forms of natural rubber.

Advantages of Emulsion Polymerization. Polymerization in aqueous emulsion has numerous overwhelming advantages over any other procedure, perhaps the most outstanding being that the reaction is always under control. There is little difficulty in handling the process and it may be stopped at any stage of the polymerization.

The procedure lends itself to the addition of other materials, either to facilitate the actual polymerization or to modify the properties of the subsequent synthetic elastic. The degree of polymerization is necessarily determined by the nature of the treatment used, i.e. the temperature and nature of the catalyst, and the time involved. In general the rate of polymerization is much more rapid when this method is used. This may be a function of available surface.

One of the great features of all emulsion processes is the absence of solvents which are invariably either toxic, inflammable or expensive. The process works at quite low temperatures and reaction is smooth and under control, there being no violent surges or other uncontrollable reactions. As a consequence there are no deleterious resinous by-products formed. In fact, emulsion polymerization eliminates most of the factors which have impeded particularly the commercial production of the synthetic rubbers. This value is further enhanced by the fact that successive batches of material do not differ in their characteristics.

No difficulty is experienced in preparing butadiene, isoprene, chloroprene, etc., as emulsions. Very concentrated emulsions can be made, but 40 per cent. diolefine appears to be the most popular proportion. The final product is obtained as a finely divided suspension, or latex. The use of protective agents enables this to keep indefinitely. There is great scope for synthetic rubbers in the form of their respective latices, although little has yet been done in this direction. This parallels the growing application of rubber latex which in 1939 had reached a consumption of 30,000 tons in the United States alone.

It is, of course, possible to obtain products which have been polymerized to an intermediate stage. In order to obtain the synthetic rubber in the solid form, generally regarded as most acceptable for processing, the final latex may be coagulated in exactly the same manner as rubber latex by the addition of acids and coagulent salts, etc.

All the familiar conditions associated with emulsions have been brought into play to deal with this problem of polymerization, e.g. the use of emulsifying agents, protective colloids, electrolytes, etc. Superimposed upon the factors necessary for the straightforward emulsification has been the addition of catalysts to promote polymerization, and also the addition of materials intended to modify the final products.

A vast range of emulsifying agents has been employed in the production of synthetic rubbers. All the well-known soaps and wetting agents have been tried. Those most frequently encountered include sodium oleate, sodium stearate, a whole range of sulphonated mineral oils, organic sulphonic acids, saponin, etc. All the familiar colloidal

materials employed in rubber latex work are encountered in the patents relating to synthetic rubbers. These, which include egg albumen, gum arabic, gelatin, glue, casein, milk, starch, destrin, carrageen moss, are claimed to exert favourable effects on the emulsion, improving the stability during heat polymerization and reducing the time required. Being water-soluble materials they tend to exert an unfavourable influence on the water-resisting qualities of the final product. A typical example is the following from an I.G. patent [15]:

Two hundred parts butadiene, 90 milk, 4 glue, 4 methyl cellulose, 2 sodium butyl-α-naphthalenesulphonate, 1 sodium isopropyl-β-naphthalene-sulphonate, 4 castor oil, and 1 urea-hydrogen peroxide compound were emulsified and heated for 7 days at 50° C. to 55° C. A white polymer, stable in air, was obtained in quantitative yield. Without the urea-peroxide compound the yield under similar conditions was less than 20 per cent.

Various claims are made that the addition of a variety of electrolytes, in addition to the protective colloids favourably affects the processing properties of the final material and even the strength. These include materials such as sodium phosphate, acetic acid, hydrochloric acid, phosphoric acid, etc. Another I.G. patent [14] illustrated this:

Four hundred parts isoprene by volume are emulsified with 500 parts water, 15 ammonium oleate, 10 trisodium phosphate, 5 parts 30 per cent. hydrogen peroxide solution, 25 parts 5 per cent. solution of glue. After standing for 190 hours at room temperature there is obtained a viscous, homogeneous latex which can be coagulated to a plastic and elastic rubber.

There are many other materials of every conceivable type which are claimed to have a good effect either on the polymerization or on the properties of the final product.

The value of many of these additions is, to put it mildly, questionable. However, it is only now with production on a large scale in full operation that effective weeding out of these materials is taking place.

Although polymerization in emulsion can be carried out without catalysts, the addition of these greatly speeds up the reaction. The most important reagents employed as in other forms of polymerization, and for plastics generally, are the oxidizing agents such as hydrogen peroxide, urea-peroxide, benzoyl peroxide, perborates, persulphates, percarbonates, ozonides, etc. Other types of catalysts include finely divided metallic oxides and salts of heavy metals, including manganese, lead, silver, nickel, cobalt and chromium. The presence of small quantities of halogen compounds such as carbon tetrachloride, hexachloroethane, trichloroacetic acid, etc. appear to have an all-round beneficial effect. This was described in another I.G. patent [16]:

One hundred and fifty parts butadiene by weight and 15 parts hexachloroethane are emulsified in a solution of 15 parts sodium stearate in 150 parts water. At ordinary or slightly increased temperature a substantially quantitative yield of synthetic rubber is obtained in 5 days. Without the hexachloroethane the yield is only 45 per cent. and cannot be substantially increased by prolonging the duration of the process.

Gerke [11] has stated that acid anhydrides such as acetic or benzoic anhydrides also appear to accelerate the rate of polymerization in the presence of inorganic peroxides.

TABLE 49. TYPICAL EMULSION REACTION MIXTURE

Butadiene	60 – 75
Styrene	40 – 25
Emulsifying agent	1 – 5
Polymerization catalyst	0·1– 1·0
Modifying agent	0·1– 1·0
Water	100 –250

From the plastics point of view, nearly every advantage claimed for production of synthetic rubbers by polymerization of diolefines in aqueous emulsions applies equally well for most synthetic resins. The trend is for their manufacture in this manner. The emulsification of the respective monomers presents no difficulties.

Conditions for Emulsion Polymerization. An excellent summary of the conditions required has been given by Mark and Rath.[23]

Our experience so far may, perhaps, be summarized in the following general way :

A series of components (between five and ten) are needed to build up the colloidal system in which the polymerization is expected to take place and to start and direct the reaction to its proper ending.

1. *The basic phase*, in which the emulsion is made This is always, or mostly, water (free from iron, lime, and organic impurities). It is always in excess and represents between 60 per cent, and 80 per cent. of the weight of the total system.

2. *The main monomer*—butadiene, vinyl chloride, etc.—to build up the backbone of the polymer to be produced. This will amount to about 60–80 per cent. of the final polymer or 15–30 per cent. of the emulsion.

3. *The additional monomers*—styrene, acrylic nitrile, acrylic esters, vinylacetate, etc.—which are present only if copolymers are to be produced. These will represent 24–40 per cent. of the weight of the final copolymer or about 5–15 per cent. of the initial colloidal system.

4. *The emulsifying agent* or agents, which enable us to produce colloidal dispersion of the monomers. Many different substances have been described and used and it seems that the actual choice of a special emulgator is of a certain importance for the success of polymerization. Aliphatic long-chain carboxylic and sulphonic acid salts, sulphonated long-chain alcohols and amines as well as aromatic alkylated sulphonic acid salts have been applied

with success. 0·2–2·0 per cent. of emulsifier, reckoned from the weight of the resultant polymer, are usually used.

5. *The stabilizer*, to prevent a premature precipitation of the emulsion. Various natural and synthetic protective colloids are recommended for this purpose, e.g. gelatine, glue, casein, starch, dextrines, methyl-cellulose polyvinylalcohol, etc. The usual amount of stabilizer is between 2 per cent. and 5 per cent. of the weight of the polymer.

6. *The regulator of surface tension*, the action of which cannot yet be clearly defined. It seems, however, that these substances have to be present to obtain and maintain the most favourable average particle size of the emulsion and to narrow down as much as possible the distribution curve of the size of the dispersed particles of the monomer or the mixture of monomers. Aliphatic alcohols of medium chain length C_5 to C_8 seem to serve this purpose best, but aromatic alcohols and amines have also been recommended. They amount to between 0·1 per cent. and 0·5 per cent. of the polymer.

7. *The catalyst*, of which the main action is presumably the acceleration of the formation of polymerization nuclei without affecting the propagation process. It seems, however, that most substances which catalyse the starting reaction act similarly towards the cessation reaction and thus the addition of too much catalyst may result in a polymer of low molecular weight. Oxygen ozone, hydrogen peroxide, organic peroxides and ozonides, persulphates, percarbonates, perborates and similar substances act as catalysts ; they usually amount to between 0·1 per cent. and 1·0 per cent. of the weight of the resultant polymer.

8. *The regulator*, to direct the polyreaction and, presumably, to act mainly as an " anti-knocking " agent, avoiding or cutting down branching and cross-linking processes during the reaction. Very little is actually known about the action of these substances. Experience has shown that chlorinated aliphatic hydrocarbons such as carbon tetrachloride, ethylene dichloride, and hexachloroethene and similar aromatic compounds have a beneficial influence on the reaction, if about 2 to 5 per cent. of the weight of the polymer is added.

9. *The P_H adjuster or buffer*. Most emulsions are very sensitive to the hydrogen ion concentration. The particle size and its distribution curve, the actual mechanism of the reaction and the stability of the final synthetic latex sometimes depend largely on the maintenance of the proper p_H. Normal buffers such as phosphates, carbonates, acetates, etc., are usually applied in appropriate amounts (2–4 per cent. of the weight of the polymer).

The above list shows that the mechanism of an emulsion polymerization is quite complicated.

They considered the action of emulsion polymerization to be polymerization of the drops of the monomer proceeding inwards from the interface with the medium. Fikentscher [10] considered that the part dissolved in the aqueous solution polymerizes, after which more was dissolved from the droplets. He based this on the fact that saturated solutions of vinyl monomers in water gradually formed emulsions of insoluble polymers. Staudinger [28] considered that polymerization in emulsion strongly favours the formation of many activated spots on

the surface of particles which give rise to a particularly reactive nucleus for promoting chain reactions and the process of polymerization is therefore accelerated.

Predominance of Emulsion Methods for Buna Rubbers. As already suggested there is strong evidence to presume that emulsion polymerization predominates in Germany, and that all other methods have been pushed into the background. The modern large-scale plants have been based on the use of this method. According to Stöcklin : [29]

It was clear from the beginning that polymerization in emulsion would be technically more valuable if it were possible to obtain a product equal to or even inferior to the sodium polymerizate. It soon became clear that in the case of the emulsion polymerization of butadiene the cyclization in the polymerization was much greater than that found in the products obtained by the sodium polymerization process. . . . Further work showed that less cyclized products with better properties from the rubber technologist's point of view were obtained if the mixtures of butadienes hydrocarbons were polymerized in emulsion. Thus Perbunan is a mixed polymerizate of butadiene and acrylic acid nitrile.

Unmistakable evidence that the emulsion process of polymerization is undoubtedly the best is the fact that the latest plants constructed in Germany have been designed to work on this system. The enormous works at Schkopau were built after the successful career of a pilot plant working the emulsion process.

Mueller [24] has described two practical examples for making Buna-S or Perbunan and -S in emulsion :

TABLE 50. BUNA EMULSIONS

Buna-N	Parts
20·0 lbs. butadiene	50
20·0 lbs. acrylonitrile	50
50·0 lbs. water	125
175 gm. sodium phosphate	1·0
100 gm. citric acid	0·5
280 gm. Aquarex D	1·5
20 gm. KCN	0·1
250 gm. carbon tetrachloride	1·5
15 gm. sodium perborate	0·075
60 gm. acetaldehyde	0·3
Buna-S	**Parts**
20·2 lbs. butadiene	50
20·0 lbs. styrene	50
50·0 lbs. water	125
1300 gm. Aquarex D	7·3
680 gm. sodium phosphate	3·75
135 gm. sodium perborate	0·75
510 gm. carbon tetrachloride	2·8
60 gm. acetaldehyde	0·3

The polymerization takes place very readily at room temperature and is completed in approximately three to five hours for Buna-N. Buna-S requires something like 40 hours to complete.

The reaction vessel should contain a stirrer in the centre: and after all materials except butadiene are weighed out and put into the vessel, the lid is tightly closed. The butadiene is added afterwards and filled into the reaction vessel through a tube and valve on the side or bottom of the vessel. This arrangement works very satisfactorily, because the butadiene being a gas at normal temperature, is shipped in steel containers under pressure and therefore can be transferred easily into the reaction vessel.

The presence of some of the ingredients need some further explanation. Aquarex D, for instance, is used as emulsifier for the monomers and has proved very satisfactory and better than Nekal, sodium-oleate, or other soaps which have been used as emulsifiers. The amount and the choice of emulsifiers and catalysts have a decided effect on the softness of the final product.

The *p*H of the system should be 6·5, i.e. not quite neutral. Otherwise separation of the emulsion and coagulation sometimes occur.

At the end of the reaction the Buna latex is separated from the unfinished part by decantation. The remainder is used again by adding it to a new batch. The reaction may be stopped by addition of phenyl-beta-naphthylamine to the Buna latex. This addition should not be made in the reaction vessel itself as phenyl-beta-naphthylamine would then act as negative catalyst on the new batch. When exposed to sunlight and air natural rubber oxidizes; whereas Buna-type rubbers, when undergoing the same conditions, tend to polymerize further and also to cyclicize. This action is prevented by adding a stabilizer, usually phenyl-beta-naphthylamine. This also acts as an antioxidant and age resister.

If any further tribute to the importance and pre-eminence of the emulsion process were necessary, it is supplied by the fact that most of the types produced in the United States are made by this method. This applies to Perbunan, Hycar, Chemigum, neoprene, etc.

Also many of the ethenoid plastics are also made in this way, e.g. the polyvinyl copolymers.

In case it has not been made quite clear, the polymerized product is obtained still in the form of an emulsion or latex. Some of the properties of Buna latices were described by Baechle.[2] They resemble rubber latex in many ways. The particles in dispersion are negatively charged, and the stability is of a similar order. The particles are spherical, unlike the rubber particles, and are about one quarter the size.

Buna latex coagulates to small flakes in contrast to the solid coagulum formed by rubber. Latices based on polymerized acrylic esters have been commercially available for a number of years. They yield elastic films and were of particular interest to the textile industries. Outstanding types include materials such as Plextol, Acryloid and Acronal.

Buna-N Latices. Buna-N latices are slightly alkaline and contain very little soapy substances. There is no tendency for bacterial growth in these latices since they are free from albuminous protective colloids. Buna latex particles carry a negative electrical charge and are therefore discharged by H-ions and coagulated. As in the case of rubber latex it is possible to change the electrical charge of the Buna particles from negative to positive. The solid content of Buna latex is generally 30 per cent. It is difficult to cream or centrifuge Buna latex because the particles are much smaller than normal rubber particles.

According to Mueller [24] suitable coagulants and creaming agents for Buna latices include the following. They are the same as operate for rubber latex.

TABLE 51. CREAMING AGENTS FOR BUNA LATEX

Coagulants	Creaming agents
Acetic acid	Caraya gum, Locust bean gum, Gum tragacanth } 0·1–0·5% on dry rubber
Formic acid	
Calcium chloride	
Calcium acetate	Iceland moss
Calcium nitrate	Alkaline solution of alginic acid
Calcium formate	Caustic soda and other alkalies
Zinc chloride	Irish moss
Ammonium acetate	Ammonium alginate (one of the most effective, the effect is accelerated by heating the system to about 60° C.
Acetone	
Methyl alcohol	
Methyl alcohol	
Alum	

When polymerization has been finished the Buna latex is decanted from the unreacted part. Any surplus of acrylonitrile can be distilled and recovered. Because of the high stability of the Buna latices, few coagulating agents are sufficiently effective to be of practical importance. Almost immediate coagulation is effected by barium chloride, ethyl alcohol, hydrochloric acid, sulphuric acid, acetic acid. Aluminium chloride and ferric chloride have a tendency to flocculate the Buna latices. Calcium chloride, calcium nitrate, tin chloride, calcium acetate, zinc chloride and magnesium chloride precipitate the Buna in the form of a gel. The following table gives the minimum amount of coagulent necessary for precipitating 100 parts of Buna-N latex.

TABLE 52. COAGULANTS FOR BUNA LATEX

	Parts
Aluminium chloride	1·5
Ferric chloride	2·0
Calcium chloride	2·5
Barium chloride	5·2
Acetone	98
Ethyl alcohol	110

Heat sensitizing and gelling agents do not appear to affect Buna latices. The hardness or toughness of the final Buna-N or -S can be controlled to some extent in their preparation. In practice other methods are necessary. Buna-S can be heat-treated or peptized with different chemicals and any degree of softness can be obtained.

Recent Patent Literature. The trend towards production of synthetic rubber by polymerization of emulsified system is strongly defined in the numerous patents taken out by the I.G. during recent years.

In one patent [17] the I.G. proposed to polymerize butadiene as an aqueous emulsion in the presence of peroxide. In another patent [20] the stress was upon the use of agents which improved the properties of the products. Thus the polymers were produced by polymerizing butadiene compounds in aqueous emulsion in the presence of such sulphur-bearing compounds as are soluble in the monomer, e.g. dialkylxanthogens. Generally less than 1 per cent. was adequate. The process could be applied to every polymerizable butadiene monomer, including isoprene and to copolymers with such monomers as styrene and acrylic acid nitrile. One example was as follows :

0·5 part di-isopropylxanthogen disulphide was dissolved in 69 parts butadiene, which was emulsified in 200 parts of 5 per cent. sodium oleate solution (containing 0·3 part ammonium persulphate). When shaken for several days a plastic polymer was produced.

In another patent [19] they proposed to polymerize a butadiene and an ethylene dicarboxylic acid in aqueous emulsion by treating with an oxidation catalyst. In an example they described how 75 parts fumaric acid ethyl ester was copolymerized with 25 parts butadiene.

Konrad and Bock,[22] of the same firm, polymerized an aqueous emulsion of a butadiene hydrocarbon with up to 40 per cent. of a compound $CH_2{=}CR.COOR_1$, where R and R_1 are hydrogen atoms or alkyl groups (i.e. acrylic, methacrylic, ethacrylic acids, esters, etc.).

Another improvement [illegible] by Müller-Conradi and Daniel,[25] who polymerized butadiene emulsion in the presence of emulsions of highly polymerized isobutylene with the aid of peroxides. The products were claimed to be far superior to those obtained from butadiene alone.

Perhaps the most interesting of these patents, which must form the background of the large-scale German production, is the following one, which has recently been published.[21] Although the importance of continuous polymerization has already been stressed, it is evident that the processes so far described have been batch processes. The I.G. have described what is probably the fundamental method in Buna production. They pointed out that hitherto copolymers of butadiene and other materials had been prepared from emulsions, but in successive batches. They proposed in this instance to introduce the emulsions continuously into the polymerization vessel. The process was achieved by having two solutions, one consisting of the polymerizable material, the other being the dispersing medium, containing emulsifying agents, polymerization catalysts, and so on. The liquids were pumped into the polymerization apparatus in such a way as to form a single emulsion. Polymerization began as the emulsion flowed into the high temperature region. The exact degree of polymerization achieved was checked by sample tests. Careful control of uniformity and the rate of flow was necessary.

General Activity with Emulsions. Although the Germans have made a special feature of butadiene polymerization from emulsions, there has been a certain amount of activity elsewhere. A great deal has been heard about Soviet efforts to make synthetic rubbers by emulsion.

It would appear that emulsion polymerization is beginning to register its importance. For example, Dogadkin, Beresan and Lapuk [8] claimed to polymerize butadiene compounds as aqueous emulsions in the presence of tautomeric substances such as diazoamino compounds.

Polymerization of butadiene in emulsion has been carefully examined by U.S.S.R. workers.[3] They prepared the latex and considered all its properties. They also considered the effects of stabilizers, the media, and the influence of catalysts on the rate of polymerization. Thus dimethyl butadiene alone polymerized in 40 days at 70° C. yielding 18 per cent. of polymer. In emulsion it took only 8 days. Butadiene without catalysts took 15 days to polymerize in emulsion, but months in the ordinary state.[4] They considered that polymerization was a chain reaction.

Synthetic rubber-like materials have been made from emulsions in this country. Thus Habgood and Morgan [12] polymerized an emulsion containing a mixture of butadiene and from 25 to 100 parts of methyl methacrylate in the presence of from 5 to 30 parts carbon tetrachloride.

Neoprene is Produced by Emulsion Polymerization. The

best-known elastomer is, of course, neoprene. This is based on a polymer of chloroprene, or 2.-chloro—1.3—butadiene. It was the first commercial synthetic rubber, appearing on the market in 1930, and is the most widely used. As in the case of the Buna rubbers, there have been very marked improvements in the quality of neoprene during recent years. These changes have largely been associated with improvements in the technique of polymerization, most notably by the introduction of emulsion methods.

The production of neoprene came about as a consequence of the work carried out by Nieuwland [26] on the polymers of acetylene. In particular he developed a method for the commercial production of monovinylacetylene by passing acetylene through cuprous chloride solution.

This work was followed up by an intensive and thorough investigation, sponsored by Du Pont de Nemours, into the possibilities of utilizing monovinyl-acetylene as a basis for producing synthetic rubber. Carothers, Williams, Collins and Kirby [5] were able to convert monovinylacetylene into chloroprene by treatment with hydrogen chloride, using cuprous chloride as catalyst. They also determined the conditions for making chloroprene polymerize to yield commercial products. This very brief description does scant justice to some of the most brilliant work in chemical history.

Like isoprene, chloroprene is capable of yielding rubber-like polymers, but owing to the presence of chlorine in the butadiene system, which renders the molecule markedly polar, it polymerizes far more rapidly than does isoprene. The influence of a halogen atom in an unsaturated system on the rate of polymerization is well shown by comparing ethylene ($CH_2 : CH_2$) with vinyl chloride ($CH_2 : CHCl$). Vinyl chloride polymerizes not only more readily but to a far higher degree than does ethylene.

Chloroprene is a colourless liquid which polymerizes with ease. It tends to change spontaneously on standing. If allowed to stand for ten days it forms a copolymer known as the μ- form, which is a resilient mass, insoluble in solvents, and somewhat similar in character to vulcanized rubber.

If polymerization is interrupted, a lower polymer is obtained (α-polychloroprene), which is soft, plastic and soluble in solvents, resembling unvulcanized rubber in many ways. This is the basis of the neoprene of commerce.

In the past there have been features of neoprene that were open to criticism, notably the bad odour and the dark colour. In the case of neoprene it has been clearly evident in recent years that these grounds

for criticism have been almost eliminated. Products can now be made in the most delicate of pastel shades, having virtually no odour.

The newer improved types are prepared by emulsion methods. Once again it should be observed that direct bulk polymerization processes tend invariably to yield by-products that are deleterious—for it becomes more strongly emphasized that the disadvantages in polymers are chiefly due to such by-products.

The polymerization of chloroprene in emulsions gives interesting results. When emulsified, chloroprene changes to the μ- polymer more quickly than when in the massive condition, the rate of polymerization being apparently at least twenty times as rapid as that of undispersed chloroprene. If chloroprene is emulsified in a solution of sodium oleate and the emulsion is allowed to stand, polymerization is so vigorous that the temperature begins to rise in about 30 minutes and may quickly reach the boiling point of chloroprene unless cooling is applied; polymerization is complete in 2 to 8 hours at room temperature. The product, which corresponds to a vulcanized latex, may be stabilized by adding a little ammonia, which neutralizes the small amount of free acid which is formed during polymerization and which would otherwise bring about gradual coagulation. Latex thus prepared is fluid so long as the concentration of polychloroprene is not more than 55 per cent. The average particle diameter is only 0·126 μ. In natural latex the particle size ranges from 0·5 to 3 μ.

The use of a number of different emulsifying agents with chloroprene has been studied by Williams and Walker.[31] Turkey-red oil, casein dispersed with sodium hydroxide or acetic acid, triethanolamine stearate, and sodium stearate all give emulsions in which chloroprene polymerizes completely within a few hours and in which the particle size is similar—viz., 0·1 to 1 μ. Carrageen moss, on the other hand, gives an emulsion which, although the particles are similar in size, does not lead to acceleration of the polymerization, the material separated from the emulsion being the plastic, α- polymer. If sodium stearate sufficient to provide a mono-molecular layer is added to a carrageen moss emulsion of chloroprene, polymerization proceeds rapidly. The nature of the interfacial layer is considered to have an important influence on the rate of polymerization.

Starkweather and Yonker[27] have described how one of the most recent types of neoprene—type G—is prepared.

By polymerizing purified chloroprene in emulsion under carefully controlled conditions, it is possible to convert it into a type of neoprene which more closely resembles rubber in its ability to be plasticized, as well as in other respects. This neoprene is not a copolymer but is made without the

use of other copolymerizable materials. This discovery is of considerable commercial importance, since it now becomes possible to make a synthetic material which can be handled in a manner similar to that used in processing smoked sheet or pale crêpe . . .

In a recent patent some of the mechanics of emulsion polymerization are described.[9] Although neoprene is not directly mentioned, the method seems likely to have a bearing on the production. Emulsions of styrene, acrylic acid nitrile, etc., containing catalysts, are polymerized by passing them through tubes having diameters not greater than 2 inches and of sinuous form having acute bends. The velocity of flow is sufficient to cause turbulence. The tube is heated to effect polymerization.

The following laboratory method illustrates how the emulsion process functions in the case of neoprene.

400 gm. chloroprene is added, with vigorous stirring, to 400 gm. water containing 5 per cent. sodium oleate. The resulting emulsion is kept at 10° C. for a period of between 24 and 48 hours, depending on the degree of polymerization desired. A little ammonia is added to counteract any acidity.

Solid neoprene is obtained from the synthetic latex in the same way as rubber is obtained from latex, by coagulation with acids and multivalent salts. Light-coloured, almost odourless products are obtained. Quite clearly neoprene becomes available as latex, a fact which obviously widely increases the scope of the material.

According to Dales,[6] neoprene latices may contain up to 50 per cent. of total solids, which upon evaporation or coagulation and subsequent washing, yield commercial neoprene. As in the case of rubber latex, these latices may be compounded and loaded with fillers, and films from them may be vulcanized.

The monomer 2.-chloro—1 : 3-butadiene, is emulsified as spherical particles of from 2 to 4 μ diameter. During polymerization these change into particles of only 0·1 μ diameter. The particles are in such violent Brownian motion that there is no tendency for them to settle, an action which would be comparable with the creaming of rubber latex (neoprene has specific gravity of 1·25, while that of rubber is 0·93).

Following on their application of the emulsion polymerization technique to the butadienes, the I.G.[18] have extended the process to substituted butadienes such as chloroprene. They polymerized 2-chloro-1.3-butadiene in the presence of organic sulphur containing compounds that are soluble in the monomer such as dialkyl xanthogen disulphides. They extended the process to polymerize chloroprene

with other monomers such as styrene and acrylic nitrile. In one example 10 parts acrylic nitrile together with 180 parts chloroprene and the catalyst were emulsified in a soap solution prior to emulsification.

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PART III

TECHNOLOGY OF SYNTHETIC ELASTIC MATERIALS

Introduction. The technology of the various synthetic elastic materials must necessarily be discussed with reference to rubber technology. Consequently the terms of reference and procedures adopted with rubber are employed in these instances. For a full consideration of rubber technology the reader is referred to any text-book on the subject.[1, 2, 3] However, it seems desirable to explain some of the terms and abbreviations that may be employed.

The chief characteristic of rubber compounds which has been

TABLE 53. SOME PHYSICAL CONSTANTS OF NATURAL RUBBER [4]

	Pure rubber	Commercial rubber	Soft vulcanized 20% S	Hard rubber 32% S
Density	0·9060	0·911	0·923	1·173
Specific heat Cals. per degree	0·449	—	0·510	0·341
Heat of combustion Cals. per gramme	10820	—	10630	7920
Refractive index n_D	1·5190	1·5190	1·5364	1·6
Dielectric constant (at 1000 cycles/sec.)	2·37	2·45	2·68	2·82
Power factor (at 1000 cycles/sec.)	0·0016	0·0018	0·0018	0·0051
Conductivity mho/cm	23×10^{-18}	420×10^{-18}	13×10^{-18}	15×10^{-18}

singled out as a standard for comparison is the tensile strength at break, with which is coupled the elongation at break. The abbreviations T_B and E_B respectively are employed for these. While these quantities serve as a convenient measure for the ultimate tensile properties of the material under consideration, yet they have little relation to the behaviour of the material under service conditions. A much more realistic appreciation is obtained from the modulus of the material, which is in effect the tensile strength at some predetermined elongation, e.g. the tensile strength at an elongation of 300 per cent. A high

modulus denotes a stiffer, more rigid material, while a low modulus indicates a soft yielding product. The abbreviation M_{300} is employed to refer to the modulus at 300 per cent. elongation. It is evident that this will give an indication of the behaviour of any elastic material at the comparatively low elongations of most service uses.

Vulcanization of course refers to the heat treatment of a material whereby it is changed from the plastic to the elastic condition. The process is referred to technically as the " cure ". The question of the state of cure, or vulcanization is technically of great importance. As the time of vulcanization of a product is increased, so the tensile strength increases until it reaches a maximum value. In the case of rubber where materials have been undercured, the tensile and other properties are inadequate ; notably the permanent set is excessive ; while where they have been overcured the ageing properties are bad and the material tends to become " short ". Consequently, the optimum technical cure is generally sought. In this connection the term " plateau effect " is encountered. This refers to rubber compounds where the nature of the vulcanization, as modified by some specific accelerator, is such that the tensile properties during vulcanization tend to reach a maximum, and thereafter instead of falling off rapidly are maintained over a period of time. Thus if a rubber compound vulcanizes to give maximum tensile properties in 30 minutes at 140° C., then with an accelerator which gives a plateau effect the properties of the product obtained in 25 minutes will not be appreciably different from those obtained in 35 minutes. Consequently any cure during that period of time will give a satisfactory material, and as a corollary the material will not be so sensitive to the vulcanizing conditions. The illustration shows why this is referred to as a plateau effect.

Accelerated ageing results are obtained by standard procedures. Heating in a Geer oven in air at a fixed temperature of 70° C. for a period simulates one type of ageing. Treatment in a Bierer-Davis oxygen bomb under high pressure of oxygen and at high temperature simulates another form of ageing. The tensile properties are taken as a measure of whatever changes may have occurred.

Hardness, which is referred to by the abbreviation H, is generally measured by use of the Shore penetration instrument.

Other properties such as abrasion resistance, tearing resistance, flexing resistance, etc., are not yet standard procedures, and reference is made wherever necessary to the specific procedure adopted.

The degree of permanent set affords a test which is of great importance in connection with synthetic elastic materials as interpreting the

extent to which they possess elastic qualities. This gives information as to what extent a product remains distorted after being subjected to stress. A sample is stretched to a definite extent, is allowed to stand for some time, after which the tension is relaxed, and the sample is allowed to retract. The percentage increase in length is the permanent set.

Resilience is one of the most characteristic features of elastic

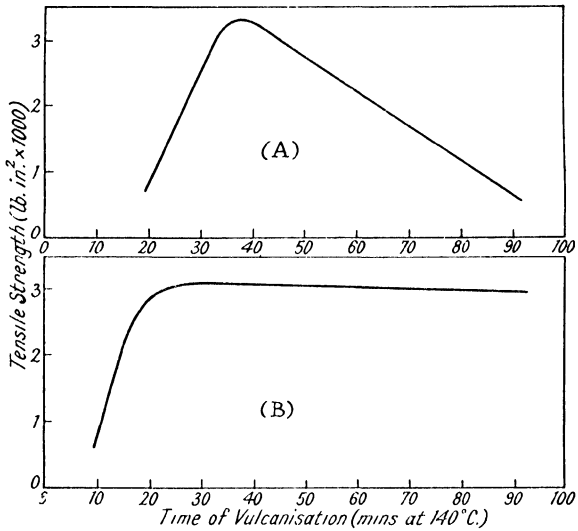

FIG. 32.—Plateau Effect.

materials, and in this respect rubber has not yet been equalled by any synthetic product. The snap or nerve of a product is a measure of this property. Actually of course, in use the material is subjected to comparatively small extensions or compressions carried out very rapidly, as in the case of a tyre. It is the resilience in such circumstances which is of importance. It is measured by the amount of energy returned by the rubber. One of the most widely used methods for doing this is to determine the height to which a steel ball or a pendulum will rebound after striking the sample. The percentage of rebound gives a measure of the impact resilience.

Hysteresis is of great technical importance. It is a measure of how much energy is lost in extension and retraction in the form of heat. In this instance, too, rubber has a lower hysteresis than any

of the synthetic materials. It is of outstanding significance when there are rapid cycles of extension and retraction such as occur in a tyre tread. High heat losses may cause overheating of the tyre. On the other hand, the rapid loss of energy is obviously of use where it is desired to damp out vibration. Hysteresis is measured by the area between the curve of extension and the curve of retraction.

Variations in the properties of natural rubber compounds are chiefly achieved by the use of various types of carbon black. The hard carbon blacks of extremely fine particle size increase the tensile strength—reinforce the rubber—but the resilience and " kick " of the rubber is decreased. Softer types of carbon black, of larger particle size, do not affect the resilience to the same degree, but on the other hand, do not give such high tensile strength—they are " semi-reinforcing " blacks. As a consequence it is necessary to vary the material to be added according to the requirements of the product. This behaviour is also shown by many synthetic elastics as will become clear in the ensuing discussion.

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CHAPTER II

ELASTOMERS—S.K.B. AND BUNA-S

IT seems quite clear from the previous discussion that more work has been based on butadiene than on any other monomer. There can be no doubt that elastomers based on butadiene lead the way in respect to output. Furthermore, the production on a vast scale in the United States is for the main part likewise based on butadiene.

At the present time the best known materials are Buna-S, Perbunan, and the slightly modified Perbunan-Extra. The former predominates, since it is the material used for tyres. These are the leading types manufactured in Germany. In the U.S.S.R. two leading types of synthetic rubber, namely S.K.A. and S.K.B., are also made from butadiene. In the United States, Buna-S, Perbunan, Hycar, and Chemigum are the leading productions based on butadiene, while butyl rubber also contains a minor proportion of this material. All of these materials (with the exception of the Russian types, and butyl rubber) are copolymers of butadiene with synthetic resin monomers. The most extensively used synthetic resin monomer is styrene, which goes into the Buna-S, while acrylic nitrile and other acrylic derivatives are used in the other materials. Recent types of neoprene and of Thiokol are also largely composed of butadiene.

The German rubbers, Perbunan and Perbunan-Extra, have been exported for some years, and there is a wide experience of them. They had gained considerable popularity in Great Britain and in the United States for their oil-resisting properties. It is only recently that their production has been inaugurated in the United States.

Buna-S is now the outstanding type in the United States. The Government has made this its standard material. The product made under Government auspices is known as GR-S. It is also made under several proprietary names including Buna-S, Butaprene-S, Chemigum IV, Hycar TT, Buton-S, etc.

The American materials Hycar and Chemigum have come out of the pilot plant stage during the last two years, and are now in full-scale operation. While Hycar has been available to manufacturers in the United States, the use of Chemigum has been entirely monopolized by the Goodyear Company. The Russian materials S.K.A. and S.K.B. have been in large-scale production for a number of years.

All these materials have the general properties of natural rubber.

They are rather more difficult to process than rubber, but, apart from Buna-S, they can all be handled on standard rubber plant. According to the German technique Buna-S does require a certain amount of special equipment. In general, the procedure is the same as with rubber, namely they are brought into a thermoplastic condition when compounding ingredients may be incorporated. The addition of sulphur and accelerators, followed by a heat treatment, converts them from the plastic condition into the elastic state corresponding to vulcanized rubber. Indeed, it is an extremely difficult task to differentiate between such products and comparable rubber products.

Obviously the ability to handle these materials on established rubber plant is a contributory factor to their continued success. In view of the enormous amount of capital sunk in such plant this is essential to their commercial success. In many respects they yield products which are far superior to natural rubber products; in some properties they are no better than rubber; they are, of course, still much dearer, although the gap is being rapidly narrowed.

Butadiene Rubber. According to the United States Bureau of Commerce,[3] the Russians in 1939 produced 60,000 tons of synthetic rubber. A considerable proportion of this production consisted of sodium-polymerized butadiene. It is referred to as divinyl rubber. The U.S.S.R. appears to be the only producer of straight butadiene elastomers, which approximate most closely, at least in chemical

$$CH_2{=}CH{-}\ CH{=}CH_2 \longrightarrow \text{-}CH_2{-}CH{=}CH{-}CH_2{-}CH_2{-}CH{=}CH{-}CH_2\ {-}CH_2{-}CH{=}CH_2{-}CH_2\text{-}$$

Butadiene

Polymerized butadiene
(probably cyclized to a considerable extent)
S.K.A., S.K.B., Buna 85, Buna 115, etc.

FIG. 33.

composition, to natural rubber. They have undoubtedly developed the technique of sodium polymerization to a very high pitch. There is an enormous volume of scientific and technical literature on the subject, although so far there has been no independent appraisal of the merits of the products. Not a great deal has as yet been heard about any of their copolymerized products, although there is evidence that these are being manufactured. On the other hand, it is known that they manufacture a chloroprene rubber, i.e. similar to neoprene, which they call Sovprene, and they also make olefine polysulphide rubbers. There is no doubt that sodium polymerized butadiene, known as S.K.B. is the predominant type.

S.K.B. is made from butadiene, which has been obtained from alcohol, while S.K.A. is made from butadiene which has been

derived from petroleum. Some indication of the extent to which these materials have been used, and still are used, is obtained from consideration of the great importance attached to the reclamation of sodium butadiene rubber. The amount of attention which has been devoted to this is a measure of the existence of a large amount of material to be reclaimed.

It is to be presumed that these sodium-polymerized rubbers have many features in common with Buna 85 and Buna 115, the comparable German types. The Germans regard these as being virtually obsolete; according to Stöcklin [18] all production ceased in 1939, and even at that time they were only using Buna 85 to make hard rubber products. The Russians confirmed the excellent opinion expressed by the Germans about the suitability of sodium butadiene rubbers for hard products. The heat resistance and mechanical properties are far better than those of comparable ebonites.

The Sodium-catalysed Buna Rubbers. It can be assumed that Buna 85 and Buna 115 have some properties in common with the Soviet products. The physical and ageing characteristics of compounds loaded with carbon black are shown in comparison with the comparable rubber mix.

TABLE 54. PROPERTIES OF RUBBER, BUNA 85 AND BUNA 115

	Natural rubber	Buna 85	Buna 115
T_B Kg. cm^2	260	175	200
E_B %	600	600	700
Shore hardness	65	65	60
Geer oven			
(32 days at 90° C.) T_B	160	155	170
E_B	350	600	625
Oxygen bomb			
(32 days at 60° C.) T_B	50	150	180
E_B	200	620	650

Processing of S.K.B. It appears that the adhesive properties of these types of synthetic rubbers are quite inadequate for the production of soft rubber articles in the ordinary way. Special treatment is necessary in order to facilitate compounding and processing.

One method for carrying this out, described by Osipovsky,[15] was to heat the material at 140° C. in air, and in this way to reduce it to a more thermoplastic condition. Another method was the use of agents having a powerful depolymerizing action, a notable one being para-nitroso dimethylaniline.

Vulcanization of sodium butadiene rubber compounds could be quite satisfactorily carried out without the use of sulphur. Oxidizing agents facilitate the process, notably benzoyl peroxide which when present to the extent of 3 per cent. effectively enabled the vulcanization of a typical compound in 15 minutes at 150° C.

The composition and tensile properties of a typical compound based on S.K.B. are shown in Table 55.

In regard to sodium butadiene rubbers the effect of accelerators is only to shorten the time and lower the temperature for combination with sulphur. The products show no qualitative benefits over straightforward vulcanization with sulphur. Zinc oxide is necessary with accelerators. In the presence of stearic acid, calcium oxide and magnesia accelerate the vulcanization. Thiuram derivatives are effective and improve heat resistance. The normal range of antioxidants function satisfactorily.

TABLE 55. TENSILE PROPERTIES OF TYPICAL SKB COMPOUND [11]

Compound	
Synthetic rubber (plasticity 0·040)	100
Gas black (Baku)	50
Sulphur	4·0
Accelerator	1·0
Softener No. 2	3·0
Zinc oxide	4·0
Softener No. 3	5·0
Tensile properties	
Vulcanization (mins. at 150° C.)	20
T_B (kg. per sq. cm.)	100
E_B (%)	555
Permanent set (%)	60

Dogadkin and Fel'dshtein [6] examined the vulcanization characteristics of sodium butadiene rubber containing various proportions of carbon black, chalk, kaolin, and silica, before and after being heated within the temperature interval of 70–200°. Large percentages of fillers caused limited swelling of the unvulcanized rubber. They considered that the limited swelling is due primarily to the structure of the system. The rubber comprises the discontinuous disperse phase and the filler forms the continuous phase producing a singular net-like structure with the rubber sealed inside the cells. Heating of the mixture reduced the proportions of fillers necessary to produce limited swelling and also caused limited swelling of the rubber itself, but in the latter case longer periods of heating were necessary. Heating at 120°–140° C. produced the following changes which are characteristic of vulcaniza-

tion: limited swelling, decreased solubility, and greater toughness. The synthetic rubber mixtures were vulcanized without sulphur by heating at 190°–200°. Under identical conditions smoked sheet mixtures could not be vulcanized. It is believed that "vulcanization" proceeds as a result of (i) interaction between the rubber and the oxygen absorbed on the rubber and the fillers, and (ii) thermal condensation of the rubber hydrocarbon.

Kusov [11] described the products obtained at 200° C., using large quantities of carbon black as filler. Material having tensile strength of 90 kg. per square centimetre and elongation at break of 400 per cent. was obtained.

There are many indications that these sodium butadiene rubbers are used in the manufacture of tyres, and according to Lebedev [13] the products have far superior abrasion resistance than the comparable rubber stocks. Other references discuss the application of sodium rubber for impregnating fabrics for making soles and heels and a wide range of mechanical goods. Gagina [8] has discussed in some detail the excellent results obtained by using sodium butadiene rubber in tyres.

Importance of Reclaiming. One of the favoured methods for reclaiming these materials for further use is to swell the products in solvents with heating, and thereafter to remove the solvent. The product could be used quite successfully for lower-grade articles.

The physical and chemical properties of the reclaimed rubber obtained by the solution method have been found satisfactory.[14] Experimental trials carried out at an artificial rubber sole factory with the products are reported to have demonstrated that soles can be manufactured entirely from the reclaimed article. So far, the rubber reclaimed from used synthetic rubber (mostly automobile tyres) has been utilized in the manufacture of rubber soles and of artificial leather. The present Soviet output of reclaimed synthetic rubber is not large, but the favourable results thus far obtained are stated to have dispelled any doubt of the practicability of the utilization of this method for the production of reclaimed synthetic rubber on an industrial scale.

Buna-S or GR-S. Far and away the major production in Germany is Buna-S, obviously because it is used for tyres. It is in fact without doubt already one of the most important materials in the world. Out of 1,100,000 tons of synthetic rubber to be made in the United States per year, no less than 845,000 tons will be Buna-S, known as GR-S.

In appearance Buna-S looks like very dark brown smoked sheet and has a definite odour of styrene. The method of production up to the formation of a fully polymerized latex has already been described.[2] The

remainder of the process to yield the raw material as supplied to the rubber works is most interesting.

In order to obtain Buna rubber from the fully polymerized emulsion, it is precipitated with acetic acid. In recent years this manufacturing process had been evolved in a most elegant manner at the Leverkusen works of the I.G.

The latex was continuously precipitated, and just like the " stuff " on the paper machine, was carried on to a continuous wire web in the form of a white thin film free from water, washed and dried. The dried film, after being compacted in a press is rolled into a large roll, and leaves the works in a suitable jute casing, which can be used again.

Buna-S is a copolymer of butadiene with 25 per cent. of styrene. It has a specific gravity of 0·92. It is rather tougher than natural rubber to the feel. The Government-sponsored Buna-S in the United States is made of butadiene 75 parts and styrene 25 parts.

Buna-S products are claimed to be far superior to rubber in heat resistance and abrasion resistance. According to Vila [21] comparison between Buna-S and natural rubber shows the following outstanding points :

BUNA-S

Superior in—	Inferior in—
Abrasion	Dynamic flex cracking
Ageing	Heat build-up
Reversion on overcure	Brittleness
Tendency to scorch in processing	Rate of vulcanization

By contrast with the Perbunans, and most other synthetic rubber-like materials they have no advantage whatever over rubber so far as oils and solvents are concerned. It is claimed that Buna-S tyres are considerably better than natural rubber tyres. According to Stöcklin, on evidence based on road tests, Buna-S tyre tread has an advantage of 35 per cent. over the best type of natural rubber tread in respect

TABLE 56. ELECTRICAL AND MECHANICAL PROPERTIES OF BUNA-S AND BUNA-SS [16]

	Specific resistance	Insulation resistance Meg. km.		T_B	E_B	T_B	E_B	T_B	E_B
	Ohm/cm		After 12 weeks at 100° C.	Kg/cm.	%	After 1 week in air at 100° C.		12 weeks in air at 100° C.	
Natural rubber .	20×10^{14}	950	600	103	270	92	220	0	0
Buna-S . . .	7×10^{14}	350	1000	52	320	57	270	52	60
Buna-SS. . .	13×10^{14}	400	4000	88	390	92	340	85	140

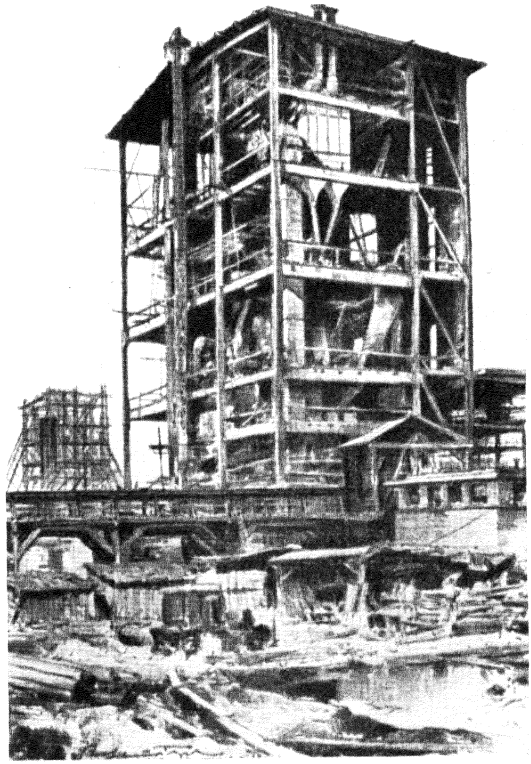

FIG. 34.—Part of the Buna Plant at Schkopau.

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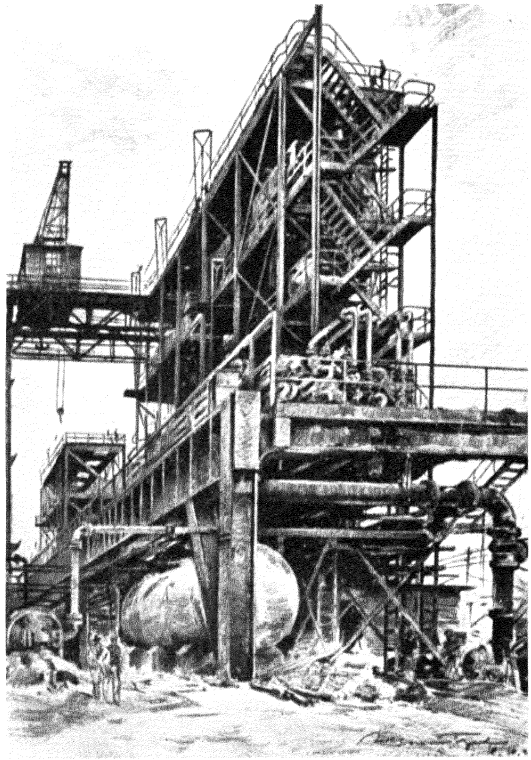

FIG. 35.—One of the Units for Preparing the Polymers at the Schkopau Works

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to abrasion resistance. This claim is not altogether unsupported by independent evidence. The largest and most critical users of rubber, the major American tyre companies, have investigated Buna-S in tyre treads, and the general conclusion is in favour of Buna-S as against natural rubber. It should also be observed that Buna-S is to be the standard material in United States large-scale production—a certain indication of its suitability for tyres.

TABLE 57. TYPICAL HEAT-RESISTING MIX [18]

Buna S	100
Kieselkreide (silica)	60
Softener	3
Antioxidant	3
Thiuram disulphide	2·5
Zinc oxide	2
Sulphur	0·12
Polyacrylic ester	16

Vulcanized from 30 to 60 minutes at 40 lbs per square inch.

Buna-S, unless previously treated, is one of the most difficult synthetic rubbers to process. It requires a special technique to break it down to a plastic condition. Although Buna-S had been developed as long ago as 1928, yet ten years elapsed before a practicable method for handling it was developed. It is now plasticized by means of hot air. The process is carried out on the largest possible scale in Germany.

Thermal Degradation of Buna-S. One of the most important problems that had to be met before Buna-S could be used on an adequate scale was to overcome the stiffness which makes it so hard to process. It can be softened by prolonged mastication in up-to-date mills, but this action consumes too much time and power. The addition of appropriate plasticizers in the required amounts had been tried, but this had an injurious effect on the quality of the final product.

In 1937 a method of reducing the molecule of Buna-S was developed by Hagen [10] which has since become known as thermal degradation or thermal decomposition. This is the method now predominantly used in Germany, and credit is given to it for the fact that Germany is now able to use synthetic rubber successfully on a large scale. Buna-S is available in the form of crumb, sheet, and shredded sheet, and the latter form is generally preferred for degradation purposes.

The shredded Buna is spread on racks to a definite, constant thickness; the racks are introduced into degradation ovens where the material is subjected to thermal treatment in the presence of air or oxygen. The main requirements for obtaining a uniform final product are thorough motion of air and uniform temperature distribu-

tion in the interior of the oven. In most modern factories special [illegible] ovens are employed which have the necessary attachment for supplying a stream of heated compressed air.

TABLE 58. AGEING OF SOFTENED BUNA-S [18]

	T_B Kg.cm²	E_B %
Room temperature. . .	230	720
Geer oven at 70° C.		
8 days	235	530
16 „	238	510
32 „	240	500
Oxygen bomb at 100° C.		
8 days	234	690
16 „	228	630
32 „	200	560

The chemistry of the degradation process has not yet been explained. It is certain, though, that the presence of oxygen is essential; no softening occurs in nitrogen or steam. A part of the phenyl-β-naphthylamine, which is incorporated as a stabilizer for the Buna prior to marketing is used up, but what remains normally suffices to give the vulcanizate anti-ageing protection.

When Buna-S is subjected to such treatment, plasticity first increases very rapidly, at the same time the viscosity of a 4 per cent. benzene solution decreases. After reaching a minimum, hardness and viscosity increase again. This minimum may be called the resinification point, for if the thermal treatment is prolonged beyond this point, the adhesive properties of the material progressively decline, the "elastic portion" increases (seriously hampering extrusion and calender work), and, if continued for a long time, a hard, brittle, translucent substance is obtained which is no longer soluble in organic solvents. It is evident, therefore, that after a certain stage of softening has been reached, a cyclization reaction develops.

In softening Buna by this method, care must be taken never to reach the point of resinification. The proper temperature and duration of treatment are thus important. For though a higher temperature increases the rate of softening, the danger of cyclization is also increased; furthermore, too high a temperature and too short a period of treatment prevent the obtaining of a uniform final product. It has been found that heating should be continued for periods of not less than 30 minutes and at a temperature of around 150° C.

Advantages and Disadvantages of Thermal Degradation. Thermal treatment of Buna-S offers various advantages—by its aid the power requirements for mixing, time for mixing, and size of pieces

treated are on a level with that usual for natural rubber; hence the mixing process becomes cheaper. With a higher degree of softening a kneading machine can be used for mixing.

Dispersion of fillers is improved, which in some cases increases the strength of the product and always reduces the amount of waste. On the other hand, the vulcanizing ability of the Buna is somewhat decreased, and the mechanical properties are also affected, the impairment depending on the degree of softening. Increased amounts of sulphur and accelerator are needed, and in general much greater care in compounding is essential.

Thermally softened Buna-S continues to show a greater tendency to shrink than natural rubber having the same plasticity, and it does not give such smooth extruded and calendered products, so that the addition of a certain amount of softener is still necessary. There is a similar difference in the processing qualities of degraded and masticated Buna-S which favours the latter. Subsequent thermal treatment of masticated Buna does not destroy this advantage so that thermal treatment of Buna-S is sometimes preceded by brief mastication.

One of the clearest statements about the handling of Buna-S or GR-S has been given by Garvey, Whitlock and Freese.[9]

Milling. Synthetic rubber differs from natural rubber in several important respects. It is tougher and consequently tends to become hotter on the mill. Also it is shorter and less thermoplastic. These differences show up as a marked difference in milling behaviour. When crude natural rubber is put on a cold mill, it is tough and knotty until well broken down. If the mill is heated to 180°–200° F., the rubber quickly smooths out, becomes soft, and is easily pulled out to a considerable extent. Under similar conditions the synthetic material smooths out somewhat more quickly on the cold mill but remains rather tough and nervy. At 180°–200° F. it becomes considerably softer, but also becomes short and weak and is rougher than on a cold mill. Some of the experimental rubbers become so short and weak that they crack on the edges or become lacy, and in extreme cases fall off the mill.

Heat Softening. With regard to oxidative or " heat " softening, tyre-type synthetic rubber is intermediate between natural rubber and the oil-resistant butadiene copolymers. Under proper conditions it can be softened in hot air, but unless the conditions are carefully controlled, the operation may actually harden the synthetic rubber. This is due to the fact that the oxidation has a double effect, a breakdown and a sort of oxidation vulcanization. In the first stages of heating, breakdown seems to be predominant and the rubber softens. Subsequently, however, the vulcanizing action becomes predominant and the rubber assumes a scorched appearance, becoming grainy, short, and hard.

Breakdown. Probably related to the heat-softening action is the mill breakdown. The synthetic rubber does not break down so much as natural rubber does. Considerably more milling is necessary for adequate break-

down and the breakdown is less obvious. Nevertheless it is important in subsequent operations. It is hard to describe accurately and should be observed on a laboratory mill. The breakdown can be obtained either before or after pigments are added. There is some indication that the addition of pigments facilitates breakdown. The important thing is that the overall milling must be adequate and that breakdown is favoured by a cool mill and a tight one.

Other methods have been tried. For example,[5] it has been proposed to treat Buna-S latex with small quantities of aromatic hydrazines such as phenylhydrazine, agitating for some hours and then passing oxygen through for 8 hours. Thereafter the latex is coagulated.

Mueller [14] suggested that a mixture of furfural or benzaldehyde phenylhydrazine (2 per cent.) was an adequate peptizing agent for Buna-S. After incorporation, the Buna-S is sheeted very thinly and heated on trays in an autoclave for 4 hours at 250° F.

Although oxygen is absolutely essential to plasticize the material successfully, yet the amount of oxygen taken up is too small to be measured. The plasticized Buna-S tends to revert to its original condition if left for any length of time. It is interesting to note that the acetone extract of Buna-S is between 6 and 7·5 per cent.[1]

Once plasticized, there is no further difficulty in processing. Thereafter, the handling follows ordinary rubber practice. One of the outstanding points about Buna-S is that when compounded without fillers, i.e. as a pure gum mix, the physical properties are incomparably inferior to those of natural rubber. Reinforcing fillers, notably carbon black, are essential to show them at their best. Fillers of all types may be incorporated according to the product being made. Sulphur and accelerators have to be added to effect vulcanization. Higher amounts of plasticizers are used than in ordinary rubber practice. In order to bring out the best physical properties, high proportions of reinforcing carbon blacks are generally added. Conditions of vulcanization and general handling are parallel to standard rubber technique. The material may be calendered or extruded, it may be moulded, etc.

Almost the greatest disadvantage of Buna-S is the lack of tack in which it is far inferior to rubber. This complicates the processing of many articles.

The tear resistance of Buna-S products is invariably inferior to that of corresponding rubber articles.

The following experimental results on tyre tread mixes based on Buna-S which has been heat treated compared with untreated material are most illuminating. It is absolutely essential to incorporate a large quantity of plasticizers in order to compound raw Buna-S. In this respect it resembles most other elastomers. But after it has been

submitted to heat treatment this is not necessary. It is also interesting to note that in common with other elastomers less sulphur and more accelerator is required than for natural rubber. The mixes were all taken to optimum state of vulcanization.

Although the Germans have had comparatively long experience in handling Buna-S, they have not overcome the processing difficulties. In fact it appears that at the present time their use of Buna-S is geared to their production of reclaim, which is an essential ingredient. It is clear that the standard range of rubber softeners perform a useful function in Buna-S by aiding the dispersion of the high loadings of blacks. But they do not give that tack which is required for the successful building up of composite articles such as tyres.

Influence of Rubber. The best method of alleviating this difficulty is by addition of either rubber or whole tyre reclaim. As part of an exceptionally fine study of synthetic rubber behaviour Drogin [7] has prepared Buna-S mixes containing 20 parts of rubber and reclaim respectively to 80 parts Buna-S. His results are summarized in the Tables 58 and 59.

TABLE 59. FORMULATION—SMOKED SHEET OR RECLAIM IN SYNTHETIC RUBBER

	Buna-S	Blend of Buna-S	
		Smoked sheet	Reclaim
Buna-S or Buna-N	100	80	80
Smoked sheet	—	20	—
Whole tyre reclaim	—	—	20
Zinc oxide	5	5	4·5
Stearic acid	1	2	1·8
Pine tar	3	3	2·75
Paraflux	3	3	2·75
Altax	1·25	1·25	1·1
Sulphur	2	2·3	1·97
Kosmobile 77	50	50	43·4
	165·25	166·55	158·27
Press cure	292° F.	292° F.	292° F.

Addition of rubber improves all characteristics and particularly processing. With reclaim, only the tensile strength is less, otherwise all properties are improved. The following Table illustrates this.

TABLE 60. DETAILED TEST DATA—SMOKED SHEET OR RECLAIM IN SYNTHETIC RUBBER

	Buna-S	Buna-S and smoked sheet	Buna-S and reclaim
Plasticity (mm.)	364	335	357
Extrusion (seconds)	5·8	4·0	5·1
Modulus at 300%	800	1675	1340
Tensile strength	2590	2710	2050
Elongation at break	620	545	425
Shore hardness	60	65	69
Tear resistance	540	508	524
Abrasion resistance	277	158	238
Percentage rebound	37	37	37
Heat build up—			
Average temp. ° F.	204°	180°	183°
Percentage compression	10·6	6·1	7·9
Percentage set	9·6	4·0	6·0
Electrical resistance	8×10^9	2×10^9	17×10^9

Properties of Buna-S Compounds. Buna-S compositions are used in Germany for the production of tyres, mechanical goods and cables. Buna-S is preferred to Perbunan for tyres because it has far superior adhesive properties which facilitate tyre construction, and also because it is cheaper. The rubbers obtained have high tensile strength, excellent fatigue resistance, and very satisfactory flexing resistance. They withstand the effect of sunlight and do not age as rapidly as rubber.

Buna-S is a pure hydrocarbon. As a result it has excellent electrical characteristics and is extensively used both for insulation and protective sheathing of cables.[4] While resembling rubber in electrical characteristics, it has much better moisture resistance and retains its electrical properties at high operating temperatures for much longer periods of time. It also has good resistance towards ozone.

Thus at 20° C. and at 50 cycles, Buna-S has a dielectric constant of 2·9 and a power factor of 0·0007.

Vulcacit A2 is the product obtained by reacting equimolecular proportions of diethylamine and mercapto benzthiazole. It appears to be admirably suited for the Buna type of elastomers. It gives products of high tensile strength, high elongation and good ageing character. It is very flat curing with a pronounced plateau effect. On the other hand Vila [21] considered that dithiocarbamates are satisfactory accelerators offering a means for hastening the slow vulcanization of Buna-S, when used in reasonable quantities. Sulphur ratios

TABLE 61. BUNA-S TYRE TREAD MIXES [10] (German)

	Buna-S		Natural rubber
	Untreated	Heat softened	
Rubber	100	100	100
Carbon black	42	42	42
Stearic acid	2	2	2
Ozokerite	1·5	1·5	1·5
Sulphur	1·3	2·2	2·6
Vulcacit AZ	1·2	1·2	0·9
Coumarone resin	12	—	—
Rosin	5	—	—
Mineral oil	5	—	—
Caoutchol	5	—	—
Zinc stearate	5	—	—
T_B Kg.cm.^{2}	200	250	280
E_B %	480	600	580
Elasticity %	44	45	50
Shore hardness	73	70	70

of the order of 2 parts per 100 Buna-S are suitable for most compounds. To obtain lowest hysteresis he recommended higher sulphur content and less accelerator.

At the present time permeability of materials towards gases and liquids is of more than normal importance. It has, of course, a profound bearing on the moulding characteristics, for one of the important factors is an adequate ability to permit air to pass through. On the other hand it is a disadvantage for applications such as balloon fabric where gas must be retained. In this respect Buna-S allows the passage of rather more air than does rubber.

TABLE 62. SPECIFIC RESISTANCE OF BUNA ELASTOMERS [16]

	Ohm/cm.	
	20° C.	0° C.
Crepe rubber	1×10^{16}	7×10^{16}
Smoked sheets	3×10^{15}	1×10^{16}
Buna-S	1×10^{14}	8×10^{14}
Buna-SS	5×10^{14}	1×10^{16}
Perbunan	3×10^{10}	5×10^{11}

TABLE 63. AIR PERMEABILITY OF VULCANIZED PURE GUM ELASTOMERS [16]

	cm^3 air / $h.cm^2.cm.mm.Hg$	
Rubber	3·4	100%
Buna-S	5·3	156%
Perbunan	0·6	18%

TABLE 64. WATER ABSORPTION [16]

	%
Rubber	6·5
Buna-S	4·5
Buna-SS	6·0
Perbunan	7·5
Perbunan-Extra	7·5

TABLE 65. WATER PERMEABILITY [16]

Mix.	Rubber	100
	Zinc oxide	5
	Sulphur	1
	Vulcacit AZ	1
	Stearic acid	2
	P.33	as indicated

	gm. water / $h.cm.^2cm.mm.Hg \times 10^{-8}$			
			Vulcanized mix with	
	Raw gum	No fillers	25 parts P.33	50 parts P.33
Rubber	27	6·2	4·8	4·7
Buna-S	18·6	12·9	9·9	7·8
Buna-SS	8·1	5·1	4·2	3·4
Perbunan	28·1	17·6	15·1	12·6
Perbunan-Extra	21·2	13·6	10·7	9·5

Buna-S compositions have remarkable ageing characteristics and resistance to heat. The following table illustrates these features.[10] The mix used was Buna-S 100; Carbon black 42; Stearic acid 2; Ozokerite 1·5; Sulphur 1·2; Vulcacit AZ 1·5. The Buna-S was strongly softened and the mix was carried to optimum cure.

TABLE 66. AGEING OF TREATED TYPICAL TREAD MIX

Ageing-period	Unsoftened; with 1% S					Strongly softened; with 2% S				
	T_B	E_B	M_{300}	E	H	T_B	E_B	M_{300}	E	H
Ordinary temperature	225	690	38	54	65	203	670	52	50	68
Geer oven at 70° C.										
8 days . . .	230	540	74	56	72	210	475	106	54	77
16 days . . .	236	525	86	57	75	204	420	121	53	78
32 days . . .	228	510	99	56	76	180	300	141	54	79
Oxygen bomb at 100° C.										
8 days . . .	227	675	54	54	72	198	570	81	52	73
16 days . . .	625	640	61	55	75	196	540	90	51	76
32 days . . .	211	640	67	56	76	180	500	105	53	78

Vila [21] has examined data pertaining to Buna-S in tyre tread mixes compared with natural rubber. The mixes contained approximately 50 parts carbon black.

TABLE 67. COMPARISON OF BUNA-S AND NATURAL RUBBER IN TYRE TREAD MIXES

Test	Buna-S	Natural rubber
M_{300} lb./in.^{2}	1200	1300
T_B lb./in.^{2}	3300	4100
E_B%	500	600
Accelerated ageing—		
Percentage change in tensile 96 hours in oxygen at 70° C. and 300 lbs.	− 14	− 32
Grasselli abrasion loss	70	200
Tear resistance (Crescent)	290	638
Max. temp. rise in Goodrich flexometer ° F. .	100	58
Dynamic flexing mins. to failure	21	130

He concluded that Buna-S is poorer in tear resistance, heat build-up and flexing, but superior in ageing and resistance to abrasive wear.

A great deal of information on compounding Buna-S has recently been made available by the R. T. Vanderbilt Company.[20] They carried out a large number of tests with materials based on Buna-S designed for tyre treads, moulded goods, inner tubes, mechanical goods and insulated wire. They compared products with similar materials based on natural rubber. Their views are summarized in the following account.

TABLE 68. TYRE TREAD MIXES [20]

	Rubber mix	Buna-S	Buna-S—sulphurless
Smoked sheet	100	—	—
Buna	—	100	100
Reogen (plasticized)	2	—	—
Stearic acid	3	—	—
Pine tar	1	—	—
Agerite resin D (antioxidant)	1	2	2
Agerite hipar (antioxidant)	1	—	—
Zinc oxide	3	3	3
Carbon black	50	50	50
Captax	1	—	1
Altax	—	1·5	—
Selenac (selenium diethyl dithiocarbamate)	—	—	2
Vandex (selenium powder)	—	—	0·2
Sulphur	3	2	—
Time of cure at 290° F.	30 mins.	45 mins.	30 mins.

Although Buna-S is comparatively soft, yet on the mill it does not readily yield a smooth plastic sheet. If the mill is used hot then the Buna-S tends to crumble. When the material is milled for an excessive time the tensile strength of the products is substantially reduced They recommended that a cool mill should be used and that overmilling should be avoided. So far as addition of other ingredients is concerned the order of mixing them may be the same as with raw rubber. The most important filler, carbon black, requires special

TABLE 69. MECHANICAL GOODS MIXES [20]

	40 hardness	50 hardness	60 hardness
Buna-S	100	100	100
Zinc oxide	3	3	3
Agerite resin D	2	2	2
Selenac	2	2	—
Captax	1	1	1
Vandex	—	—	0·2
Kalvan	100	—	—
Thermax (soft)	—	25	—
Channel black (hard)	—	25	50
Time of cure at 308° F.	8 mins.	8 mins.	15 mins.

TABLE 70. INNER TUBE MIXES [20]

	Parts.	Parts.
Smoked sheet	100	—
Buna-S	—	100
Reogen	2	—
Stearic acid	1	—
Paraffin	1	—
Agerite resin D	2	2
Zinc oxide	3	3
P.33	40	60
Carbon black	—	10
Sulphur	0·75	1
Altax	1·5	—
Methyl zimate	0·25	—
Telloy (tellurium)	0·5	—
Butyl Eight (ultra-accelerater)	0	2
Time of cure at 308° F.	8 mins.	8 mins.

consideration because of the difficulty of dispersing it. It should be added in small amounts at a time, and completely dispersed before adding more. Most other fillers disperse quite readily. It is recognized that the properties of articles based on rubber depend on satisfactory dispersion of compounding ingredients; this factor is even more important in the case of Buna-S. It is necessary to adhere closely to an established mixing procedure.

TABLE 71. INSULATION MIXES [20]

	B.4	A.7	B.7	X
Buna-S	100	100	100	—
Smoked sheet	—	—	—	100
Stearic acid	0·75	0·75	0·75	0·75
Agerite resin D	3	3	3	3
Zinc oxide	15	15	15	15
Mille mar	36	—	36	36
Whiting	90	—	—	90
Kalite No. 1	33	25	25	33
Kawan	—	100	100	—
Tysonite	—	36	—	—
Litharge	1	5	5	9
Selenac	4	—	4	—
Altax	—	0·5	—	0·5
Methyl zimate	—	0·5	—	0·5
Sulphur	—	2	0·75	2
Vulcanization	300 ft./minute	300 ft./minute	450 ft./minute	450 ft./minute

The physical properties of Buna-S materials are considerably improved by allowing the compounded materials to rest for some hours and then remilling through tight rolls. It should be pointed out that the best rubber practice normally allows the mixed material to rest for at least 24 hours before it is used. Comparative tests on the rate of vulcanization suggested that Buna-S stocks in general did not introduce scorching difficulties. The Vanderbilt researches suggested that softeners are essential to obtain satisfactory processing properties with Buna-S. Their use does lower the modulus and tensile strength while increasing elongation. They could not find any really satisfactory softener for conferring tack on Buna-S. While stearic acid could be used, and had a softening effect, it was not really necessary for vulcanization as in the case of rubber. Among the many fillers they tested carbon black gave the best results for tensile strength, modulus, and elongation. Other fillers gave materials which were invariably much inferior in strength.

They found quite clearly that Buna-S was far inferior to rubber where no fillers were present. Reinforcing pigments are absolutely essential to give satisfactory physical properties in the vulcanized material. Apart from carbon black and other blacks the most interesting filler was coated calcium carbonate of very fine particle size (Kalvan). Microscopic examination showed that Buna-S wetted the treated calcium carbonate but not untreated whiting. This gave a softer stock, but also resulted in a lower tensile strength. The coated calcium carbonate was, however, far superior to straight whiting, giving a better curing rate and superior physical properties.

While sulphur and accelerators gave effective vulcanization the amounts and ratios differed from those employed with natural rubber. The Buna-S materials prepared with sulphur donating accelerators were found to be superior to suphur containing compounds in some respects. They also found that drying in combinations of accelerators and sulphur the rate of cure was invariably slower than with crude rubber. However, satisfactory combinations were found. They recommended the use of antioxidants to obtain the best ageing properties, even though some antioxidant is already present in the unprocessed Buna.

The physical properties of the materials that they tested all showed lower tensile strength, lower elongation, and lower tear resistance than natural rubber compounds. Usually they have lower resilience and hardness under comparable conditions. The Buna materials showed superior ageing characteristics, especially when determined in the oxygen bomb.

TABLE 72. COMPARATIVE PROPERTIES FOR PRODUCT MIXES [20]

	M.	T_B	E_B	M	T_B	E_B	Impact resilience	H.	Permanent set (percentage)	Compression set (percentage)
Tyre tread mixes										
Rubber	1525	3960	575	1490	1890	410	37	64	—	—
Buna-S	1360	2900	520	1490	2410	490	34	61	—	—
Buna-S—sulphurless	1365	3280	545	1690	3060	480	35	61	—	—
Inner tube mixes										
Rubber	410	3340	700	515	2860	665	—	40	—	—
Buna-S	530	1700	755	705	1410	610	—	50	—	—
Mechanical goods mixes										
Buna-S (40 hardness)	245	1140	760	450	985	475	36	40	20	39·8
(50 ,,)	600	1650	630	890	1550	520	40	50	10	34·2
(60 ,,)	1160	3020	510	1570	2710	450	32	60	11	21·3
Insulation mixes	*									
Rubber B.4	450	1940	495	490	1830	495	—	—	—	—
Buna-S A.7	270	425	455	330	680	470	—	—	—	—
Buna-S B 7	425	720	440	615	1010	405	—	—	—	—
Buna-S X	450	895	460	620	1025	385	—	—	—	—

* M200.

They arrived at some interesting conclusions in connection with the possible uses of Buna-S for tyre treads and mechanical goods. Their tensile tests on Buna-S compounds at low elongations showed that these had 80 per cent. the " kick " of natural rubber on the initial pull. After " massaging " four times they obtained 90 per cent. of the strength. They noted that results from other sources confirmed that products used at low elongations such as tyre tread and moulded items gave satisfactory results.

The Use of Reclaim. They[20] also tried out compositions of Buna-S containing reclaimed rubber. Reclaim helped the processing considerably, but reduced the physical properties more than a comparable load of reclaim on natural rubber.

They made up three equivalent combinations of whole-tyre reclaim with Buna-S, and with smoked sheets. A mix containing 50 parts of Buna-S and 100 parts of whole-tyre reclaim gave tensile properties almost equal to another mix containing 75 parts of Buna-S and 50 parts of reclaim. The use of the first mix would therefore represent a considerable saving in Buna-S with very little loss of tensile properties. Ample tack was produced in these mixes by the use of 3 per cent. to 5 per cent. of Reogen (a mixture of mineral oil, sulphonated petroleum oil, and normal butyl alcohol) on the reclaim. Although Reogen is not a tack producer for Buna-S, it does act on the reclaim and provides tack for the combination. With this 50 Buna-S

TABLE 73. COMPARATIVE RECLAIM MIXES [20]

	A 1	A 2	A 3	B 1	B 2	B 3
Smoked Sheet	75	50	25	—	—	—
Buna-S	—	—	—	75	50	25
Whole-tyre reclaim	50	100	150	50	100	150
Reogen	2	2	2	—	—	—
Stearic acid	3	3	3	—	—	—
Pine tar	1	1	1	—	—	—
Agerite resin D	1	1	1	2	2	2
Agerite hipar	1	1	1	—	—	—
Zinc oxide	3	3	3	3	3	3
Sulphur	3	3	3	2	2	2
Captax	1	1	1	—	—	—
Altax	—	—	—	1·5	1·5	1·5
Channel black	50	50	50	50	50	50

—100 reclaim mix, the comparative effect of four fillers, channel black soft gas blacks (P 33 and Thermax), and finely divided calcium carbonate (Kalvan) was determined. Although channel black gave the best overall results, greater loadings of the soft blacks gave some physical properties such as resilience and adhesion to steel that were better.

They carried out examination of insulation compounds applied on wire. The insulated wires were vulcanized continuously, in the case of the Buna-S mixes being passed through a 100-foot tube at

TABLE 74. PROPERTIES OF BUNA-S—RECLAIM COMBINATIONS [20]

	M_{300}	T_B	E_B	Aged 48 hours in oxygen bomb at 300 lbs. and 80° C.			Impact resilience	H	Permanent set percentage	Compression set percentage
				M_{300}	T_B	E_B				
A_1	1370	3300	570	1635	2470	460	34	70	40	21·1
A_2	1350	2560	515	1565	2110	410	31·5	71	45	18·1
A_3	1300	1930	450	1425	1585	365	30·5	70	40	20·8
B_1	1275	1980	440	1685	2080	375	35	64	15	24·5
B_2	1430	1925	400	1485	1865	400	32	66	20	21·7
B_3	1170	1520	405	1315	1560	375	30	64	20	25·6
15 min. cure at 290° F.							20 min. cure			20 min. cure

TABLE 75. BUNA-S AND RECLAIM MIXES [20]

	B 2	B 4	B 5	B 6
Buna-S	50	50	50	50
Whole-tyre reclaim	100	100	100	100
Agerite resin D	2	2	2	2
Zinc oxide	3	3	3	3
Sulphur	2	2	2	2
Altax	1·5	1·5	1·5	1·5
Channel black	50	—	—	—
P 33	—	60	—	—
Thermax	—	—	60	—
Kalvan	—	—	—	100

TABLE 76. TENSILE PROPERTIES OF BUNA-S—RECLAIM MIXES [20]

	M	T_B	E_B	Aged 48 hours in oxygen bomb at 300 lbs. and 80° C.			Impact resilience	H	Permanent set	Compression set
				M	T_B	E_B				
B 2	1430	1925	400	1485	1865	400	32	66	20	21·7
B 4	660	1300	525	725	1140	505	39	52	22	21·3
B 5	765	1250	490	820	955	380	44	51	20·5	24·2
B 6	465	1180	550	570	955	510	33·5	53	26	32·7
15 min. cures at 290° F.							20 min. cure			20 min. cure

TABLE 77. ELECTRICAL PROPERTIES OF BUNA-S—INSULATION MIXES [20]

Type	S.I.C.	Power factor	S.I.C.	Power factor	S.I.C.	Power factor	S.I.C.	Power factor
	Measured in mercury at 25° C.		After 24 hours' immersion in water at 50° C.		After 3 days' immersion in water at 50° C.		After 14 days' immersion in water at 50° C.	
B 4	2·84	0·0065	3·36	0·0301	3·51	0·0324	3·76	0·0396
A 7	3·69	0·0118	4·03	0·0251	4·16	0·0286	4·43	0·0305
B 7	3·16	0·0114	3·39	0·0114	3·51	0·0132	3·71	0·0148
X	2·81	0·0058	3·22	0·0208	3·31	0·0226	3·48	0·0235

200 lbs. steam pressure. The rubber compound was vulcanized through a 180-foot tube at 220 lbs. steam. Their tests confirmed the suitability of Buna-S compounds for wire insulation.

With the evolution of the large-scale production of Buna-S in the United States a number of proprietary products have appeared. All are Buna-S, but nevertheless show somewhat different properties according to the source of manufacture. These differences will in due course be eliminated.

An interesting and informative study carried out by Drogin illustrates these features particularly in relation to the properties of natural rubber. He used the following types:

Buna-S (Naugatuck) made by the U.S. Rubber Co.
Buna-S (Buton-S) made by the Firestone Tyre & Rubber Co.
Buna-S (Chemigum IV) made by the Goodyear Tyre & Rubber Co.
Buna-S (Hycar TT) made by the Hycar Chemical Co.

As a matter of interest the first two companies were licensed to make Buna-S by the Standard Oil Co., of New Jersey, who had the information available from the I.G. Farbenindustrie. The latter two companies had evolved their own methods of production prior to coming into the Buna-S production scheme under the Government auspices.

GR-S Properties Compared with Rubber. Drogin [7] compared these elastomers with smoked sheet for such properties as elasticity, tensile strength, modulus, elongation, hardness, tear resistance, and so on. There were marked differences in the materials. He compared them in pure gum mixes, that is, without any filler loading, and then

TABLE 78. COMPOUNDS EMPLOYED [7]

	Pure gum		Reinforcing black		Semi-reinforcing black	
	Rubber	Buna-S	Rubber	Buna-S	Rubber	Buna-S
Elastic	100	100	100	100	100	100
Zinc oxide	5	5	5	5	5	5
Stearic acid	1	1	3·5	1·5	2	1·5
Altax	1	1	1	1·25	0·65	1·25
Pine tar	—	—	3	3	—	1·5
Paraflux	—	—	—	3	—	1·5
Sulphur	2	2	2·85	2	2·85	2
Dixie 20/Kosmos 20	—	—	—	—	60	60
Kosmobile 77/ Dixiedensed 77	—	—	50	50	—	—

Press cured to optimum tensile values at 292° F.

proceeded to study the influence of different types of carbon black at various loadings. His main object was to evaluate the influence of different types of carbon black, the hard reinforcing channel blacks, the softer semi-reinforcing materials, the soft non-reinforcing blacks and so on. His results gave a very excellent picture of the best type of carbon blacks to use for any specific purpose. He showed quite clearly the importance—in fact the absolute necessity—of using a black filler in order to obtain the best characteristics with the elastomer. For example, he found that the best loading of reinforcing carbon black such as Kosmobile 77 was 50 parts per 100 of elastomer; whereas in rubber the best results are obtained at about 40 parts carbon black. It is of interest to observe the difference in the rubber composition and the Buna-S composition required to give balanced comparable materials.

TABLE 79. COMPARISON OF MIXES CONTAINING CARBON BLACKS [7]

(Natural Rubber Properties rated as 100 in each case)

	Pure gum					Reinforcing black					Semi-reinforcing black				
	Smoked sheet	A	B	C	D	Smoked sheet	A	B	C	D	Smoked sheet	A	B	C	D
Plasticity	100	56	51	40	59	100	80	66	58	86	100	48	44	34	42
Extension	100	—	—	—	—	100	36	39	16	32	100	33	45	19	25
Modulus	100	—	—	—	—	100	59	55	83	62	100	63	66	92	60
Tensile	100	15	13	21	11	100	74	64	73	74	100	80	56	78	78
Elongation	100	74	55	78	52	100	121	110	102	120	100	124	116	95	122
Hardness	100	74	89	100	100	100	94	94	97	94	100	94	92	100	92
Tear	100	17	15	37	9	100	33	40	27	27	100	48	47	37	43
Abrasion	100	—	—	—	—	100	87	73	151	115	100	87	78	105	85
Rebound	100	74	78	85	81	100	88	77	90	90	100	91	79	91	91
Heat build-up %	—	—	—	—	—	—	59	67	44	58	—	53	42	51	42

A = Naugatuck Buna-S. B = Buton-S. C = Chemigum IV. D = Hycar TT.

With semi-reinforcing carbon black such as Kosmos 20 Drogin found an addition of 60 parts on the 100 to be most suitable both for rubber and Buna-S. So far as the softer carbon blacks, such as P 33 and Thermax are concerned, these gave much lower reinforcement of the Buna-S. On the other hand, they process more easily and larger amounts could be added. The cure is much more rapid. The tensile strength obtained is about the same and the heat build-up is lower. The resilience of these compounds is also rather improved.

Drogin also tried the behaviour of 60 parts lampblack and acetylene black in natural rubber and Buna-S rubbers. He found lampblack to have effects somewhat similar to those shown by semi-reinforcing

TABLE 80. SIX DIFFERENT BLACKS IN BUNA [7]

(50 parts per 100 Buna-S)

	Kosmobile-S Dixiedensed-S	Kosmobile 77 Dixiedensed 77	Dixie 40 Kosmos 40	Dixie 20 Kosmos 20	P 33	Therma
Plasticity (mm)	404	380	360	307	277	270
Extrusion (seconds)	15 5	11·6	4·9	3·3	3·0	3·1
Modulus at 400%	1300	880	1095	1530	625	490
Tensile strength	3250	2780	2600	1915	1700	1575
Elongation at break	475	615	525	475	720	890
Shore hardness	65	63	60	56	51	48
Tear resistance	408	331	349	200	164	145
Abrasion resistance	197	163	224	223	522	765
Percentage rebound	38	40	45	50	50	53
Heat build-up :						
Average temp. ° F.	181°	190°	189°	165°	160°	190°
Percentage compression	6·0	8·1	6 6	3·8	4·2	9 2
Percentage set	4·0	6·4	6·0	4·0	6·0	10·0
Percentage shrinkage	4·3	6·7	4 8	11·5	11·0	10·6
Electrical resistance	$1·9 \times 10^6$	13×10^8	$10\,4 \times 10^6$	34×10^8	35×10^8	34×10
Process of manufacture	Channel	Channel	Special furnace	Furnace	Furnace	Furnac
Type	Hard	Soft	Reinforcing	Semi-reinforcing	Soft	Very soft

black, e.g. Kosmos 20. Acetylene black behaved in a manner betwee this and the reinforcing hard black, e.g. Kosmobile 77. Acetylen black showed a much higher heat build-up. The conductance wa

TABLE 81. FORMULATION—BUNA-S TREAD COMPOUND [7]

	Dixiedensed 77 Kosmobile 77	Dixie 40 Kosmos 40	Dixie 20 Kosmos 20
Buton-S	100	100	100
Zinc oxide	5	5	5
Stearic acid	2·5	2·5	2·5
Pine tar	1·3	1·3	1·3
Wool grease	2·4	2·4	2·4
Bardol	2·4	2·4	2·4
Agerite powder	0·8	0·8	0·8
Sunproof	1·7	1·7	1·7
Santocure	1·4	1·4	1·4
Sulphur	1 8	1·8	1·8
Black	50	55	60
	169·3	174·3	179·3
Press cure	280° F.	280° F.	280° F.

outstandingly good, which indicates its application for conducting synthetic rubbers, parallel to conducting rubber.

The most important fact brought out by Drogin was that the best type of black to use was a specially prepared furnace black. In this case Kosmos 40 is of the reinforcing type, approaching hard reinforcing channel black in reinforcement, but much easier to process. It is faster curing, has higher modulus, better resilience, and lower heat build-up than channel black.

A consequence of this conclusion, substantiated by other workers, is that the United States Government has arranged for new plants for the manufacture of such special furnace blacks for use with synthetic rubbers.

TABLE 82. DETAILED TEST DATA—BUNA-S TREAD COMPOUND [7]

	Dixiedensed 77 Kosmobile 77	Dixie 40 Kosmos 40	Dixie 20 Kosmos 20
Black loadings	50	55	60
Plasticity (mm.) [a]	362	318	260
Extrusion, seconds [b]	2·4	1·7	1·4
Modulus at 300% [c]	1100	1625	1200
Tensile strength (maximum) [c]	2215	2080	1615
Elongation at break [c]	460	360	370
Shore hardness [c]	61	60	55
Percentage tensile depreciation [d]	12	4	35
Tear resistance [c e]	545	282	242
Abrasion resistance [c f]	162	100	168
Percentage rebound [c g]	39	42	45
Percentage shrinkage [h]	6·3	4·8	9·6
Flex resistance, flexes [i]			
Incipient cracking	405	1275	405
Deep cracking	1550	2525	1050
Final break	2210	3380	1150
Heat build-up [c k]			
Average temp. ° F. [l]	175°	166°	161°
Percentage compression	6·2	2·5	1·3
Percentage set	6·0	3·2	3·2
Electrical resistance [m]	$3{\cdot}2 \times 10^8$	$1{\cdot}6 \times 10^5$	$6{\cdot}8 \times 10^8$

[a] Williams plastometer, at 70° C.
[b] Firestone-Dillon plastometer, 15 lbs. pressure.
[c] For cure which produced maximum tensile strength.
[d] Aged 24 hrs. in oxygen bomb at 80° C. and 300 lbs. oxygen pressure.
[e] Winkelmann test, crescent-shaped piece.
[f] Grasseli abrader. [g] Lupke-type machine.
[h] Shrinkage of a standard dumbell test piece.
[i] De Mattia machine, stroke 3-inch, r.p.m. 300.
[k] Goodrich flexometer, stroke 0·150-inch, load 147·5 lbs., r.p.m. 1800.
[l] Average of 30-minute cycle.
[m] Measured with Volt Ohmyst Jr., calculated to ohms-cm.[3]

The excellent all-round character of these special furnace blacks is brought out rather more clearly by Drogin's study of them in tread formulations based on Buna-S.

TABLE 83. SUMMARY OF TEST DATA—BUNA-S TREAD COMPOUND [7]

	Dixiedensed 77 Kosmobile 77	Dixie 40 Kosmos 40	Dixie 20 Kosmos 20
Black loadings	50	55	60
Plasticity	100	114	139
Extrusion	100	141	171
Modulus	100	148	109
Tensile	100	94	73
Elongation	100	78	80
Hardness	100	98	90
Tear resistance	100	52	44
Abrasion resistance	100	162	96
Flex resistance	100	153	52
Rebound	100	108	115
Heat build up	100	− 9° F.	− 14° F.

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CHAPTER 12

ELASTOMERS—PERBUNAN, HYCAR O.R., CHEMIGUM

The Properties of Perbunan and Perbunan-Extra. Production of Perbunan is carried out on plant identical to that used for Buna-S, and by the same procedure, i.e. by emulsion polymerization.

Perbunan is a copolymer of butadiene and acrylic acid nitrile. It has a nitrogen content of 7 per cent., corresponding to about 25 per cent. acrylic nitrile. According to Moll, Howlett, and Buckley[9] the Perbunan being made by the Standard Oil Company of New Jersey consists of 74 per cent. butadiene and 26 parts acrylic nitrile. An increase in the proportion of acrylic nitrile was found to enhance the resistance to oils and solvents. Simultaneously, however, the synthetic rubber became more thermoplastic with an accompanying decrease in rubbery properties. The best balance is obtained when the acrylic nitrile content is about 35 per cent. This modified product is Perbunan-Extra.

They are pale, rubbery materials without marked odour or taste. They are particularly distinguished by their outstanding resistance to swelling by petrol, lubricating oil, and many organic solvents. Apart from this, vulcanized products have other superior physical properties. Both types are better than natural rubber in withstanding heat, in their resistance to abrasion, and in their ageing characteristics. The raw materials are insoluble in aliphatic hydrocarbons, but are freely soluble in aromatic hydrocarbons and chlorinated solvents, they also dissolve in ketones such as acetone.

Both the favourable and unfavourable properties of Perbunan are attributed to its internal structure. Whereas rubber is thought to consist of open long-chain molecules based on isoprene, Perbunan is considered to have a cyclized molecule. Although composed of a large number of butadiene and acrylic nitrile units, it is thought that a mass of long-chain molecules have been formed to yield a cyclized structure. This would provide a plausible explanation for the differences of plasticizing and also its resistance to solvents.

The Perbunans are best handled on two roll mills such as are widely used for rubber processing. As a preliminary, they must be broken down just in the same way as rubber is masticated. The object is to render the material thermoplastic, so that fillers and other ingredients may be added. The breaking down of Perbunan is much

more difficult than with rubber. This is one of the chief drawbacks of the material. At one time it could not be worked in internal mixers, such as the Banbury, which is the backbone of large-scale production. This has recently been overcome. Thus Moll, Howlett and Buckley found that Perbunan can be mixed in the Banbury at the high temperature of 105° C. in the presence of 0·9 part xylyl mercaptan. The time required is between 5 and 20 minutes. Only small batches of Perbunan can be handled at a time. For example, only 30 lbs. can be used on a 60-inch mill. The rolls have to be kept cool and very close together, when the initial breakdown then takes about a half-hour. This initial " nerve " of Perbunan is never eliminated by overmastication ; it cannot be " killed " in the same way as rubber.

The softening procedure for Buna-S does not work with these other derivatives. However, other chemical methods are being developed with some success. The following method illustrates one angle. According to Baechle : [1]

Small amounts of asymmetric derivatives of hydrazine are introduced into the polymerizates before working up, for example phenylhydrazine, nitrophenylhydrazine, aminophenylhydrazine, and tolylhydrazine. The hydrazine derivative can be added to the rubber mixture during milling or to the emulsion-polymerizate, as it assumes the form of a latex, about 0·1 per cent. of the hydrazine derivative being used. The action of the addition is to make the polymerizate become plastic and flowable on the rolls. Adhesive surfaces can be given to the polymerizates by brushing them with the hydrazine derivatives.

Parallel with the plasticizing action there is an increase in solubility of the polymerizate so that it is now applicable for the preparation of solutions. When the hydrazine derivative is added to the polymerizate in emulsion form it is advantageous to inject air or oxygen, optionally, together with the addition of oxygen-transferring heavy metal salts.

Unfortunately this type of material is very toxic.

Gerke [7] has also achieved some success in plasticizing this type of material. He described how a plastic conversion product of a mixed ploymer of a conjugated 1,3-diene with an alpha-beta-unsaturated nitrile is prepared by heating a mixture containing the mixed polymer and an organic nitroso compound selected from *p*-nitroso-dimethyl aniline, nitroso-beta-naphthol, and *p*-nitroso-diethyl aniline, for a time and at a temperature sufficient to reduce the viscosity of the mixed polymer and confer on it a greater tack than possessed by the original material.

Once rendered partly thermoplastic, plasticizers and softeners are added to aid the process. Perbunan works very dryly and lacks tackiness, consequently the softeners normally used with rubber are not adequate.

The Use of Plasticizers. Perbunan is much less thermoplastic than natural rubber. A suitable selection of plasticizers greatly facilitates the improvement of plasticity and also aids such other properties as tackiness, the extrusion process, etc. Another important point is that most available plasticisers also lower the cost of the compound. In the normal way the addition of softeners would be of the order of 5–10 per cent. of the amount of Perbunan. For exceptional purposes the plasticizer content may be as high as 150 per cent.

Four types of plasticizers may be used with Perbunan. The general range of plasticizers employed in plastics technique and lacquer technique such as dibenzyl ether, triphenyl phosphate, phthalic acid esters, dibutyl sebacate, etc., are very effective. They all have a marked softening effect on the material, but nevertheless profoundly improve the elasticity of the vulcanized composition. These plasticizers swell the Perbunan, but do not affect the processing properties to any great extent.

It is essential to add additional softeners to enhance the tackiness of the unvulcanized material. As a matter of fact this is a very important feature of nearly all synthetic elastics. They greatly affect such processes as lamination and the building of all plied material as in the manufacture of beltings or hose. In most cases these softeners reduce the elasticity of the vulcanized material. Amongst the chief materials that are used are rosin, coumarone resin, rosin oil, alkyd resins, coal tar, pine tar, etc. It will be recognized that these materials perform a precisely similar function with natural rubber compounds.

Perbunan compounds do not extrude and calender so well as natural rubber owing to the fact that they have considerable nerve and are lacking in plasticity. Consequently suitable materials must be added to facilitate extrusion and calendering. Typical materials which help these features include alkyd resins, lanolin, and factices.

There is one other type of softening material which should be considered in connection with Perbunan. The outstanding property of Perbunan is the resistance to oils and solvents. In order to attain a maximum resistance to these solvents, it is obviously essential that materials used as plasticizers, should, as far as possible, be insoluble in petrol and oil. Examples of such softeners are triphenyl phosphate, alkyd resins, trichlorethyl phosphates, etc.

In this connection Stöcklin [14] showed that addition of another class of synthetic rubber-like material profoundly enhanced the oil-resisting properties of Perbunan. He found that addition of polysulphide condensation rubbers of the thioplast type greatly improved the already excellent oil-resisting properties of Perbunan. These materials were

mixed in on the rolls. The products were found to have remarkable swelling resistance and other physical properties. It should be noted that this procedure of adding thioplast to other synthetic rubbers has proved very successful. For example, similar materials are added to neoprene and also to the latest type of Thiokol—Thiokol RD—which contains butadiene.

Thus a typical mix employed for Perbunan to be used in contact with petrol, comprises Perbunan 75, Thiokol F 25, Dibutyl phthalate 5, plus the usual accelerators, etc.

Strangely enough, one of the best softeners for Perbunan is natural rubber. It is found that additions of up to 20 per cent. do not greatly detract from the swelling characteristics while facilitating the processing. The primary effect of using any great amount of rubber together with Perbunan is to lower the resulting oil resistance and to detract seriously from the ageing characteristics and ability to withstand high temperature service.

Other plasticizers recommended include tributyl phosphate, dibenzyl sebacate, butyl acetyl, cricinoleate, etc.

Plasticizers for Elastomers. Plasticizers employed for synthetic elastic materials in many cases differ from those normally employed for rubber technology. Among the most extensively used are materials such as tricresyl phosphate, dibutyl phthalate, dibutyl sebacate, etc. These are widely used in the manufacture of lacquers, varnishes, coatings, etc., and in the plastics industry.

The properties which are sought in plasticizers, apart from the ability to mix, include :

(*a*) Non-volatility and non-inflammability.
(*b*) Good retention by the material, i.e. there must be no sweating.
(*c*) Good water resistance.
(*d*) Resistance to petrol and oils.
(*e*) Low freezing point.
(*f*) Odourless, chemical stability, non-toxicity, etc.
(*g*) Good electrical properties.

Very few come up to all these requirements, and plasticizing is invariably a compromise.

Tricresyl phosphate is a colourless, odourless liquid, with a specific gravity of 1·175. It has a high boiling point of 295° C. at 13 mm. pressure. It freezes at − 35° C. It has a very low water solubility—less than 0·002 per cent. at 100° C. It is probably the most widely used plasticizer. It has a high temperature stability, and is unaffected by acids and alkalis. It has good fire-retarding properties.

Another very widely used plasticizer is dibutyl phthalate, which is a clear, colourless liquid, boiling at 340° C. and freezing at − 35° C. The specific gravity is 1·048 at 20° C. It is miscible with most organic solvents and oils, but has an extremely low water solubility amounting to 0·001 per cent. at 20° C.

Another less well-known plasticizer, which is, however, attaining great importance particularly for elastomers, is dibutyl sebacate, which has a specific gravity of 0·940 at 25° C., and a boiling point of 340° C. This also has a very low solubility in water—less than 0·1 per cent.

Addition of Filling Materials to Perbunan. Filling materials are always added to Perbunan, not only because they are necessary to cheapen the product but because the unloaded Perbunans yield vulcanized products which are much weaker than the corresponding rubber articles and have very limited scope. The usual range of rubber fillers are widely used, including zinc oxide, china clay, whiting, lithopone, etc.

As with rubber, the best properties are brought out by the use of strong reinforcing fillers. From this point of view and from the point of view of cost, Perbunan is usually compounded according to the requirements. All classes of hard carbon blacks produce products with high tensile strength and good abrasion resistance. They enable the production of materials having tensile strength quite as high as the best obtainable with natural rubber, e.g. about 5,000 lbs. per square inch. They also yield Perbunan compounds having the optimum values for hardness and resistance to tear. However, they do not give the best values with regard to permanent set, the ability to bond to metal and the rebound elasticity.

It is found that addition of semi-reinforcing softer blacks, while giving somewhat lower tensile strength and hardness, yet give a better balance of physical properties and result in the best all-round products. They produce compounds having better flexibility, a maximum of rebound elasticity, less permanent set, better bonding to metals, and the resistance to fatigue and flexing is also augmented.

With the exception of magnesia and magnesium carbonate, which tend to cause hardening up of Perbunan stocks, almost every white filler can be used as in the case of rubber. In some cases some of these fillers do not give the same tensile strength as they do in rubber. Nevertheless they are very useful in compounding Perbunan for special purposes.

Zinc oxide plays a similar rôle to that which it plays in rubber compounds, and is primarily useful in small amounts to activate the accelerators. Usually from 2 to 5 per cent. is adequate for this purpose.

It is found that larger quantities of the order of 15 parts are helpful with mercaptobenzthiazole as an accelerator in order to achieve a strong bond to metal. As in rubber, zinc oxide helps to maintain the tackiness of compounds, which are to be plied together as in belt and hose friction materials. Since zinc oxide is not easily wetted and dispersed by Perbunan, it is desirable to add it early in the compounding process to ensure thorough dispersion.

Other white fillers such as clay, whiting, blanc fixe, and barytes are primarily useful in Perbunan only as cheapeners, and as might be expected, this is achieved at the expense of the tensile strength, elasticity, and permanent set. These inert fillers perform a very useful function by aiding processing, and their presence materially improves the extrusion and calendering properties of Perbunan.

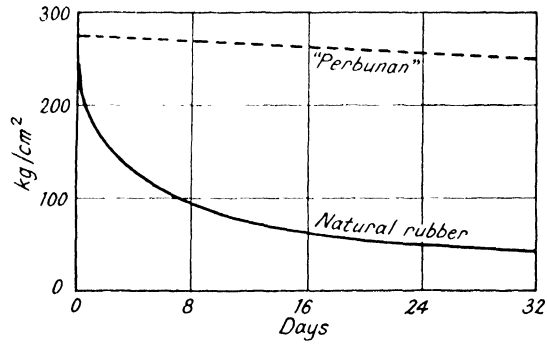

FIG. 36.—Tensile Strength of Perbunan and Rubber Tyre Tread Compounds during Ageing in an Oxygen Bomb at 60° C.[12]

This type of elastomer as manufactured contains about 2 per cent. of antioxidant phenyl-β-naphthylamine, a quantity which is adequate to protect it for all normal applications. It darkens on exposure to light, and consequently limits the use of Perbunan for light-coloured articles. As in the case of rubber, the best heat-resisting compounds are made with thiuram accelerators, and for such applications it is desirable to add a small further amount of antioxidant.

It is essential to add waxes in Perbunan compounds which are to be made into mechanical goods or any product which may have to stand up to sunlight or be subject to flexing. In this respect Perbunan appears to be just as vulnerable as rubber. The most suitable waxes include paraffin wax, ozokerite, ceresine, petroleum waxes, etc. In addition to the protection thereby afforded, they also assist the processing of the compounds.

As in the case of rubber, stearic acid is used with Perbunan to assist in the dispersion of carbon black, and to act as an activator for various accelerators. Up to 3 per cent. may be employed to advantage. It does not mix into Perbunan very easily, and is generally added together with fillers. Stearates may be added to Perbunan in very much the same manner as to rubber.

Vulcanization Characteristics. The vulcanizing behaviour of Perbunan is very similar to that of rubber; rather less sulphur is necessary for soft products, about 2 per cent. being generally used. Selenium and tellurium are also effective.

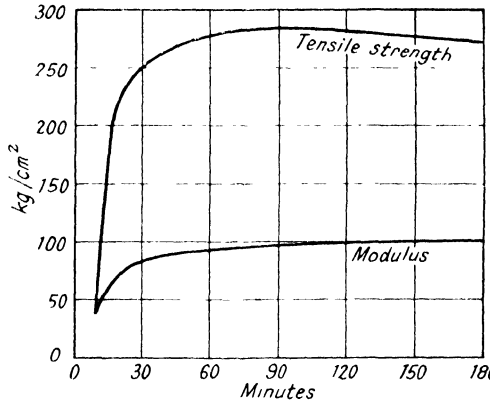

FIG. 37.—Tensile Strength and Modulus of a Perbunan-Carbon Black Mix during Progressive Vulcanization.[12]

The normal vulcanizing temperatures employed with Perbunan compositions is between 125° and 150° C., while the time of vulcanization in general varies from 10 to 60 minutes. Continued heating of Perbunan vulcanizates is accompanied only by slight hardening and can be regarded as a form of after-vulcanization; there is no tendency for tackiness or resinification to occur as in the case with rubber.

The table on the next page illustrates the effect on various properties of variations in the sulphur content of a specimen Perbunan compound.

From this table it is easy to see that in this particular compound, which is typical, a sulphur content over 2 per cent. produces two principal effects. First, the higher ranges of sulphur produce rapidly increasing hardness and modulus, while the elongation correspondingly decreases. Optimum tensile strength is attained with a sulphur content not greater than 2 per cent.

TABLE 84. INFLUENCE OF SULPHUR ON PERBUNAN [8]

Perbunan	100
Dibutyl phthalate	10
Coal tar	5
Rosin	5
Stearic acid	2
Zinc oxide	5
Spheron	30
Altax	1·25
Dibutylamine	0·25
Sulphur	as in the table following

Press cure 40 minutes at 141° C

Sulphur	T_B lbs./in.²	E_B %	M300	H
1	3180	750	420	50
2	3400	650	560	55
3	2820	500	1000	58
5	1970	300	1970	61
7·5	1820	200	—	65
10	1660	175	—	70

The use of accelerators in the vulcanization parallels the ordinary rubber practice. The most useful types include mercaptobenzthiazole, benzthiazyl disulphide, particularly when used together with diphenylguanidine or di-orthotolyl guanidine. The organic ultra-accelerators function precisely as with rubber. As with rubber the dangers of premature vulcanization during processing must be considered.

As in the case of rubber, added resistance to heat is obtained by using ultra-accelerators which carry their own sulphur of vulcanization, notably the thiurum disulphides. Such heat-resistant products are much superior to their rubber prototypes. They show no tendency to tackiness, nor does the phenomenon of reversion occur. Prolonged exposure to heat merely causes slight hardening up.

Hard Rubbers Based on Buna Elastomers. With more than 30 per cent. of sulphur, hard materials result which in some respects are superior to ebonite, notably in resistance to solvents and in greater heat resistance.

A very informative study on hard rubbers obtained from Buna elastomers has been made by Gartner.[4] He prepared comparable mixes based on the elastomers and subjected them to electrical tests.

He found that Buna-S hard rubbers were almost as good as those made from natural rubber, while those made with Buna-SS were superior. As might be expected, those made with Perbunan were not so good, but were better than expected.

TABLE 85. COMPOSITIONS OF THE HARD RUBBER MIXTURES [4]

No.	Natural rubber		Buna-85		Buna-S		Buna-SS		Perbunan		Perbunan-Extra	
	1	2	3	4	5	6	7	8	9	10	11	12
Rubber (percentage by weight)	75·0	73·3	73·3	71·7	77·8	76·0	79·1	77·3	79·7	78·5	79·7	78·5
Sulphur (percentage on rubber)	32·0	35·0	35·0	38·0	27·0	30·0	25·0	28·0	24·0	26·0	24·0	26·0
Natural rubber	100·0	100·0	—	—	—	—	—	—	—	—	—	—
Buna-85	—	—	100·0	100·0	—	—	—	—	—	—	—	—
Buna-S (Defo 250)	—	—	—	—	100·0	100·0	—	—	—	—	—	—
Buna-SS (Defo 400)	—	—	—	—	—	—	100·0	100·0	—	—	—	—
Perbunan	—	—	—	—	—	—	—	—	100·0	100·0	—	—
Perbunan-Extra	—	—	—	—	—	—	—	—	—	—	100·0	100·0
Sulphur	32·0	35·0	35·0	38·0	27·0	30·0	25·0	28·0	24·0	26·0	24·0	26·0
Vulkacit DM	1·5	1·5	1·5	1·5	1·5	1·5	1·5	1·5	1·5	1·5	1·5	1·5
Totals	133·5	136·5	136·5	139·5	138·5	131·5	126·5	129·5	125·5	127·5	125·5	127·5

Hard rubbers are widely employed on account of their resistance to corrosion. So Gartner also studied the behaviour of the various elastomer hard rubbers on contact with the more usually encountered chemical agents over long periods of time. Table 86 summarizes the results obtained.

The elastomer hard rubbers displayed exceptionally good resistance to even the most exacting corrosive agents.

TABLE 86. ELECTRICAL PROPERTIES OF HARD RUBBERS (1000 V.) [10]

Rubber	Sulphur	Ohms per cm. $\times 10^{15}$		tan δ (50 Hertz)		Dielectric constant (50 Hertz)	
	%	(1)	(2)	(1)	(2)	(1)	(2)
1. Natural rubber	32	8·4	Higher than 10^{16}	0·0056	0·0050	2·9	2·9
2. Natural rubber	35	8·8	Higher than 10^{16}	0·0056	0·0066	2·9	2·9
3. Buna-85	35	10·0	Higher than 10^{16}	0·0076	0·0067	2·9	2·9
4. Buna-85	38	10·0	Higher than 10^{16}	0·0077	0·0078	3·0	3·0
5. Buna-S	27	6·8	Higher than 10^{16}	0·0057	0·0050	3·0	3·0
6. Buna-S	30	4·7	Higher than 10^{16}	0·0047	0·0051	2·9	2·9
7. Buna-SS	25	10·0	Higher than 10^{16}	0·0029	0·0035	2·9	2·9
8. Buna-SS	28	10·0	Higher than 10^{16}	0·0033	0·0045	3·0	3·0
9. Perbunan	24	2·6	Higher than 10^{16}	0·0014	0·0084	4·0	4·0
10. Perbunan	26	5·4	Higher than 10^{16}	0·0096	0·0088	3·9	3·9
11. Perbunan-Extra	24	5·0	Higher than 10^{16}	0·0098	0·0101	4·2	4·2
12. Perbunan-Extra	26	3·2	Higher than 10^{16}	0·0093	0·0114	4·1	4·2

(1) Original state.
(2) After 14 days in air oven at 100° C.
The compositions are given in Table 85.

Processing of Perbunan Compounds. All the usual processing methods applied to natural rubber may be used with equal success in handling Perbunan compounds. The precautions to be taken for various fabrication processes are much the same as with natural rubber. As is the case with every material there are certain knacks which can only be acquired by experience.

Press-curing of Perbunan presents no difficulties as the material flows extremely well. The plateau effect in the curing of Perbunan renders the time of cure less critical than with natural rubber, since overcure does not greatly lower the physical properties.

TABLE 87. CHEMICAL STABILITY OF THE HARD RUBBERS

Reagent	Very satisfactory	Unsatisfactory
Water (8 weeks at 95° C.)	Buna-85, Buna-S and Buna-SS vulcanized in steam Natural rubber	
Hydrochloric acid (12 weeks at 20° C.)	Natural rubber Buna-85 Buna-S Buna-SS Natural rubber (All equally good)	Perbunan Perbunan-extra
Sulphuric acid (Dilute) (12 weeks at 20° C.)	Natural rubber Buna-85 Buna-S Buna-SS (All equally good)	Perbunan Perbunan-extra
Hydrofluoric acid (2 weeks at 20° C.)	Heavily loaded blends of natural rubber with Buna-85 Neoprene Buna-SS	Perbunan Perbunan-extra
Nitric acid (8 weeks in 32% at 20° C.)	Buna-SS (Both vulcanized in hot air)	Perbunan Perbunan-extra
Chlorine gas (4 weeks at 70° C.)	Buna-85 vulcanized in steam Natural rubber	Perbunan Perbunan-extra (Both vulcanized in steam)
Sodium Hypochlorite (8 weeks at 20° C.)	Buna-85 Buna-S Buna-SS Perbunan Perbunan-Extra. (In all cases, particularly when containing high percentages of sulphur and vulcanized in hot air)	
Benzene (8 weeks at 20° C.)	Perbunan-Extra (with high proportions of sulphur)	Natural rubber Buna-85 Buna-S Buna-SS

Steam-curing of Perbunan compounds works perfectly well, generally yielding vulcanized stocks rather harder than if the same stock is press-cured.

TABLE 88. PROPERTIES OF COMPARABLE VULCANIZED PRODUCTS

Basis	T_B kg./cm.	E_B %	M_{300}	H	Pendulum elasticity
Raw rubber	260	600	70	65	50
Perbunan	300	600	90	70	45
Buna-S	275	650	80	65	50

Calendering or frictioning of Perbunan compounds presents no difficulty if they are designed for the purpose. In general, any normally plasticized Perbunan compound may be calendered into thin sheets without trouble if the roll temperatures are suitably adjusted.

TABLE 89. AGEING OF COMPARABLE MIXES LOADED WITH CARBON BLACK

Basis	Original		Geer oven (90° C.) 32 days		Oxygen bomb 32 days	
	T_B	E_B	T_B	E_B	T_B	E_B
Raw rubber . .	260	600	130	350	50	200
Perbunan . . .	290	560	260	400	250	600
Buna-S . . .	270	765	225	575	230	600

Tubing or extruding of Perbunan proceeds very easily when the compound is plasticized with those softeners particularly recommended for this purpose. In general the barrel and worm of the tuber should be thoroughly cold, and the die should be only sufficiently warm to assure that the stock extrudes smoothly.

Bonding Metal and Perbunan. The bonding of Perbunan to metal is comparatively simple to achieve in the case of iron, steel, and ferrous alloys generally. An intermediate coat of chlorinated rubber is used as a bonding agent. The metal surface should be thoroughly cleaned and free of grease in any case; it should preferably be sand-blasted, pickled or treated with an abrasive paper to produce a slightly roughened surface to improve the bond. Then there should be applied to the properly prepared metal surface two or three coats of

a 15 per cent. solution of chlorinated rubber (125 cp. viscosity) dissolved in toluene. The best bond will result if, before vulcanization, the raw Perbunan compound can be formed so that it will conform fairly well to the metal surface and hence flow as little as possible in the mould. It is preferable to join the coated metal and the preformed Perbunan while the last coat of chlorinated rubber is at least still somewhat moist with solvent and tacky.

From the electrical viewpoint, Perbunan has little to offer. Thus it has a dielectric constant of 15, and a specific resistance of 10^7 ohms/cm^3. It is virtually a semi-conductor and finds some use as such in the new field of conducting rubbers.

Oil Resistance of Perbunan. The outstanding property of Perbunan is the solvent resistance, particularly as shown by properly compounded vulcanized products. The influence of numerous types of solvents and oils is summarized in the following table. It is remarkable how the tensile strength is retained after contact with these solvents and oil.

TABLE 90. SWELLING OF UNPLASTICIZED PERBUNAN COMPOUND AFTER 8 WEEKS AT ROOM TEMPERATURE [8]

Original Tensile Strength 2600 lb./in.^{2}

	Percentage increase in weight	Tensile strength lb./sq. in. Swelled sample
Petroleum fraction, propane, butane, petrol, mineral oil, etc.	0– 10	2100/2500
Transformer oil	0– 10	2400
Fuel oil	0– 10	2300
Paraffin oil	0– 10	1850
Benzol, toluol, xylol	50–100	700
Carbon tetrachloride	50–100	850
Methylene chloride, chlorbenzene, etc.	more than 100	400/700
Esters, ketones, aldehydes, amines	50–100	400/600
Alcohols	0– 20	1700/1850
Glycols	0– 10	2400/2500
Palm oil, fish oil, butter	0– 20	2100/2500
Linseed oil	10– 20	1950
Oleic acid	20– 50	2500

The swelling action of different types of solvents on Perbunan compounds varies widely. It is true that the more highly loaded a Perbunan compound is the less it will swell in a given solvent, although this is much less important than with the natural rubber compounding. There is no great difference between low and high loadings so far as solvent swelling is concerned. For minimum values of solvent swelling or absorption, it seems essential that Perbunan compounds should be fully cured or even slightly overcured.

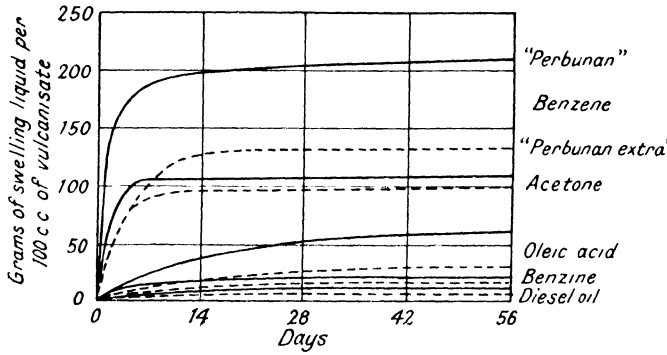

FIG. 38.—Swelling of Perbunan in Various Solvents.[12]

TABLE 91. HOSE COMPOUND WITH HIGH RESISTANCE TO SWELLING [13]

	1. *Tube and cover.*		2. *Friction.*
100·0	Perbunan-Extra	100·0	Perbunan-Extra
8·0	Rosin	50·0	Dibenzyl ether or coal tar fuel oil
3·0	Softener III		
25·0	Dibenzyl ether	15·0	Carbon black
15·0	Carbon black	30·0	P.33
120·0	Thermax, P.33 or Gastex	5·0	Zinc oxide
125·0	Whiting	1·3	Sulphur
5·0	Zinc oxide	1·0	Vulkacit AZ
2·2	Sulphur		
1·5	Vulkacit AZ		

Cure in steam : 40 to 50 min. : 45 lbs. per sq. in.

	T_B.	E_B.	M_{300}.	H.	E.
Physical properties of mixing (1)—					
with Thermax . . .	65	360	59	76	28
with Gastex . . .	90	225		85	21
with P.33	78	480	56	77	20
Physical properties of mixing (2)—					
with dibenzyl ether . .	72	910		30	51
with coal tar fuel oil . .	84	1050		33	47

		Benzol	Coal tar fuel oil	Petrol	Fuel mixture
Swelling of the tube stock (1) in 24 hours at 70° . .		45%	90%	0·2%	11%
Test immediately after swelling	T_B	31	28	71	60
	E_B	140	150	190	180

The fuel mixture consists of 75% petrol, 10% benzol, and 15% alcohol.

None of the common alcohols and glycols used for anti-freeze purposes swells Perbunan appreciably. But many applications of Perbunan compounds for service in contact with anti-freeze liquids require good resistance.

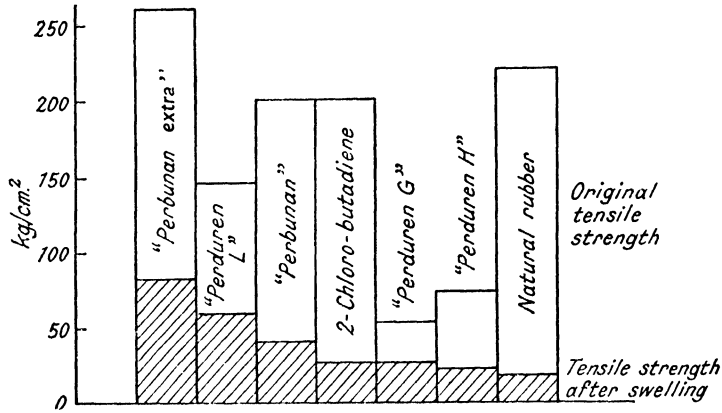

FIG. 39.—Tensile Strength after Swelling for 8 weeks in Turpentine at 20° C.[12]

Apart from the better solvent resistance and heat-resisting properties of Perbunan compounds, it is claimed that they have far superior resistance to abrasion. A Perbunan tyre tread mix is claimed to be considerably better in this respect than a corresponding tread mix of rubber.

Resistance to Heat and Cold. The resistance of Perbunan compounds to low temperature is, in general, similar to that exhibited by natural rubber compounds. When properly compounded Perbunan may be used at temperatures of 300° F. At the other end of the scale, it cracks at − 45° F.

Heat resistance of Perbunan compounds is inherently superior to that of natural rubber products. Perbunan does not develop tackiness, nor does reversion occur when it is exposed to elevated temperatures. The primary effect of prolonged exposure of Perbunan compounds to heat is to cause a gradual increasing surface hardness while the tensile strength is at first increased, then gradually decreased as the elongation and rebound elasticity fall off. At the present time maximum resistance of Perbunan compounds to high temperatures seems to be accomplished along the same lines as with rubber, through the use of tetramethyl-thiuram disulphide, with little or no sulphur.

Uses of Perbunan. Perbunan and Perbunan-Extra are widely employed in the production of:

Gaskets, packings, seals, food containers, motor-car parts, petrol hose, oil-resistant sheetings, etc.

They are attached to metal parts and find great application for use in engineering both in extension and under compression.

TABLE 92. HEAT-RESISTING PERBUNAN COMPOUNDS[13]

Perbunan	100·0	100·0
P.33	30·0	30·0
Thermax	30·0	30·0
Zinc oxide	1·0	1·0
Softener III	3·0	5·0
Vulkacit Thiuram	2·5	2·5
Antioxidant MB	2·5	2·5
Sulphur	0·1	0·07
Crêpe	12·0	—
Dibenzyl ether	—	10·0

	T_B.	E_B.	M_{250}.	E.	H.	T_B.	E_B.	M_{250}.	E.	H.
Cure at 45 lbs. per sq. in.										
30 min.	93	760	30	48	56	99	980	24	55	54
60 „	105	740	34	47	57	105	845	28	55	56
Aged in air at 150° C.										
48 hours	117	385	67	45	68	144	385	84	45	72
	123	387	68	46	68	159	437	84	45	72
96 „	87	275	78	42	71	102	275	94	42	74
	96	275	85	42	71	78	237	—	42	74
120 „	57	156	—	35	74	49	106	—	35	78
	42	100	—	35	75	41	90	—	36	78
Aged in transformer oil at 150° C.										
48 hours	57	331	35	56	46	117	470	45	55	56
	51	320	33	56	46	105	465	42	55	56
96 „	36	262	34	55	44	72	331	48	52	58
	35	260	32	54	44	70	330	46	51	58

Spreading and dipping Perbunan compounds are readily prepared from a wide range of unvulcanized stocks. Thus it is possible to spread and dip cements or solutions of such compounds as will give vulcanized goods ranging from very soft, resilient products to the consistency of hard rubber.

The Use of Perbunan for Spreading and Dipping. Perbunan is successfully used in the manufacture of sheetings and dipped goods. Gloves are the chief products made by dipping. Gloves for various industrial purposes resistant to oils, benzene, weak and highly concentrated acids, are now made from Perbunan, and they are claimed to be far superior to those made of natural rubber; in fact, for some purposes where they are used, natural rubber cannot be employed at all.

All kinds of nipples and teats are also made. It has not yet been

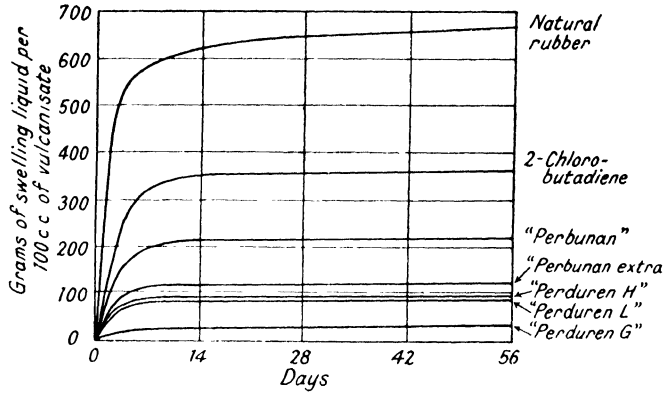

FIG. 40.—Swelling of Perbunan compared with Other Elastics in Carbon Tetrachloride at 20° C.[12]

possible to achieve the transparency that had become usual in natural rubber goods of this type, but this is not really necessary.

Dipped goods made of Perbunan are, of course, very resistant to oils and solvents.

The manufacturing process, while similar to that followed when natural rubber solutions are used, offers various difficulties which have to be overcome. The Perbunan must be thoroughly broken down. Difficulties are also encountered in preparing solutions. With efficient mixers it is possible to complete the production of Buna solutions in about four hours. The appropriate solvent for the different types of

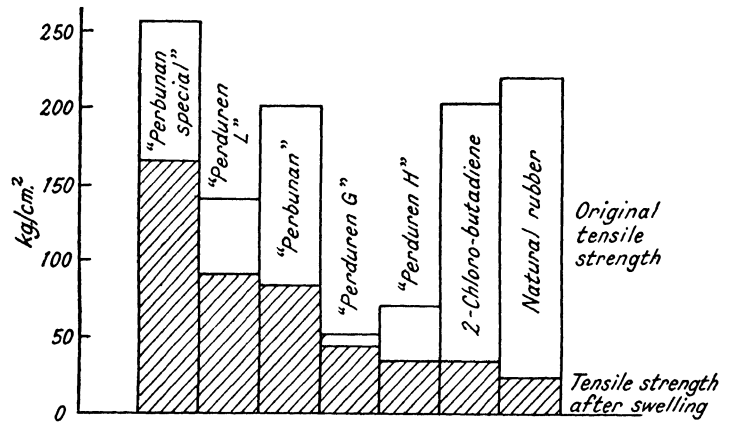

FIG. 14.—Tensile Strength after Swelling for 8 weeks in Carbon Tetrachloride at 20° C.[12]

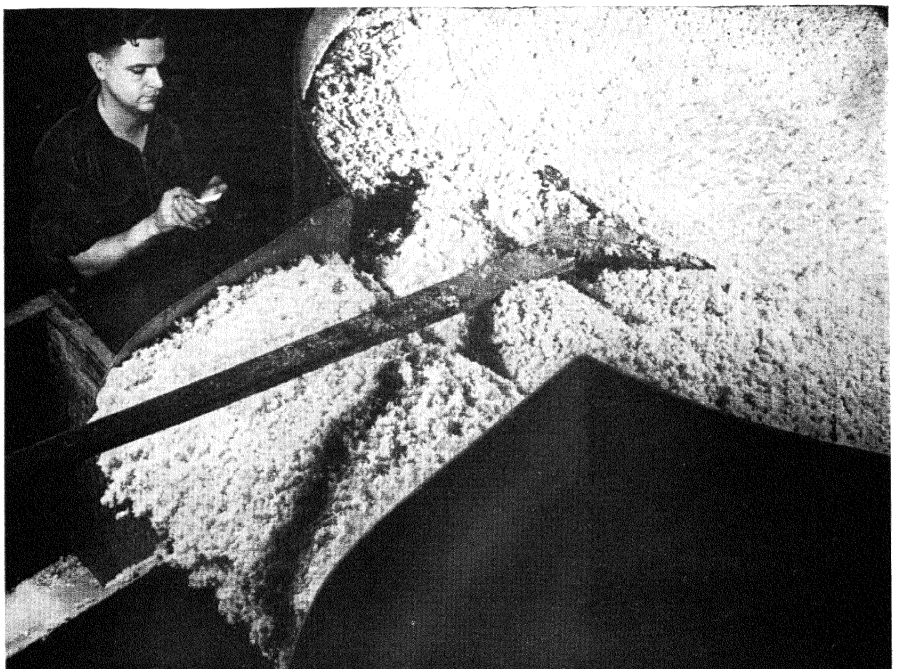

FIG. 42.—Hycar Elastomer being Washed before being Worked into Sheets.

[*To face page* 213.

Buna must be carefully selected. For Perbunan mixes toluene is the preferred solvent.

Another source of trouble is the right concentration and viscosity of Buna solutions. But once the solutions have been properly prepared, the actual dipping process is simpler than with natural rubber solutions. For one thing it is much easier to obtain a Buna solution free of bubbles. One hour after stirring, the latter is usually perfectly free from bubbles, and the dipping process can be interrupted at will to add fresh solution. In addition the dipping and drying operations can be effected more rapidly. However, Buna solutions are generally less concentrated, thus requiring more dippings to obtain the same thickness in the finished goods.

When the goods are finished and have to be rolled, the lower adhesive power of Buna also causes trouble.

No changes have to be introduced in the vulcanization process, generally hot-air curing, which, if anything, is simpler than with natural rubber, because the vulcanization plateau of Perbunan is wider and a slight deviation from the heating limits in either direction is not nearly so unfavourable in its effect on the product.

The cured goods are removed from the moulds in the usual manner, but here again the structure of Perbunan becomes apparent, and removal is more difficult.

Perbunan-Extra. Perbunan-Extra has even better oil- and solvent-resisting properties than the ordinary Perbunan. The larger proportion of acrylic acid nitrile present is thought to lead to a lesser degree of cyclization in the molecule. As a result, it is more easily rendered thermoplastic, and is generally handled with less difficulty than Perbunan. In all other respects its behaviour follows very closely that of the parent material.

Moll, Howlett and Buckley have shown that for Buna-N materials resistance to swelling in solvents is greater as the proportion of acrylic nitrile increases. On the other hand the cold crack temperature becomes worse, i.e. the temperature of cracking becomes higher.

Hycar. Hycar is the trade name for a group of synthetic rubbers which have been available since 1939, produced by the Hydrocarbon Chemical and Rubber Co., which is jointly owned by the Phillips Petroleum Co., and the B.F. Goodrich Co. The latter company manufactures articles from these synthetic rubbers which are sold under the name of Ameripol. The leading type is Hycar O.R., a synthetic rubber based on butadiene and acrylic nitrile. It contains about 25 per cent. of the latter. It is an amber, crêpe-like material whose specific gravity is 1·00. It has a pleasant odour. It can be

blended with rubber and reclaimed rubber in all proportions, with neoprene, Thiokol, polyvinylchloride, etc.

More recently Hycar T.T. has become available. This is actually similar to Buna-S and is one of the Government-sponsored synthetic rubbers. It has already been considered in the discussion of butadiene-styrene elastomers.

While Hycar O.R. is the oil-resistant type, there is another type known as Hycar O.S. which is soluble in oil. In all other respects they are very similar. They can be blended together if desired. It has been found that they can be mixed with polyvinyl chloride, with beneficial results all round.

Almost everything that has been said about Perbunan can be applied equally well to Hycar O.R. Oil resistance of the latter is claimed to be superior. Oil resistance, heat resistance, and the resistance to oxygen, are the outstanding advantages.

The same difficulties are encountered in breaking it down and compounding, and similar methods are adopted to overcome these difficulties. For example, only small batches can be handled on the mixing mill.

One feature that invites comment is the importance which is assigned to its use for tyres. Apparently Ameripol tyres, based on Hycar, have been very sympathetically received by the public in the United States in spite of the higher cost. It is interesting to note, according to Semon,[11] that these tyres have less tendency to skid than the natural rubber ones.

TABLE 93. EFFECT OF SOFT COAL TAR ON HYCAR O.R. COMPOUND [5]

	Parts by weight.		
Hycar O.R.	100	100	100
Zinc oxide	5	5	5
Phenyl-β-naphthylamine	1	1	1
Benzthiazyl disulphide	1	1·25	1·5
Sulphur	1	1·25	1·5
Channel black	50	50	50
Stearic acid	1	1	1
Soft coal tar	5	25	50
Vulcanized for 20 minutes at 310° F.			
T_B lb. in.^{2}	3,500	3,200	2,400
E_B per cent.	450	600	675
Shore Hardness	74	70	66
Percentage volume change immersed in			
Hexane 48 hours at 25° C.	+3	0	0
Circo light oil 48 hours at 100° C.	+6·1	0	−8·4

The difficulty of compounding Hycar O.R. is reflected in the use of larger proportions of plasticizers. Similar types of plasticizers and softeners as these used with Perbunan are equally effective. Thus esters, ethers, and ketones used as plasticizers for lacquers and plastics, such as dibutyl phthalate, tricresyl phosphate, etc., are very effective with Hycar O.R. They yield snappy resilient materials. The usual run of softeners used with natural rubber, e.g. pine tar and coumarone resins, etc., are also extremely useful. Suitably selected plasticizers can, however, be added in large quantities without unduly affecting vital properties.

The behaviour of filling materials appears to follow more closely the behaviour in natural rubber than in Perbunan. Optimum tensile strength is obtained by the use of channel black in loadings comparable

Tensile strength (maximum)	2840	2950	2850
Elongation at break	420	315	260
Shore hardness	65	70	75
Tear resistance	1165	475	400
Abrasion resistance	175	17	4
Percentage rebound (*a*)	53	43	17
Heat build-up, average temp. ° F., (*b*), (*c*)	130°	171°	161°
Percentage compression	4·3	2·8	1·1
Percentage set	4·0	2·4	2·0
Shrinkage	4·8	6·7	3·8
Electrical resistance (*e*)	23×10^3	3×10^8	4×10^8

TABLE 95. COMPOUNDS EMPLOYED [3]

	Pure gum		Reinforcing black		Semi-reinforcing back	
	Rubber	Perbunan or Hycar O.R.	Rubber	Perbunan or Hycar O.R.	Rubber	Perbunan or Hycar O.R.
Elastic	100	100	100	100	100	100
Zinc oxide	5	5	5	5	5	5
Stearic acid	1	1	3·5	1·5	2	1·5
Altax	1	1	1	1·25	0·65	1·25
Pine tar	—	—	3	3	—	1·5
Paraflux	—	—	—	3	—	1·5
Sulphur	2	2	2·85	2	2·85	2
Dixie 20/Kosmobile	—	—	—	—	60	60
Kosmobile 77/ Dixiedensed 77	—	—	50	50	—	—

Sulphur is necessary for vulcanization, being used in rather lower quantities than in rubber. The usual run of accelerators are employed performing the same function as in natural rubber, slightly higher amounts being needed. Thiuram accelerators giving off free sulphur are likewise employed for preparing heat-resisting products. As with rubber careful control is necessary in order to avoid scorching.

TABLE 96. REINFORCING BLACK IN PERBUNAN AND HYCAR [3]

	Smoked sheet	Buna-N	
		Perbunan	Hycar O.R.
Plasticity (mm.)	245	454	467
Extrusion (seconds)	2·2	11·3	24·2
Modulus at 300%	1450	2160	2300
Tensile strength	4075	3600	4030
Elongation	565	415	450
Hardness	64	70	75
Tear	1360	328	381
Rebound	48	40	18
Abrasion (*a*)	202	19	4
Heat build-up ° F. (*b*)	137°	181°	183°
Shrinkage (*d*)	2·9	7·7	6·8
Electrical resistance (*e*)	$7·5 \times 10^6$	21×10^7	11×10^7

TABLE 97. COMPARISON OF RUBBER AND BUNA-N [3]

(Rubber properties rated at 100 in each case)

	Pure gum			Reinforcing black			Semi-reinforcing black		
	Smoked sheet	Perbunan	Hycar O.R.	Smoked sheet	Perbunan	Hycar O.R.	Smoked sheet	Perbunan	Hycar O.R.
Plasticity	100	39	40	100	34	60	100	34	36
Extension	100	—	—	100	19	9	100	11	5
Modulus	100	—	—	100	114	159	100	139	180
Tensile	100	25	40	100	88	99	100	104	100
Elongation	100	67	73	100	74	80	100	75	62
Hardness	100	129	129	100	109	117	100	108	115
Tear	100	30	35	100	24	28	100	41	34
Abrasion	100	—	—	100	1055	5950	100	1030	4380
Rebound	100	81	37	100	83	38	100	81	32
Heat build-up %	—	—	—	—	44	46	—	41	31

Mercapto benzthiazole accelerators are found to be quite effective. Dibenzthiazyl disulphide is as useful for Hycar O.R. as it is for rubber stocks, there being little fear of scorching during processing. Zinc oxide and litharge has been found to be an excellent accelerator for Hycar O.R. mixes. Five parts of zinc oxides and 10 parts litharge are normally used.

TABLE 98. HYCAR TYRE TREAD MIX

	Parts by weight.	
Hycar O.R.	100	100
Stearic acid	0·5	0·5
Plasticizer	25	25
Benzthiazyl disulphide	1·25	1·25
Channel black	55	55
Zinc oxide	5	5
Anti-oxidant	1	1
Sulphur	2·5	3
Cure at 45 lb./in.²	30 minutes	20 minutes
T_B lb. in.²	2900	2900
E_B per cent.	577	610

Since Hycar O.R. is supplied with 2 per cent. of phenyl-β-naphthylamine, normally there is no necessity for further additions of anti-oxidants. Thus in a tread type of mixing the sulphur content would be 1·25, and a typical accelerator addition 1·25 parts benzthiazyl disulphide.

The outstanding property of Hycar O.R. is the excellent resistance to a wide variety of solvents. In this respect it is superior to Perbunan, especially as regards the newer types of aviation petrol. It is very little affected by aliphatic solvents, oils, by alcohols, water, etc. The performance is greatly dependent upon compounding. The behaviour of various compounds has been described by Garvey, Juve, and Sauser.[6]

TABLE 99. RECIPES OF COMPOUNDS STUDIED [6]

Compound	A Tread	B Low set	C Gasoline hose tube	D Heat resistant	E Soft stock	F Clay loading	G Soling	H Pure Gum	I Fast-curing
Hycar O.R.	100·0	100 0	100·0	100·0	100·0	100·0	100·0	100·0	100·0
Zinc oxide	5·0	5·0	5·0	5·0	5·0	5·0	5·0	5·0	5·0
Age resister	—	—	—	5·0	—	—	—	—	—
Mercaptobenzthiazole	—	—	—	3·0	—	—	—	—	1·5
Benzthiazyl disulphide	1·25	1·0	1·0	—	1·5	1·5	1·25	1·0	—
Tetramethyl thiuram disulphide	—	—	—	3·0	—	—	—	—	—
Di-ortho tolyl guanidine	—	—	—	—	—	—	—	—	0·25
Crude lauric acid	1·5	1·5	1·5	1·5	—	—	—	1 0	—
Sulphur	1·25	2·0	1·0	—	1·5	1·5	1·5	1·0	1·25
Channel black	50·0	—	—	50·0	—	—	75·0	—	50·0
Gastex	—	50·0	100·0	—	—	—	50·0	—	—
P. 33 black	—	—	—	—	25·0	—	—	—	—
Clay	—	—	—	—	—	75·0	—	—	—
Soft coal tar	3·5	—	—	10·0	—	—	25·0	—	20·0
Dibutyl phthalate	—	20·0	20·0	—	50·0	20·0	—	—	—

Time of cure, 45 minutes at 155° C.

They are affected by aromatic hydrocarbons such as benzene, by many chlorinated solvents (except carbon tetrachloride), by acetone and other ketones.

The tensile strengths obtainable are comparable with those obtained in rubber compounds, while elongations are similarly dependent upon the amount of fillers.

Hycar O.R. products have good resistance to heat, especially when compounded specially for this purpose. They can be used at 300° F. and in a few limited applications, even at 400° F. They tend to become harder and tougher under such conditions, in contrast to the behaviour of rubber. Their behaviour at low temperature is inferior to that of rubber compounds as they tend to become leathery

at — 10° C. Elastic properties may be maintained by the use of plasticizers such as dibutyl phthalate, in which case a temperature of — 35° C. can be reached before becoming leathery. The crack point is said to be as low as — 50° F.

The resistance to ageing is also superior to that of rubber.

TABLE 100. EFFECT OF SOLVENTS ON HYCAR O.R.[6]

Solvent	Percentage volume change of compound								
	A	B	C	D	E	F	G	H	I
	48-hour immersion at room temperature								
Hexane	1·5	0·0	0·0	3·0	—6·1	0·0	0·0	4·5	0·0
Benzene	127·4	104·8	86·1	102·4	114·7	90·7	76·3	209·6	135·4
Carbon tetrachloride	36·8	26·0	23·4	36·8	11·7	20·8	25·1	64·3	36·8
Acetone	176·0	151·5	144·9	234·5	191·7	147·4	105·1	345·1	224·6
X-70 gasoline	4·5	1·5	3·0	4·5	—9·2	3·3	2·2	9·2	3·7
95% ethanol	9·2	3·0	3·0	7·6	—10·0	3·0	3·0	14·9	7·6
Distilled water	0·0	0·0	3·0	1·5	0·75	0·0	0·75	0·0	1·5
S.A.E. 20-W oil	0·0	—1·5	0·0	0·75	—6·1	—0·75	0·0	0·0	0·0
95% kerosene +5% benzene	0·75	0·0	0·0	1·5	—4·5	0·0	0·0	2·2	0·0
	48-hour immersion at 100° C.								
Circo X light oil 95% kerosene +5% benzene	9·2	0·0	0·0	5·3	—19·1	0·0	4·5	14·9	4·5
	11·6	0·0	0·0	6·1	—17·4	18·2	6·1	0·0	4·5

In general, the applications are very similar to those of Perbunan. It is widely employed for gaskets, packings, petrol tube, and generally where petrol, oil, or heat conditions are likely to be encountered. Hycar O.R. compositions may be bonded to metals by the technique described for Perbunan using chlorinated rubber as adhesive.

Garvey and Sarbach [5] have described how ebonite can be made from Hycar O.R.—15. They suggested the following compositions:

TABLE 101. COMPOUND SUITABLE FOR ACCUMULATOR CASE.

Hycar O.R.	100	—
Sulphur	40	For vulcanization
Clay	50	For processing, moulding and acid resistance
Cumar	10	To confer tack and smoothness
Dioctyl phthalate	10	
Dibutyl metacresol	6	

TABLE 102. COMPOUND FOR HIGH-QUALITY SMALL MOULDINGS.

Hycar O.R.	100	—
Sulphur	40	—
Zimate	2	Accelerator
Iron oxide	75	For processing, high tensile and moulding
Oil	15	To confer tack and smoothness
Tricresyl phosphate	5	
Rosin	5	

Chemigum. Chemigum is the name for a series of elastomers which are derived from petroleum, and are based on butadiene. According to Dinsmore [2] it is a butadiene copolymer of a modified Buna type. While butadiene is the main constituent, there are various synthetic resins, other than styrene and acrylic nitrile which have been successfully developed as copolymer. It is an amber-coloured crêpe-like material. It has an aromatic odour and its specific gravity is 1·06.

Chemigum is made in three grades of hardnesses. It physically resembles brown crêpe, is very tough, and has a distinctive odour. It processes more easily than other synthetic rubbers, although the addition of fillers, plasticizers, etc., is very much in line with those used normally. The most effective plasticizer is pine tar. On the other hand Chemigum will not take up stearic acid. It is best worked on a cold mill and the mill capacity of a 40 per cent. black master batch is two-thirds that of a rubber mix. It can be handled without difficulty in the Banbury mixer. The important advantages are the increased tensile strength, the resistance to ageing abrasion, and to oils and solvents generally. It is also much more resistant to oxygen than rubber. Although very soft and plastic when hot, yet it lacks tackiness. Natural rubber can be blended with this material in almost any proportions, this being done most readily by combining black master batches. Addition of 15 per cent. of crude rubber produces good surface tackiness without having any serious effect on such properties as oil resistance. It is not quite as resilient as rubber. Thus comparable mixes showed Chemigum to have a rebound resilience of 53 per cent. as against 66 per cent. for rubber. Another grade of Chemigum IV is the Government Buna-S material made by the Goodyear Company.

It is much less soluble than rubber in solvents, notably in petrol. The Goodyear Rubber Company, which makes Chemigum, is the sole user, and the first uses have included petrol hose, hydraulic brake-sealing rings, gaskets, and similar types of products which come in contact with oil. Production of tyres has also commenced.

Copolymerization Products. Although no information has been forthcoming about the specific composition of these materials, a lead can be obtained from some of the patents connected with their production.

For example, in one recent patent [15] it was stated that improved rubber-like materials were obtained by the copolymerization of 1 : 3-diolefines such as the butadienes, $CH_2 : CR.CR : CH_2$, and acrylic acid esters of the form $CH_2 : CR.COOR^1$, where R is a hydrogen or an alkyl group preferably but may be aralkyl or aryl, while R^1 is a saturated aliphatic hydrocarbon radical of four or more carbon atoms, with a branched chain, or is an unsaturated aliphatic or araliphatic radical. Polymerization was effected preferably in emulsion at a temperature of about 50° C. in 100–300 hours. Diolefines that may be used include 1 : 3-butadiene, methyl butadiene, and dimethylbutadiene. Esters suitable include numerous acrylates such as isobutyl-secondary butyl-, isoamyl-, 2-methyl and 3-methyl amyl-, 2-2-dimethyl butyl-, and various heptyl esters.

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CHAPTER 13

ELASTOMERS—NEOPRENE

Introduction. The first commercial synthetic rubber was neoprene. This made its debut in the United States in 1931, having been developed by the Du Pont de Nemours concern. Neoprene is a polymer of 2,-chloro-1 : 3-butadiene.

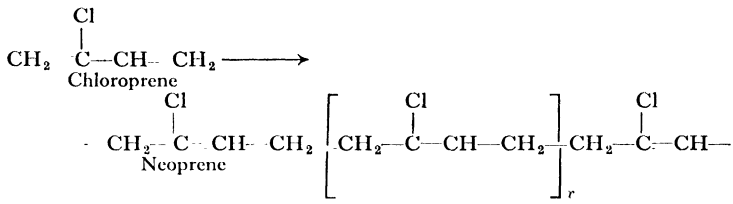

FIG. 43.

The leading figures in the development of neoprene were Nieuwland and Carothers. This fact shows how close is the relationship between plastics and synthetic rubbers, for Carothers was also the genius behind the production of nylon, that amazing series of synthetic resins which have already attained great importance. This mutual interest in synthetic rubbers and synthetic resins is evident in all manufacturing quarters during recent years.

The story of its discovery started in 1925. Du Pont's were seeking a synthetic rubber which would have properties superior to those of rubber. It was already quite clear that natural rubber could no longer satisfy many industrial requirements and they thought that there would be a market for a more expensive material for special purposes. They could not find a starting point. In 1925 they learned that Nieuwland, of Notre Dame University, had been able to produce monovinylacetylene by passing acetylene through aqueous cuprous chloride. This was commercially practicable.

Chloroprene rubber was discovered, as the outcome of the work on the polymerization of acetylene carried out by Nieuwland.[17] Nieuwland discovered that on passing acetylene into a concentrated solution of cuprous chloride, made with the aid of ammonium chloride or salts of amines, and allowing the reaction mixture to stand, liquid polymers of acetylene could be obtained. Of these the trimer, divinylacetylene ($CH_2 : CH.C \vdots C.CH : CH_2$) could most readily be obtained in good yield. This material could readily be polymerized to a synthetic

resin.[16] When completely polymerized it gave a clear, colourless resin, distinguished by the possession of a noteworthy resistance to chemical attack and insolubility in all the solvents which were examined. An intermediate polymeric product from divinylacetylene is now on the market under the designation S.D.O. (synthetic drying oil). When applied in films and exposure to the air, it undergoes conversion to the final polymer, which is very resistant to chemical and solvent attack.

Under appropriate conditions of reaction, acetylene treated with cuprous and ammonium chlorides gives monovinylacetylene which is a dimer of acetylene. Vinylacetylene is a liquid which boils at 5° C. It polymerizes readily to form first a viscous oil and finally a hard, resinous solid.

Preparation of Chloroprene. In the capable hands of Carothers [1] and his team of workers, over a period of five years, this yielded the desired material. First they were able to prepare chloroprene, i.e. 2-chloro-1 : 3-butadiene. Chloroprene is a colourless liquid having a characteristic odour not unlike ethyl bromide. It boils at 59·4° C. and has a density of 0·958. This was obtained by treating monovinylacetylene with hydrogen chloride in the presence of cuprous chloride. By analogy with isoprene they called this "chloroprene". The product polymerized spontaneously to yield material like vulcanized rubber.

It was evident that here was their synthetic rubber. But the process of polymerization had to be brought under control. It was found that by interrupting the polymerization a soft resilient rubbery polymer was obtained which resembled natural rubber in many ways. This was polychloroprene, resembling vulcanized rubber.

When kept in the absence of light at room temperature, chloroprene becomes completely polymerized in ten days to a transparent, resilient, elastic mass resembling soft vulcanized rubber. The product has a tensile strength of about 140 kg. per square centimetre and an ultimate elongation of about 800 per cent. Like vulcanized rubber, it cannot be worked on a mill to a smooth sheet, being non-plastic; it swells strongly but does not dissolve in rubber swelling agents. Completely polymerized chloroprene is known as μ-polychloroprene. If polymerization is carried only part of the way, a plastic material is obtained which is analogous to milled, unvulcanized rubber, and which has been designated α-polychloroprene. The α-polymer can be manipulated on a mill much like raw rubber, various materials being incorporated with it if desired. It can then be transformed into the μ-polymer by heating or otherwise completing polymerization process. The further polymerization of the intermediate, or α-polymer, to the

fully polymerized product, the μ-polymer, is analogous to the transformation of milled raw rubber (plastic and soluble) to vulcanized rubber (elastic and insoluble).

It is a most interesting fact from the structural angle, as Sebrell and Dinsmore [19] have shown, that neoprene is the only elastomer which gives an X-ray diagram when stretched, just as rubber does.

When heated it proceeds to the insoluble condition. At ordinary temperatures the process is slow, but at 130° C. the change occurs inside five minutes. The change is accelerated by a number of materials, among them magnesia, zinc oxide, zinc chloride, ferric chloride, and primary aromatic amines such as aniline, benzidine, etc.

Obviously it was a long and tedious process to work out all the conditions necessary for commercial production. In due course this was successfully achieved, and in 1931 neoprene appeared on the market.

Subsequent Developments. In the early days there were many disadvantages. The material had a strong pungent odour, and poor colour, while the stabilization was not too good. These defects were thought to be due to the presence of small amounts of oily low polymers. With the passing of time, these faults have been almost completely eliminated. New methods of production have been introduced.

For many years most neoprene was prepared in the massive condition, and while improvements were made, it was not found possible to eliminate the disadvantages.

The most profound changes have been brought about by utilizing the method of emulsion polymerization. This avoided the production of the varied by-products which cause the obnoxious odour and conferred the poor colour. The change in procedure was in line with developments in other fields of synthetic polymers where precisely similar improvements were being obtained by the same technique. The surprising feature about this is that the general rubbery product and the processing behaviour differed considerably according to the method of polymerization used. This has given rise to the different types of neoprene. Thus the leading type for many years was Neoprene E. To this has been added Neoprene G, the emulsion polymer, which has little odour, and can be successfully used to make light-coloured products. A still better product is Neoprene GN. There are a number of less important variants of these types.

Polymerization in emulsion form has resulted in the formation of a neoprene latex. The solid neoprene is obtained from this by coagulation in precisely the same manner as rubber is obtained from latex. As a corollary this neoprene latex is used as such. Films may be

FIG. 44.—Neoprene after being Polymerized.

[*To face page* 224.

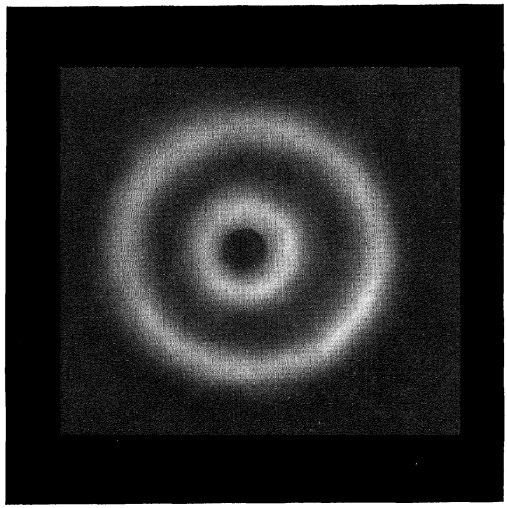

FIG. 45.—X-ray Photograph of Neoprene (Sebrell and Dinsmore).

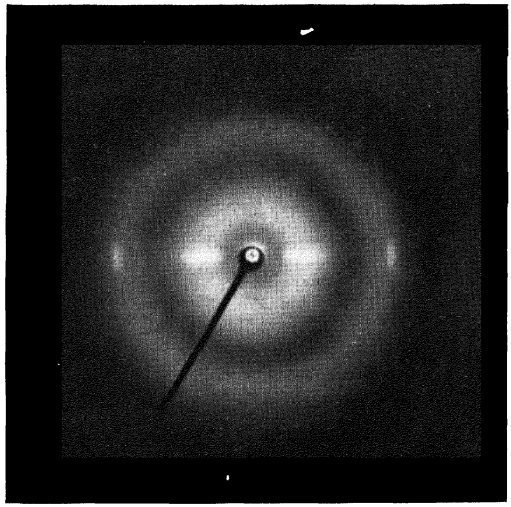

FIG. 46.—X-Ray Photograph of Stretched Neoprene (Sebrell and Dinsmore).

[*To face page* 225.

made and vulcanized. Impregnation, coating, dipping, and other similar processes may be carried out.

TABLE 103. TYPICAL NEOPRENE [3] LATEX (Type 57)

	Parts by weight.
Neoprene	100
Lithopone	10
Zinc oxide	5
Sulphur	2
Phenyl β-naphthylamine	2
Sodium dibutyldithiocarbamate	0·8

(All fillers were dispersed)

FILM CHARACTERISTICS

Dried and cured for 30 minutes at 141° C.	
T_B lb./in²	4500
E_B %	900
M_{600}	600
Aged 14 days in Bomb under 300 lbs. pressure of oxygen	
T_B lb./in²	4950

This is the synthetic rubber which now has a history of more than ten years behind it and whose merits may be based on solid experience. Its career has been one of steady but not spectacular progress. It was never set up as a competitor against rubber but merely for use where rubber could not give satisfaction. Production has been confined to satisfy the steadily growing commercial demand. Recently under the pressure of current events there has been an enormous expansion in production, an output of 100,000 tons is said to be the objective.

There have not been many types of neoprene. The methods of production have been responsible for slight differences in behaviour. As industrial demands arose for these varied types they were brought on to the market to meet the definite need. But fundamentally the material has remained the same. It has always been a straight chloroprene polymer. Only recently has there been a departure from these principles. The latest introductions to the range are based on butadiene copolymers with chloroprene.

Neoprene is now quite generally accepted by the rubber industry, and is regarded as a standard material. There has been great consumer interest, led by the motor industry. Its present status as a standard material in rubber technology is a tribute to its excellent properties.

Neoprene scores over almost every other synthetic rubber inasmuch as its handling presents no difficulties. With minor reservations it

can be handled just in the same way as rubber. This is, of course, an invaluable asset.

Neoprene has a very high chlorine content, nearly 40 per cent. As a result it is virtually non-inflammable and does not support combustion. This accounts for many of its applications, notably in the cable industry.

The property about which most has been heard is the resistance to oils and solvents. It is impervious to vegetable oils, mineral oils, greases, etc., being merely slightly swollen by them, without any marked loss of strength. It is almost unaffected by paraffin, hydrocarbons, and many other solvents. It is swelled and dissolved by chlorinated hydrocarbons, and by aromatic hydrocarbons.

There is no questioning its superiority over rubber where these agents are concerned. It is incomparably better, and even where neoprene is attacked to some extent, it still retains the greater part of its physical properties.

Neoprene compositions have excellent resistance to chemical corrosion, particularly against strong acids. Thus it is widely used for lining tanks which contain sulphuric acid, hydrochloric acid, acetic acid, etc.

Behaviour of Neoprene E. Neoprene E can be handled in much the same manner as rubber. Standard rubber manufacturing plant is eminently suitable. It may be milled and mixed on ordinary open rolls, or in internal mixers such as the Banbury.

A very important feature is that the full-sized batch as is used for rubber may be handled. In these respects neoprene is far in advance of other synthetic elastic materials, e.g. of the butadiene class, which require a modified technique. Although the raw material is well stabilized, nevertheless it tends to vulcanize spontaneously when heated, and consequently it must be stored under suitable conditions. In normal factory conditions raw neoprene may be stored for periods of at least twelve months. On the other hand, compounded unvulcanized material has a tendency to scorch, and this must be carefully watched.

Neoprene does not require to be broken down in the same manner as rubber. All that is necessary is to reduce it to a thermoplastic condition when compounding ingredients may be added.

Neoprene is quite different from rubber, and consequently the formulation of its compounds are unlike those of rubber. The essential ingredients in processing neoprene are magnesia, wood rosin, and zinc oxide. Zinc oxide is the vulcanizing agent accelerating the setting up processes caused by heat. It corresponds to the use of sulphur in ordinary rubber compounds, and is used in the proportion

of 5 parts to 100 parts of neoprene. Ten parts of magnesia are added, and exert a general stabilizing influence tending also to retard the scorching effect promoted by the use of zinc oxide. Ten parts of wood rosin has an all-round beneficial effect on the physical properties of the final product.

The mechanism of the action of these materials is not yet fully understood. In the case of the wood rosin the important factor is undoubtedly the content of abietic acid. Magnesia not only neutralizes any hydrogen chloride that may be formed under the influence of sunlight or oxidizing conditions, but is also found to increase the tensile strength of the product. Litharge can be used where water resistance makes the presence of magnesia undesirable.

The milling of neoprene is carried out at medium temperatures; neither excessively hot nor unusually cold rolls being desirable.

The order of adding ingredients is:

1. Factice (if used)
2. Magnesia
3. Portion of Softeners and Resins
4. Antioxidant
5. Sulphur (if used)
6. Fillers
7. Remainder of Softeners.

Softeners. The use of plasticizers and softeners is of considerable importance in the manipulation of neoprenes. Vegetable oils such as linseed oil, cotton-seed oil, rape oil, castor oil, and mineral oils are also quite generally employed. The various rubber substitutes are also of great assistance in processing. Apart from these the standard range of plasticizers such as tricresyl phosphate, triphenyl phosphate, chlorinated naphthalene, chlorinated paraffin, etc., are also widely used.

Rubber substitutes, notably dark substitute, play a very important part in the compounding of neoprene. Considerable loadings may be used, and greatly assist extrusion and calendering processes, while giving excellent vulcanized materials. Pine tar is almost interchangeable with wood rosin; the other standard rubber softeners are also used to some extent as and where desirable. Coumarone resins have an excellent capacity for conferring tackiness on mixes. Lubricating materials chiefly employed are paraffin wax and stearic acid.

Filling Materials. Large quantities of fillers are incorporated into neoprene compositions. They serve the dual purpose of lowering the cost of the products, and also increase the scope of their application. All the materials used in rubber compounding are equally useful in this case.

The most important fillers are in the carbon black class. The hard channel blacks do not exert anything like the same reinforcing effect as in rubber, and since their use introduces processing difficulties they are not extensively employed alone. On the other hand, the softer blacks give a very desirable improvement in practically every property. The hardness, abrasion, and tensile strength are considerably enhanced. In the normal way the largest possible amount of black filler is incorporated purely from a cost angle.

TABLE 104. EFFECT OF FILLING MATERIALS ON NEOPRENE E MIXES [8]

(Cured: 60 mins. at 141° C.)

Parts by weight.

Neoprene type E	100	100	100	100	100	100	100	100	100	100
Light calcined magnesia	10	10	10	10	10	10	10	10	10	10
Wood rosin	5	5	5	5	5	5	5	5	5	5
Cotton-seed oil	5	5	5	5	5	5	5	5	5	5
Mineral oil	10	10	10	10	10	10	10	10	10	10
Sulphur	1	1	1	1	1	1	1	1	1	1
Zinc oxide	10	10	10	10	10	10	10	10	10	10
Thermatomic black	—	115	170	230	—	—	—	—	—	—
China clay	—	—	—	—	115	170	230	—	—	—
Whiting	—	—	—	—	—	—	—	115	170	230
T_B (kgs./cm. sq.)	178	125	107	98	74	67	64	66	45	—
E_B %	930	350	250	180	500	193	77	693	600	—
Permanent set %	1	2	3	3	5	6	—	1	3	—
H	31	67	80	93	69	80	91	62	72	83
% swelling in Diesel oil at 70° C.	61	42	31	30	42	38	32	49	41	—

In fact, the successful use of neoprene depends upon the amount of filler added. So far as black fillers are concerned, it has been found that:

(*a*) For a given degree of oil resistance, as large a volume as possible of a soft black (thermatomic black) should be employed for all but the most severe conditions.

(*b*) When service conditions call for a soft stock having a fairly high tensile strength, slightly harder blacks, such as P.33, should be used.

(*c*) When hard stocks with high tensile strength are required, a mixture of soft black with channel black should be used. For heat-resisting products, thermatomic black is far and away the best.

Among the other common filling materials china clay and zinc oxide show some reinforcing action. Clay however yields rather dead pro-

ducts which have high permanent set. Barytes gives slight reinforcement and is perhaps the best filler for light-coloured products.

Vulcanization of Neoprene E. Sulphur is not essential for the vulcanization of neoprene, this function being performed by zinc oxide. It can, however, have very beneficial results. There is evidence that advantageous results are achieved by the use of sulphur in all cases except where heat resistance is the important feature. It has a profound accelerating effect on the vulcanization of neoprene. Singularly enough, the use of above 3 per cent. of sulphur retards any

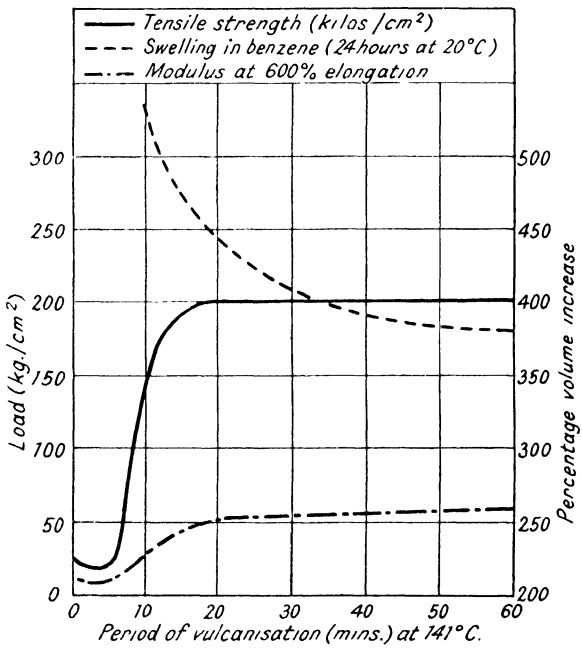

FIG. 47.—Vulcanizing Behaviour of Neoprene.[14]

tendency of a neoprene mix to set up during storage. The mechanism of the action of sulphur is not understood, although the inability to extract any of it indicates that there has been some chemical combination. The time for vulcanization of neoprene E materials is 60 minutes at 141° C. or the equivalent.

There is a pronounced plateau effect in the vulcanization of neoprene so that the material is not particularly sensitive to over-vulcanization.

There has not been much progress in effecting acceleration of the

vulcanization of neoprene. A number of materials have been found which profoundly stimulate the setting up in a manner comparable with the use of fast accelerators in rubber. Addition of certain types of phenols are significant in this respect. Among these are resorcinol, catechol, and pyrogallol. The use of 0·25 part of catechol to 100 of neoprene profoundly accelerates vulcanization.[14] The effects are shown in the table. Other materials which appear to be capable of exerting

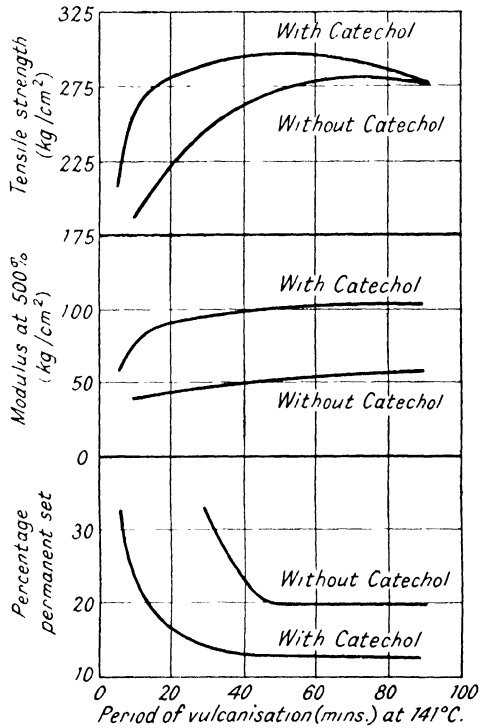

FIG. 48.—Effect of Catechol on Neoprene.[14]

a similar accelerating effect include hexamethlyenetetramine, triethanolamine, etc.

Behaviour of Neoprene G. The foregoing comments have applied to materials based on neoprene E. In recent years neoprene has been made by emulsion polymerization and the material obtained differs in many respects. In particular it is practically odourless. The raw material is much more rubber-like than neoprene E. This

is neoprene G, and it vulcanizes more rapidly, it has greater tensile strength, is more resilient, and shows superior abrasion resistance.

There are notable differences in compounding it, and in processing. In this instance, for example, wood resin performs no useful function, and is not employed. Rather large quantities of magnesia and zinc oxide are used, the latter having a more pronounced vulcanizing effect. Materials based on neoprene G are tackier than those made with neoprene E. They also retain this tack for a much longer period of time. It is rather strange to find that materials of the guanidine class, notably diorthotolyl guanidine act as plasticizers in this case. Neoprene G compounds in the normal way require only 30 minutes at 141° C. for vulcanization.

TABLE 105

	Type E	Type G
Neoprene	100	100
Light calcined magnesia	10	7
Wood rosin	5	—
Zinc oxide	5	5

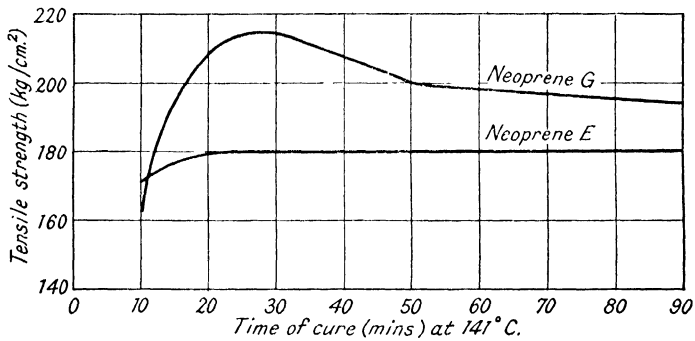

FIG. 49.—Comparison of Vulcanizing Behaviour of Neoprene E and Neoprene G.[8]

Other typical rubber accelerators in this instance act as retarders of vulcanization tending to prevent scorching during processing. A typical example is benzthiazyl disulphide when used to the extent of 1 per cent. This action is specific to neoprene G.

Sulphur is not employed since it exerts no advantageous effect. Compounding of neoprene G with filling materials, plasticizers, and so on, follows the practice with neoprene E. The products, while retaining all the oil-resisting qualities, have higher tensile strength, less permanent set, and better resilience.

According to Catton and Fraser,[2] it appears that neoprene compositions swell less when vulcanized at higher temperatures than at lower temperatures to an equivalent cure as judged by modulus.

The effect of fillers on neoprene G has been exhaustively studied by Catton and Fraser. The swelling of neoprene vulcanizates after immersion in solvents (particularly those derived from a petroleum base) is dependent only on the dilution of the neoprene by the compounding pigments, even though these pigments may be of the reinforcing type.

This is in sharp contrast to the behaviour of rubber compounds. In these, Scott,[18] Ishiguro,[11] and Naunton, Jones and Smith [15] have shown that the resistance to swelling of rubber vulcanizates in solvents is due to the dilution of the compound in the case of non-reinforcing

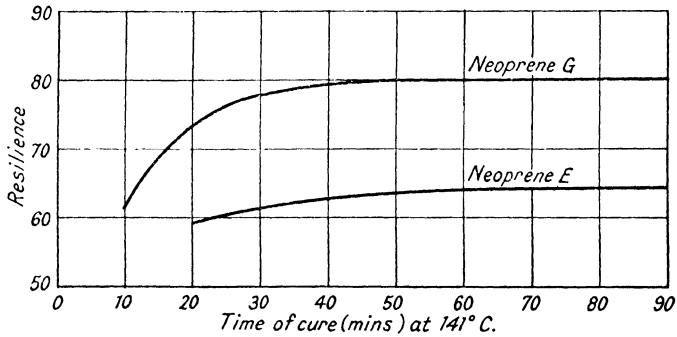

FIG. 50.—Comparative Resilience of Neoprene E and Neoprene G.[8]

pigments, whereas in the case of reinforcing pigments the increased resistance to swelling is due in part to the increased modulus of the compound.

Recent trends have somewhat altered the order of popularity of the various types. So that at the present time Neoprene type GN, a general purpose type of neoprene, is being produced and used in much larger quantities than E and G or the speciality types. Neoprene type GN should be used unless extraordinary service conditions dictate the selection of a type of neoprene especially developed for some particular property.

Processing Neoprene. In general the processing of neoprene compositions subsequent to mixing presents no unusual difficulties. They may be calendered and extruded in the same manner as rubber. Obviously the necessary temperature conditions must be evolved by

trial depending upon the nature of the stock. Heavily loaded stocks are easier to calender and are less sensitive to temperature variations. Neoprene is susceptible to comparatively small temperature variations, so that temperature control is of greater importance even than with rubber. Neoprene G stocks behave more like rubber than any of the other types. Normally neoprene can be calendered at lower temperatures than rubber. Frictioning and coating are also widely employed procedures with neoprene, and here, too, the behaviour of neoprene G approaches most closely to natural rubber.

For extrusion purposes dark substitute is a particularly useful ingredient, while small amounts of paraffin wax and stearic acid are used for lubricating purposes.

Solutions of Neoprene. Aromatic solvents such as toluene, benzene, etc., and chlorinated solvents such as trichlorethylene and carbon tetrachloride dissolve neoprene. Doughs made in this way are used for spreading on to fabrics. Solutions are used for dipping. The solutions are less viscous than corresponding rubber ones, and larger amounts of solid can therefore be taken up. The vulcanizing ingredients are added to neoprene on the mill and thin sheets are then dispersed in solvent in the usual solution mixers. No breakdown is required as with rubber.

Small amounts of diphenyl guanidine effectively inhibit any tendency for gelation of neoprene E solutions, but are ineffective with neoprene G. Vulcanization is generally carried out by hot air treatment.

The Bonding of Neoprene to Metals, etc. Neoprene can be very successfully bonded to metals, wood, and other surfaces, a fact of considerable commercial importance. Yerzley [20] has carried out extensive work on this subject, and has described methods for securing excellent adhesion by neoprene. Particularly interesting in this connection is the use of chlorinated rubber cements. By using this it is possible to bond neoprene to most metals and alloys, such as iron, steel, aluminium and its alloys, magnesium, zinc, lead, etc. The technique involves applying coats of chlorinated rubber solution on a perfectly clean surface which has been slightly roughened. Several coats are applied, and the calendered neoprene sheet is rolled on before the final coating is dry. The article is then vulcanized either in steam or in a press. The neoprene mix should be of medium hardness in order to achieve a satisfactory result. In many instances, particularly with magnesium alloys, it is helpful to add 10–15 per cent. of red lead to chlorinated rubber. This process of adhesion can be used to apply neoprene to glass and enamel surfaces.

It is interesting to observe how this technique employing chlorinated rubber is applicable to almost every elastomer.

Neoprene GN. According to Du Pont de Nemours the type of neoprene which will be in greatest supply in the future is likely to be neoprene GN. This is supplied as unplasticized material, and has to be plasticized as part of the compounding procedure. Vulcanized neoprene GN materials have all the leading properties of neoprene G, excelling it in some respects. For example, white stocks and coloured stocks may be prepared which maintain their colour even when exposed to sunlight.

Neoprene GN is best plasticized by the addition of diorthotolyl guanidine often referred to as DOTG. In the ordinary way 0·5 per cent. is required; greater additions result in the formation of soft materials.

Neoprene GN may be handled on mixing mills or internal mixers. It is rather more difficult to compound than other types, and the technique of handling must be carefully studied. In the usual way it should be handled on warm rolls (between 50° and 60° C.) with a fairly tight nip. In these circumstances it forms a sheet in a short time when the plasticizer should be added. It is preferable to add the plasticizer together with some filling material, such as whiting, in order to avoid milling difficulties. Thereafter magnesia is added, and then the main filling ingredients and softeners. Finally zinc oxide is added. In these circumstances mixing normally takes something like half an hour for satisfactory completion. The following mix only takes 30 minutes, at 141° C. for vulcanization:

Neoprene GN	100
DOTG	0·5
Stearic acid	0·25
Light calcined magnesia	4
Zinc oxide	1

No rosin is required for handling neoprene GN. It differs from neoprene G in requiring much less zinc oxide.

The following mixing illustrates the use of a semi-reinforcing carbon black:[8]

TABLE 106.

	Parts by weight
Neoprene type GN	100
Vulcafor DOTG	0·5–1 0
Stearic acid	0·25
Nonox S	2
Light calcined magnesia	4
S.B.I. carbon black	28·8
Zinc oxide	1

Cures at 141° C.	Modulus (Kgs/cm.²)		T_B (Kgs/cm.²)	E_B %	H
	300%	500%			
7½ mins.	23	60	144	1010	41
15 ,,	67	135	216	800	55
30 ,,	83	163	212	700	57
60 ,,	86	174	206	600	58

The usual range of additional compounding agents may be incorporated into neoprene GN stocks. The following details illustrate the formulation of mixes suitable for extrusion : [8]

TABLE 107.

Neoprene, type GN	100	100	100
G.810	—	2·5	—
Dark substitute	20	20	20
Light calcined magnesia	4	4	4
Thermatomic black	70	150	175
Mineral oil	10	10	10
Tricresyl phosphate	5	0	10
Neozone D	2	2	2
Nonox NSN	2	2	2
Vulcafor MBTS	0 5	0·5	1
Paraffin wax	0·5	0·5	1
Zinc oxide	5	5	5

PHYSICAL TEST RESULTS ON PRESS-CURED SHEETS

(30 mins. at 141° C.)

Hardness (° Shore)	50	65	75
Tensile strength (kg. per sq. cm.)	110	90	110
Percentage elongation at break	700	290	330
Resilience (% at 50° C.)	58	50	47
Diesel oil figure	39	33	27

Neoprene GN is considered to be particularly good from the point of view of application at low temperatures, and the following mix was found to give a crack point of — 52° C.

Neoprene GN	100
G.810 plasticizer	1·5
Light calcined magnesia	4
Stearic acid	1
Nonox S	2
Lampblack	100
Dibutyl phthalate	50
Zinc oxide	1

The behaviour of neoprene GN in general at low temperatures is favourably influenced by the use of plasticizers such as dibutyl phthalate or dibutyl sebacate.

Outstanding Properties of Neoprene Compounds. Properly

compounded neoprene yields materials having physical properties which are in line with comparable rubber products. They are quite as extensible and as strong. Under ordinary conditions the abrasion resistance is better than rubber; but where there is contact with oils or greases neoprene is incomparably superior. This also applies to the other physical properties, for rubber rapidly loses all its resistance whereas neoprene is little affected.

Where special conditions have to be encountered, it is fairly obvious

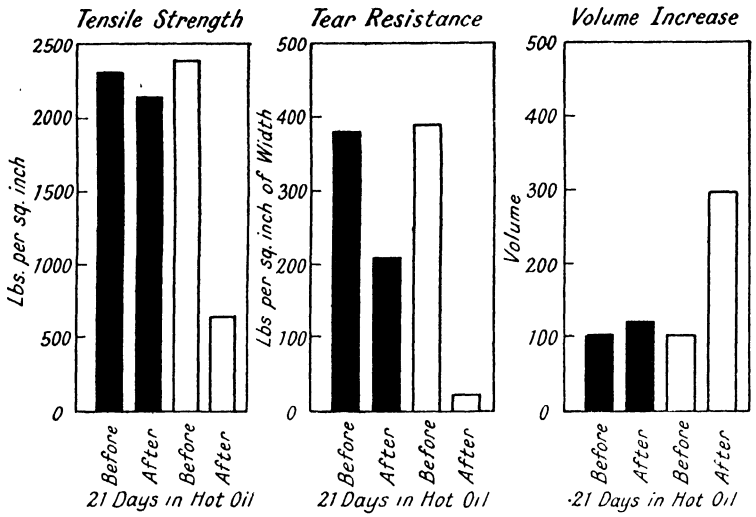

FIG. 51.—Effect of 21 Days' Immersion in Lubricating Oil at 100° C. on Physical Properties of Neoprene (Black Column) and Rubber.[8]

that modifications in the composition of the materials must be made. Compounding of neoprene for oil resistance in general involves the presence of high loadings of fillers and a minimum addition of softeners which may be leached out by the oils or solvents present.

In general, the processing procedure already described is adopted, and while black fillers are chiefly employed, especially soft carbon blacks, yet for light-coloured mixing barytes, whiting, china clay, zinc oxide, etc., may be employed. The usual softeners are added. In this connection it is interesting to note that it is of advantage to use as a softener the actual oil with which the product may be in contact, and particularly the quantity which in the ordinary way would be taken up during contact.

For best oil resistance it is also advisable to have a very advanced state of vulcanization. It has been found that additions of soft

hioplasts, which are of course highly resistant to the effect of oils nd solvents, confer beneficial properties on the oil resistance of ieoprene products, particularly in the case of aromatic and chlorinated olvents which do to some extent swell neoprene rather badly. One ype that is widely used in this country is known as Vulcaplas. About ;o per cent. of this can be added without interfering greatly with most ıf the properties of the product.

Recently even better results have been obtained by the use of nother thioplast known as Novoplas A. This is particularly suited for ıse with neoprene GN. Additions of Novoplas A up to 20 per cent. ıave little adverse effect on the physical properties. Larger additions lo reduce tensile strength and elongation but greatly improve resistance o oils and solvents.

TABLE 108. NEOPRENE E MIX CONTAINING A THIOPLAST [8]

(Cure: 60 mins. at 141° C.)

Neoprene, type E	80
Vulcaplas	20
Rubber substitute	10
Light calcined magnesia	10
Wood rosin	5
Spindle oil	15
Seekay wax A.68	5
Thermatomic black	100
Zinc oxide	5
T_B (kgs./cm. sq.)	80
E_B %	456
H.	61
Elasticity (°Shore)	72

Neoprene has excellent resistance to heat, far superior to that of ubber. This is however dependent upon correct formulation of naterials.

The following composition is a typical heat resisting type.

TABLE 109. HEAT RESISTING MIX [8]

Neoprene GN	100
Magnesia	4
Nonox NSN	2
Phenyl α-naphthylamine	4
Thermatomic Black	50
Mineral Oil	5
Zinc oxide	15

Cure for 40 mins. at 141° C.

This mixing was still serviceable after 5 days ageing at 150° C. which s very arduous treatment.

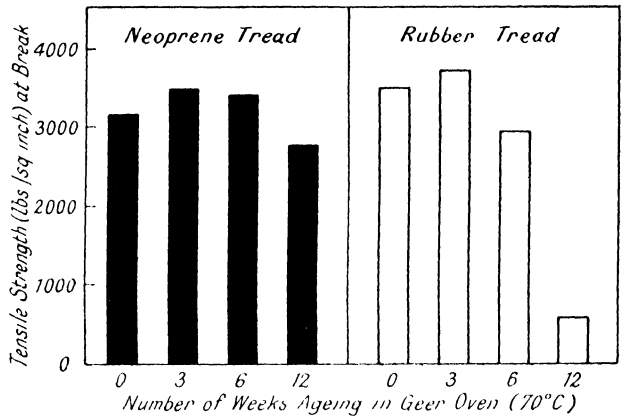

FIG. 52.[8]

Neoprene products gradually become harder and tougher on exposure to heat, in contrast with the degradation of rubber products. In this connection sulphur is always omitted when heat-resisting

TABLE 110. BEHAVIOUR OF COMPARABLE NEOPRENE AND RUBBER MIXES IN VARIOUS SOLVENTS AND OILS [8]

Immersed in	Temp. °C.	Compound	Percentage increase in volume		
			24 hrs.	3 days	7 days
Motor petrol	28	neoprene	29	29	33
		rubber	84	84	88
Paraffin (lamp oil)	28	neoprene	14	23	23
		rubber	73	78	78
Paraffin (lamp oil)	100	neoprene	36	36	36
		rubber	142	254	disintegrated
Motor oil	28	neoprene	1	1	1
		rubber	5	7	11
Motor oil	100	neoprene	4	8	10
		rubber	57	108	131
Benzene	28	neoprene	168	172	174
		rubber	113	114	122
Cotton-seed oil	28	neoprene	—	1	2
		rubber	6	8	15
Linseed oil	28	neoprene	1	3	4
		rubber	2	4	7
Turpentine	28	neoprene	50	67	88
		rubber	113	116	135

materials are being made up. Another very vulnerable aspect of rubber is the rapidity with which it is broken down by sunlight, whereas neoprene is virtually unaffected. Oxidation is far less a menace to neoprene than it is to rubber. This is further reflected in the successful manner in which neoprene stands up to ageing, always a bugbear in the use of rubber. This is confirmed both by accelerated tests and by natural life tests. Large amounts of antioxidants are usually incorporated. Also vulcanization is carried as far forward as possible.

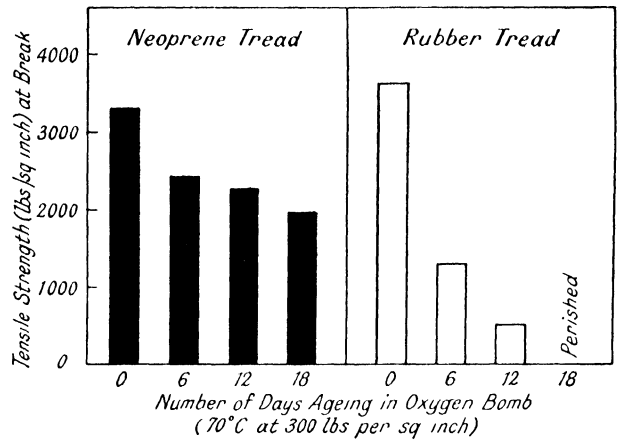

FIG. 53 [8]

Neoprene compounds are virtually unaffected by sunlight, and are also remarkably resistant to attack by ozone. It withstands the effect of strong mineral acids for long periods of time, and for this reason is used to line tanks, and apparatus used with such acids; naturally ingredients must not be added which will be attacked by the materials with which neoprene will be in contact.

The behaviour of neoprene at low temperatures is of considerable importance at the present time. Neoprene in general does not retain its flexibility to such low temperatures as rubber, becoming leathery at about − 30° C., and brittle at about − 40° C. Nevertheless, by the addition of suitable plasticizers in larger quantities than are normally used for compounding the low temperature range, it may be extended as far as − 60° C., retaining the resistance to oil.

Reclaiming of Neoprene. Large quantities of neoprene are being successfully reclaimed at the present time. The technique is much

simpler than with rubber. One method depends upon milling the scorched or vulcanized neoprene with soaps. The general outline of the method is to mill the scorched material, and add small successive additions of the soap, usually a proportion of about 5 per cent is adequate to disperse the neoprene and make it run smoothly. If it is difficult to get the mill started, a small addition of raw neoprene is utilized to act as a compounding medium.

Another method for achieving this is to add small amounts of tricresyl phosphate. It has been found that as little as 2 per cent. does a remarkable job in replasticizing vulcanized scrap neoprene. Small proportions of naphthalene are extremely useful in aiding the reclaiming procedure. The reclaimed material can be used again rather along the lines of rubber reclaim. Additions of raw neoprene aid the compounding, and also the subsequent processing, without greatly affecting the other properties, although it is inadvisable to use very large quantities.

According to Fraser [6] neoprene reclaim may replace as much as 50 per cent. of the new reclaim without greatly impairing the physical properties of medium or low-grade mechanical goods.

Applications of Neoprene. Neoprene was developed for uses where rubber gave unsatisfactory service or could not be used. As a result it has acquired an enormous spread over industries of every description. It has been used for fittings of every type in motor engines. It has become almost a standard engineering material, being specified wherever oil, heat and abrasive conditions are encountered. It has the odd property of damping out vibration to a much greater extent than rubber. These same properties make it invaluable in aircraft production, its value being further enhanced by its virtual non-inflammability. In the same way it is widely used in shipbuilding. It goes without saying that it is extensively employed wherever oils and solvents are handled, as in oil-refining plants, and for hose and accessories in garages.

It is utilized for many forms of clothing, such as aprons, hoods, boots, etc., in works where corrosive materials are being produced. It is used for making conveyor belts, for handling materials where the influences of oil together with abrasion must be overcome. Printers employ it for a variety of purposes, including their rollers and their plates.

Neoprene is widely used as sponge where oil resistance is required. It is prepared along the lines used in ordinary rubber practise. A gas-evolving agent such as sodium bicarbonate is incorporated as blowing agent.

TABLE 111. EFFECT OF NEOPRENE RECLAIM [7]

(Cured : 60 mins. at 141° C.)

	Parts by weight.	
Neoprene, type E	100	80
Neoprene E reclaim	—	20
Light calcined magnesia	10	8
Wood rosin	5	4
Soft black	100	100
Mineral oil	5	4
Tricresyl phosphate	5	—
Nonox S	2	2
Sulphur	1	1
Zinc oxide	10	8
T_B (kg. per sq. cm.)	143	141
M_{300}	106	136
E_B %	462	340
H	65	73
Elasticity (Shore)	64	50
% Volume increase in diesel oil	32	32

And so one could go on for a long time cataloguing the innumerable applications throughout the industry.

The electrical properties of neoprene are inferior to those of rubber. According to Yerzley [21] neoprene compounds having just sufficient

TABLE 112. SPONGE NEOPRENE

Neoprene GN	100
Magnesia	4
Zinc oxide	1
Sodt Black	50
Dibutyl Phthalate	25
Liquid Paraffin	10
Oleic Acid	2
Sodium bicarbonate	10

Cured for 90 minutes at 141° C.

added ingredients to ensure proper vulcanization, at 1000 cycles, had dielectric constant of 7·5, power factor of 0·03 and specific resistance of 10^{12}. It also takes up more moisture. Yet its other properties are so advantageous that it is employed in cable manufacture. Its chief function here is for sheathing cables which have to be non-inflammable, abrasion resistant, able to withstand oils, solvents, etc. It also resists the influence of ozone to a far greater extent than does rubber.

Little effort had hitherto been made to manufacture ordinary tyres from neoprene. It could not compete on cost with rubber. Also the scale of a manufacture was not large enough for this market. It has been established that tyres can be made which are at least as good as

those based on natural rubber. In fact, under severe service conditions such as experienced by truck tyres, neoprene has been found to be definitely superior, and solid tyres based on it are made in the United States.

Great strides have recently been made in the use of neoprene for adhesive solutions. These have a number of advantages over rubber solutions. These include (*a*) superior ageing characteristics, (*b*) resistance to oil and grease, (*c*) better penetration into porous surfaces and inproved anchorage, (*d*) the higher solid deposition per coat. On the other hand they have lower initial strength. Another disadvantage is the inability to use cheap petroleum hydrocarbons, involving either more expensive or more toxic solvents. Earle [5] has made the following comparison in relation to neoprene GN or KN:

TABLE 113. NEOPRENE CEMENTS

Property of cement	Rubber	Neoprene
Choice of solvent	Wide	Narrower: insoluble in petroleum solvents
Practical solubility range	Limited	Three to four times more soluble
Initial film strength	Good	Fair
Penetration of porous surfaces	Poor	Excellent
Ageing of uncured film	Poor	Excellent
Ability of properly compounded film to cure at room temperature	Good	Good
Stability of solution	Good	Good
Resistance to oil and grease	Poor	Excellent
General resistance to corrosive chemicals	Fair	Excellent
Dielectric resistance	Good	Fair

Neoprene adhesives are being used for bonding neoprene to itself, to wood, metals, fabric, etc. It is also applied for bonding leather, fabric, cork, paper and other materials. The solutions are of great importance for lining tanks merely by painting them with the solution, drying and curing by steam or hot water.

Other Modifications of Neoprene. An interesting example of a modified type is neoprene KN.[16] This produces materials with properties similar to those obtained from types G or GN. However, type KN differs from other types in that it can be plasticized to a much greater extent by the use of chemical plasticizers. The new neoprene is said to offer possibilities in the manufacture of the following types of compositions: (1) heavily loaded compounds;

(2) base compounds for cements; (3) compounds containing other types of neoprene; and (4) compounds to be cast in special moulds.

The recommended plasticizers are Latac (hexamethylene ammonium hexamethylene-dithiocarbamate) and DOTG (di-ortho-tolylguanidine). The maximum effect is obtained with 1 per cent. Latac or 4 per cent. DOTG. The former is preferred because of imparting room temperature stability and a rapid accelerating effect at vulcanizing temperatures. At 80° C. untreated type KN has a Williams plasticity of 86, and untreated GN, 245; with 1 per cent. Latac, KN has a plasticity of 12, and GN, 81.

When vulcanized, the following highly loaded compound had a Shore hardness of 100; neoprene type KN, 100; Latac, 2; extra light calcined magnesia, 8; soft carbon black, 250; neozone A, 2; medium process oil, 10; paraffin, 2; and zinc oxide, 20. Yet the unvulcanized compound was sufficiently plastic to flow easily in a curing mould. This compound illustrates the wetting properties of plasticized KN and shows that the extreme plasticization does not lower the hardness of the vulcanizate.

Lightly loaded neoprene KN compounds dissolved in common neoprene solvents (toluene, benzene, xylene, etc.) produce cements having a much lower viscosity than similarly compounded cements made from any other type of neoprene. Obviously, one dip or brush coat of a cement made from KN will deposit a heavier film than will a cement of the same viscosity made from another type of neoprene. Frequently in the lining of tanks and the covering of metal and other surfaces, a heavier coating than can be economically applied by the use of brushing cements is desired. This can be achieved by trowelling if the solids content of the cement is increased to form a more viscous compound.

When very tacky or extremely plastic unvulcanized compounds are needed KN may be used as the sole basic material in lightly loaded compositions. However, the wide range of plasticity obtainable with mixtures of KN and other neoprene polymers are of interest in the formulation of friction stocks, roll coverings, lathe-cut goods, shoe stocks, and other compounds requiring building tack.

The substitution of KN for other types of neoprene in certain soft-type compounds results in an unvulcanized consistency approaching that of a trowelling compound. This consistency makes it possible to pour the compounds at elevated temperatures, and the lack of volatile solvents eliminates excessive shrinkage. However, such pourable compounds are softer and will display a higher shrinkage than milled compounds. Thus it is possible to shape objects by casting

methods, unsuitable for use with normal neoprene compounds; for example, soft-roll coverings can be applied to shafts by casting in a cylinder, or irregular-shaped objects can be vulcanized in plaster of Paris, wood or soft metal moulds.

Casting compositions, pourable at 80° to 90° C. can be prepared but special procedures are needed in mixing and casting for the removal of entrapped air. Vulcanization is carried out for long periods at low temperature. By modifying the procedure, rubber moulds may be used.

Other Modifications. Until comparatively recently the manufacturers of neoprene did not deviate from the policy of basing their neoprene types on the single monomer—chloroprene. It was found however, that chloroprene could advantageously be copolymerized with other synthetic resin monomers to give superior products.

TABLE 114. TYPICAL COMPOSITIONS OF NEOPRENE I AND Z [8]

	Type I		Type Z	
Neoprene	100	100	100	100
Light calcined magnesia	10	10	10	10
Wood rosin	2	5	2	5
Pine tar	8	10	8	10
Nonox S	2	2	2	2
Kosmos T	35	—	35	—
Lamp black	—	110	—	110
Tricresyl phosphate	—	5	—	5
Sulphur	1	2	1	2
Zinc oxide	5	5	5	5
Cure 30 mins. at 153° C.				
T_B kg./cm.^{2}	262	137	262	137
E_B %	731	279	731	279
H	78	87	64	81
% Swelling in diesel oil (11 days at 70° C.)	1	−1		
Cotton-seed oil			2·5	
Transformer oil			2·5	

Comparable standard neoprene mixes swell 55% in diesel oil and 30% and 20% respectively in cotton-seed or transformer oils.

Notable additions to the range include neoprene I and neoprene Z which are copolymers. From the processing angle both these are similar to neoprene G, although they are not plasticized by guanidines From the vulcanizing aspect they resemble neoprene E. Although not essential for vulcanization, a little sulphur is generally used Typical neoprene I mixes are vulcanized for 80 minutes at 141° C. while neoprene Z mixes take 30 minutes at 153° C. These more recen

types have even better resistance to oils and solvents than their predecessors which is the chief reason for their introduction.

It is known, too, that chloroprene is also treated together with styrene and acrylic nitriles respectively, analogous to the Buna rubbers. The outstanding effect which is obtained by copolymerization is a further decrease in the already low degree of swelling in oils.

Other Chloroprene Elastomers. Not all the work on chloroprene rubbers has been carried out in the United States. The other synthetic rubber-producing countries were interested at a very early stage. In the U.S.S.R., for example, one of the leading types has been Sovprene, a chloroprene rubber. The properties of the Sovprene materials were described as long ago as 1935.[13] Frequent references in the literature confirm activity in this direction. Thus, according to Kosloff and Gimpelwitz,[12] the preparation of chloroprene from a solution of vinylacetylene in xylene gave a yield of 53 per cent. as against 32 per cent. by the standard method. A recent account described how Sovprene was made in many grades of varying plasticity which also differ in their processing properties, and showed how these were applied for different purposes.

The I.G. in Germany have taken out numerous patents relating to chloroprene rubbers. For example,[9] they extended the method of catalyzing monovinylacetylene to chloroprene by the use of cuprous chloride by adding alkali metal salts. In another patent [10] they copolymerized chloroprene together with acrylic acid nitrile and styrene, respectively. In addition they described how chloroprene when polymerized in the presence of small amounts of sulphur containing compounds gave superior products.

Du Pont de Nemours [4] in a recent patent also claimed that polymerization in the presence of 0·25 per cent. sulphur gave improved materials. Emulsions containing up to 60 per cent. chloroprene were polymerized at temperatures that could go up to 100° C. The reaction could be stopped at any desired stage by adding a small amount of an inhibitor such as phenyl-β-naphthylamine.

In Japan, Hurukawa and Nakamura [7] have described the preparation of vinylacetylene from acetylene and have developed a synthesis of chloroprene.

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CHAPTER 14

ELASTENES—POLYISOBUTYLENE, BUTYL RUBBER, ETC.

EFFORTS at the polymerization of olefines such as ethylene, propylene, isobutylene, etc., have been carried out for many years, mainly with the object of obtaining improved motor fuels. Among the numerous new synthetic products that have resulted from this work, several have already attained considerable importance in the plastic field, and in the rubber field. As might be expected from the lack of a conjugated system of double bonds, all such materials are thermoplastic.

The outstanding commercial polymers of ethylene is the group generally known as polythene and sold as Alkathene, developed by the Imperial Chemical Industries, Ltd. This is one of those materials where plastic properties predominate. On the other hand, polyisobutylene as developed by the I.G. Farbenindustrie, and the Standard Oil Development Company has predominantly elastic properties, although still thermoplastic.

The deliberate introduction of a predetermined number of conjugated double bonds into materials such as polyisobutylene by copolymerization with small quantities of diolefines such as butadiene, has enabled the Standard Oil Development Company to prepare thermosetting synthetic rubber materials—the butyl rubbers.

Styrene is, of course, another olefine. The polymer polystyrene does show very distinct rubbery properties in the upper temperature range, but since it is in no sense elastic at normal temperatures, it is not considered in detail here. In fact its pronounced brittleness is one of its greatest defects which has not yet been overcome by any plasticizing. It is interesting to note also that Buna-S could quite well come into this group of materials, since it is a pure hydrocarbon derived from an olefine (and a diolefine).

All these materials being pure hydrocarbons they are characterized by outstanding electrical properties.

Polythene. Polythene is the generic name given to solid polymers of ethylene. The molecular weight of these may vary from 3,000 up to 50,000.

The best-known product, it is a tough, horn-like, white translucent material which has considerable flexibility. It is very inert and has great resistance to corrosion ; it has outstanding resistance to moisture

and by virtue of its being a pure hydrocarbon it has exceptional electrical properties. Although insoluble in all solvents at ordinary temperatures, above 70° C. it becomes freely soluble in benzene, toluene and other aromatic solvents, in chlorinated hydrocarbons, in aliphatic hydrocarbons and in natural oils. It is quite insoluble in water, alcohols, acetone, ether, vegetable oils, etc.

Polythene is unaffected by ultra-violet light and ozone. Nor is it prone to oxidation under ordinary conditions. It has a marked softening point between 100° C. and 115° C. above which it is a viscous fluid. This sudden transition from solid to liquid is in contrast to most thermoplastics. When heated in air it begins to decompose at about 200° C. It burns quite freely.

It is very resistant to concentrated nitric acid and hydrochloric acid even at high temperatures, but is affected by strong sulphuric acid. It is not affected by strong alkalis.

The electrical characteristics are superb, only equalled by polyisobutylene and polystyrene.

TABLE 115. ELECTRICAL CHARACTERISTICS OF POLYTHENE AT 50 CYCLES

Dielectric constant.	2·2
Breakdown voltage.	1000 volts per mil.
Resistivity (ohms/cm^3)	$> 10^{17}$
Power factor	0·0005

The tensile strength of moulded polythene is of the order of 2000 lbs. per square inch. When extended there is no tendency for retraction which indicates the absence of marked elastic properties, which only become at all marked near the melting point. It has good impact resistance. Oddly enough, it does not suffer appreciably from cold flow until very close to the melting point. The only great disadvantage is the softness, as a consequence of which it can be cut, scratched, or deformed quite easily.

It may be compounded and mixed with other materials on the mixing mill or in an internal mixer at fairly high temperatures. Materials such as rubber, paraffin wax, polyisobutylene, etc., may be added. Fillers may also be incorporated in quite large volume at the expense of flexibility while making the material brittle.

Polythene may be moulded or extruded or formed into films. It is extensively employed in cable manufacture and for electrical uses.

Polyisobutylene (or Polyisobutene). The class of materials generically known as polyisobutylene (or polyisobutene) has already acquired considerable commercial importance. Chemically they can-

not claim any relationship to rubber, or any of the elastomers already described. Yet the high molecular weight products are more rubbery than rubber !

Polyisobutylene is a polymer of isobutylene. This is a by-product of petroleum processing, is obtained in great quantities from " natural gas " and is also available as a by-product in various industrial processes. It is made in the United States from petroleum derivatives, whereas in Germany industrial by-products are the source. The U.S.S.R., too, has rich sources of isobutylene, which are being utilized.

The lower members of the series are viscous fluids which become progressively more solid and rubbery as the molecular weight is increased. Both fluid and solid products have wide industrial application. Commercial materials include those sold as Vistanex by the Standard Oil Company in the United States, as Oppanol by the I.G. in Germany, and as Isolene by F. A. Hughes & Co., Ltd., in this country.

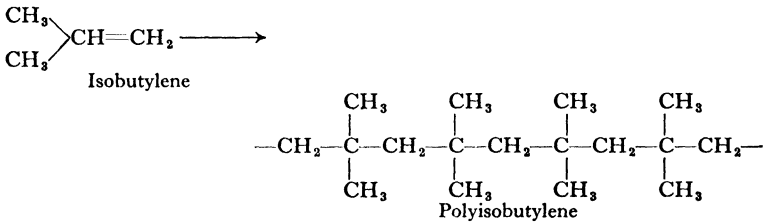

FIG. 54.

Rubber-like polymers of isobutylene are of comparatively recent origin. The other lower polymers had been known for some time. In 1873, Butlerov and Gorianov [2] described the polymerization of isobutylene to yield liquid products, using sulphuric acid or boron fluoride as catalysts. Quite recently Otto and Müller-Conradi obtained products which approached the solid condition, reaching molecular weights up to 10,000. Following upon this, a joint research scheme carried out by the Standard Oil Development Company and the I.G.[20] resulted in the production of high molecular weight compounds, definite rubbery solids. The essential feature for the production of high molecular weight rubbery polymers is to carry out the process at very low temperatures, e.g. below − 50° C. Molecular weights of the products ranged from 25,000 up to 400,000. The speed of reaction is extremely rapid often being a fraction of a second.[22]

The manufacturing procedure has been outlined in various patents. For example, isobutylene polymerizes readily in the presence of boron

fluoride at low temperatures, below — 10° C., and the lower the temperature the higher the molecular weight of the product.

Temperature	Molecular weight
— 80° C.	70,000
—103° C.	200,000

Small amounts of impurities in the isobutylene adversely affect the polymerization, reducing the molecular weight to 10,000.

The I.G.[7] have found that small amounts, 0·5 per cent. of materials such as sulphuric acid, nitric acid, formaldehyde, phenol, cresol, and so on, have a notable accelerating effect on the reaction. Added to the isobutylene they shorten the time of reaction, and in many cases considerably increase the molecular weight of the polymer. They also reduce the amount of catalyst involved. According to Mann,[10] an improved process for producing hydrocarbon polymers of high molecular weight from isobutylene comprises adding the olefine in liquid condition to a reaction zone and providing at least three gallons of propane per gallon of isobutylene, bubbling boron fluoride through the liquid and agitating for a short time to bring about polymerization, meanwhile maintaining the temperature below — 20° C., by evaporation of a portion of the propane, but maintaining a sufficient portion in liquid condition to produce an easily flowing mass with the polymer, then adding a normally liquid oil to the polymer-propane mixture and removing the propane.

Properties of Polyisobutylene. The lowest polymers, the dimers and the trimers, are clear, free-flowing liquids. As molecular weight increases so does the viscosity. According to Thomas, based on penetration data, the change-over from viscous fluid to elastic solid occurs at a molecular weight of about 27,000. All the products are odourless and tasteless. The specific gravity is about 0·9, varying but slightly with change in molecular weight. Those polymers with molecular weight less than 80,000 have quite low tensile strengths, but when greater than 150,000, the strength is high enough to be measured on tensile testing machines, without any modification.

From the chemical standpoint, polyisobutylene differs from rubber chiefly in being a saturated hydrocarbon, in contrast to the profound unsaturation of rubber. Both are long-chain pure hydrocarbons, and both have a regular distribution of short aliphatic side chains. X-ray examination shows that polyisobutylene behaves very much like rubber. Brille and Halle [1] showed that when stretched it gave an X-ray diagram very similar to that of stretched rubber. The X-ray photographs obtained by Sebrell and Dinsmore[12] illustrate this feature. The

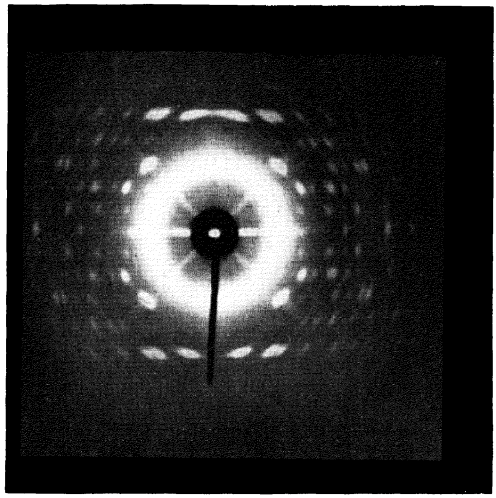

FIG. 55.—X-Ray Photograph of Vistanex (Polyisobutylene) Unstretched (Sebrell and Dinsmore).

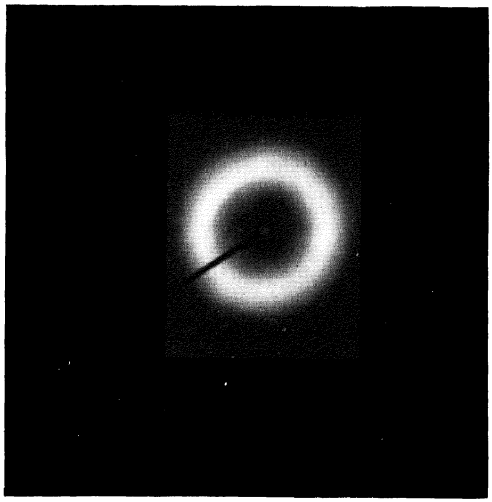

FIG. 56.—X-Ray Photograph of Vistanex Stretched (Sebrell and Dinsmore).

[*To face page* 250.

inescapable elasticity of polyisobutylene, a fully saturated material, is very significant. For it shatters the many theories which attributed elasticity to forces connected with unsaturation. These are no longer tenable.

The physical properties are closely akin to those of rubber. The commercially available types, such as Vistanex, resemble rubber. They are colourless, clear materials, very rubbery to the feel. They are much less thermoplastic than rubber. These characteristics do not become marked to any degree below 100° C. Polyisobutylene can be moulded at about 200° C., decomposing at 350° C. It is, however, profoundly affected by sunlight, which after long exposure tends to break it down and make it very tacky. The action is one of depolymerization and is analogous to what occurs with rubber. There is a loss of strength and elasticity in each instance. The use of small amounts of fillers, notably carbon black, greatly inhibits the influence of light.

An outstanding property of this material is the exceptional resistance to corrosive influences, which is almost unequalled. It withstands, almost indefinitely, the effect of virtually all concentrated and dilute acids, with the exception of nitric acid, to which polyisobutylene succumbs only after long exposure. Above temperatures of 80° C., it is however attacked by strong sulphuric and nitric acids. The same degree of resistance extends also to concentrated and dilute alkalis.

Oxidizing agents have no effect upon polyisobutylene. Even ozone has no effect upon it, a property which is found to be very useful. The resistance to the action of ozone is of considerable importance. By contrast the effect on rubber is devastating. This is attributed to the double bonds, the unsaturation of rubber, along the lines described by Harries. According to this reasoning, polyisobutylene, a saturated material with no double bonds, should be unaffected by ozone. This is the case. Moreover, it is found that the presence of appreciable quantities of polyisobutylene exerts a profound protective effect against ozone. These high powers of resistance can be directly attributed to the saturation of the molecules.

Polyisobutylene will not, however, stand up to chlorine and bromine. In these cases new products are formed which appear to have intrinsic merits and are being developed.

The solubility of polyisobutylene in solvents is very similar to that shown by rubber. It is insoluble in solvents such as alcohol, glycerol, acetone, etc. The resistance to water is superb, the take-up over very long periods being virtually nil ; in this it is far superior to rubber. It swells in fats, greases and oils. It swells and dissolves in petrol, benzene, toluene, chlorinated solvents, etc. Mineral oils, paraffin

wax, and similar materials also exert a pronounced solvent action. Nevertheless solutions are far more difficult to make than in the case of rubber. Considerable milling and breakdown of the molecule is necessary to facilitate the preparation of solutions.

The temperature range of the elastic properties is remarkably wide, in fact the greatest known. Sheets do not become brittle even at − 70° C., nor do they soften and melt together at temperatures as high as 180° C. A very surprising feature is that in spite of the rubbery nature of the material, at ordinary temperatures there is no rebound or bounce. Yet at 100° C. its rebound behaviour is quite as good as that of rubber. Polyisobutylene shares these temperature oddities with polystyrene, which, although brittle at ordinary temperatures, becomes extremely rubbery above 80° C., and with polyvinyl chloride which also shows enhanced elastic behaviour at slightly elevated temperatures.

TABLE 116. EFFECT OF MOLECULAR WEIGHT ON BRITTLE POINT [13]

Material	Approx. wt. mol.	Appearance	Brittle point ° C. (±0·5°)
Polyisobutylene . . .	1,500	Viscous liquid	− 23
Polyisobutylene . . .	10,000	Very viscous liquid-solid	− 50·2
Polyisobutylene . . .	100,000	Elastic solid	− 50·2
Polyisobutylene . . .	200,000	Elastic solid	− 50·2
Polyethylene	Low	Soft waxy	− 15
Polyethylene	High	Tough, waxy, but hard	− 68·5

The electrical properties are outstanding characteristics of polyisobutylene. They are equalled only by the other pure hydrocarbon plastics polystyrene and polythene. The power factor is extremely low throughout a very wide range of temperatures, the dielectric constant is low, while the insulation resistance is very high. Coupled with the resistance to moisture, it is a superb electrical material, and finds wide application by virtue of this.

TABLE 117. ELECTRICAL PROPERTIES OF POLYISOBUTYLENE [11]

Temperature	Power factor at 800 cycles	Dielectric constant	Specific resistance ohm/cm.	Breakdown voltage
20° C.	0·0004	2·3	$>10^{15}$	23 kv./mm.
85° C.	0·0005	2·2	$>10^{15}$	

Processing of Polyisobutylene. The high molecular weight polyisobutylenes are very gristly rubbery solids. Before any filling materials can be added, these must be broken down on a mixing mill or internal mixer. In the early stage on the mill they have much more nerve or kick than rubber. Breakdown is more pronounced at low temperatures than at high, in this respect resembling the behaviour of rubber. The effect of mastication is to break down the long molecules into shorter ones. At high temperature softening is chiefly a thermoplastic effect and is reversible, so that when the material becomes cold again all the original nerve is recovered. As in the case of rubber, the solubility is greatly affected by this treatment, as is the viscosity of such solutions. The latter property gives a measure of the molecular weight.

TABLE 118. EFFECT OF MILLING ON POLYISOBUTYLENE [15]
(initial molecular weight 200,000)

Time of milling (minutes)	Maximum temp. (° C.)	Final molecular weight
5	52	163,000
10	66	158,000
20	93	156,000
35	115	144,000

Polyisobutylene has a remarkable capacity for taking up filling materials. Loadings of 1000 per cent. and more are not only possible, but offer little difficulty, and give quite attractive flexible material. As the amount of filler taken up increases, so the temperature of mixing must be lowered; otherwise there are no snags. Polyisobutylene appears to be quite indifferent to the nature of the filler. Any fillers may be added. Only carbon black has any pronounced influence on the properties, increasing the tensile strength and lowering the elastic limit.

Polyisobutylene is compatible with numerous other materials such as bitumens, waxes, oils, resins, synthetic resins, etc. These do not exert any appreciable plasticizing or softening action. In fact, this process is reversed, for in many instances polyisobutylene is used to confer specific qualities on these materials. Thus it reduces brittleness and confers flexibility and ductility at low temperatures, particularly in the cases of waxes, resins, polystyrene, etc. In the case of rubber it confers increased water resistance, enhances the electrical properties, improves resistance to ozone and oxidation, and retards ageing.

Polyisobutylene and its compositions can be handled by the normal methods of the rubber industry. That is to say, they can be extruded, calendered, moulded, etc. But owing to the " nerve " of the material they are much more difficult operations to carry out, worse even than with

the elastomers. In the case of the pure materials much higher temperatures are necessary than are normally used with rubber. All these operations are made much easier by addition of compounding ingredients. Mouldings must be chilled before removal from the moulds.

The one outstanding defect of polyisobutylene is the cold flow which is very pronounced. Subjected to slight load for any length of time there is permanent deformation. The only way to overcome this is to add rubber or an elastomer, although montan pitch minimizes the effect. So far, no satisfactory method of vulcanizing or setting polyisobutylene has been devised that might overcome this defect. Sulphur has no effect, nor has zinc oxide, etc. A reaction does proceed with sulphur chloride, but this is not yet a practical procedure. At any rate at present no change can be produced which will produce the desirable characteristics implied by vulcanization, namely change of solubility, improved mechanical properties, etc.

Applications of Polyisobutylene. The chief applications of these materials have been more in the nature of plastic compositions than direct rubber applications as in the case of the elastomers and other synthetic rubber-like materials.

TABLE 119. SOME PHYSICAL PROPERTIES OF POLYISOBUTYLENE (molecular weight 200,000)

	T_{B_2} kg.cm.	E_B %	Set %	Rebound Energy	H
Polyisobutylene . . .	60	1000	4	12	35
Rubber mix	160	700	7	66	42
Polyisobutylene + 50% carbon black	105	730	14	8	45
Rubber mix + 50% carbon black	320	450	20	50	65

Straightforward mixes of polyisobutylene and fillers or modifying agents such as clay, whiting, talc, carbon black, cork, coumarone resin, bitumens, etc., have been used for many purposes. Acid-resisting linings, gaskets, packings, insulation, adhesives, sealing compounds, are among typical applications.

The chief application of polyisobutylene has been to modify and improve the properties of rubber articles, notably with regard to resistance to heat, to ozone, and resistance to acid.

Polyisobutylene and rubber are easily miscible in all proportions, the rubber plasticizing the polyisobutylene on the mixing mill. According to Longman [9] the following proportions are found to give the best results:

1. For cable insulation 60–65 parts Vistanex polyisobutylene to

40–35 parts of rubber gives the best ozone resistance to be had with physical properties maintained at an acceptable level.

2. For compounds resistant to acids, alkalis, and corrosive salts, the maximum amount of polyisobutylene possible is recommended. Physical requirements for this type of application are usually low, so that the rubber content can be set at a much lower percentage approximating to 20–25 per cent.

3. Heat-resisting compounds such as steam hose, conveyor belt covers, etc., usually contain fairly high loadings of carbon black. Actual production has shown that ratios of 50–60 parts of polyisobutylene to 50–40 parts rubber are quite practicable. Singularly enough in these cases additional vulcanizing ingredients must be added for the polyisobutylene, even though alone these ingredients have no effect whatever.

There is already considerable activity in the production of modified derivatives from isobutylene. Thus the Standard Oil Development Company [19] have prepared chlorinated materials. The polymers of isobutylene are chlorinated under conditions of heat and sunlight, the latter being particularly effective. Until a 50 per cent. content of chlorine is reached elastic properties are retained. This material has high resistance to heat and is non-inflammable and has been recommended for cable insulation.

The fully chlorinated material containing 75 per cent. chlorine is a white brittle inelastic powder which shows some promise in the field of coatings.

A.X.F. Another rubbery olefine polymer which has gained some commercial use is known as A.X.F.[14] This material, which is both elastic and plastic, is prepared by the action of ethylene dichloride on certain aromatic hydrocarbons in the presence of aluminium chloride. With benzene the structure of the resulting material is thought to be:

$$—C_6H_4—CH_2—CH_2—C_6H_4—CH_2—CH_2—C_6H_4—CH_2—CH_2—$$

This product has excellent chemical resistance and although little used alone, is fairly extensively employed to confer oil resistance, ozone resistance, and corrosion resistance to rubber compounds. Alone it has a maximum tensile strength at break of 500 lb. per square inch and an optimum elongation up to 600 per cent.

Butyl Rubber. The fact that polyisobutylene possessed elastic properties showed that these were independent of unsaturation, but that vulcanization did hinge on this. The Standard Oil Development Company [21] set out to produce a polymer having only the limited amount of unsaturation required for vulcanization. Upon completion of the

vulcanizing operation, such a product should give a rubbery product which was substantially saturated, and should have the chemical stability of a typical saturated paraffin.

This was the principle that eventually resulted in the development of butyl rubber, which is a copolymer of olefine, with a small amount of diolefine. There were obvious economic advantages in being able to use as the main raw material in this process chiefly a simple olefine, such as isobutylene rather than a diolefine such as butadiene.

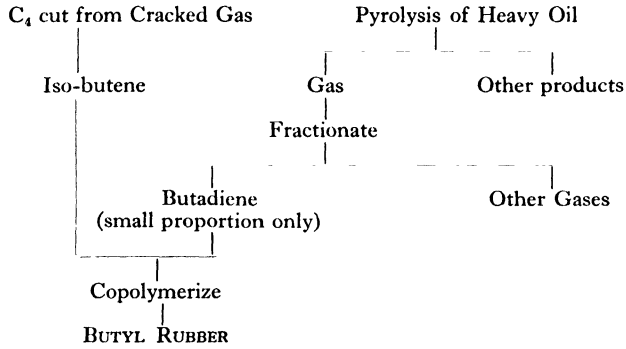

FIG. 57. Butyl Rubber from Cracked Gas.

The term butyl rubber is a generic term, because variation of the types and quantities of olefine and diolefine employed make it possible to obtain products having very different properties, although they all have the one feature in common, that of limited controlled unsaturation.

Butyl rubber in the present instance describes a hydrocarbon product with an unsaturation less than 5 per cent. of that found in natural rubber, and having a molecular weight between 40,000 and 80,000. It is a soft white material which has no odour or taste. It has the extremely low density of 0·91. It stretches very easily.

Actually a number of types have already appeared and been examined, the degree of unsaturation varying between 1 and 5 per cent. that of rubber.

Manufacture of Butyl Rubber. The method adopted to produce these new copolymers has been described in the patent literature.[16] An aliphatic iso mono-olefine such as isobutylene and a hydrocarbon compound having a conjugated system of alternate single and double bonds and having at least one olefine linkage, e.g. butadiene, isoprene, or styrene, are treated at a temperature below 0° C. with a Friedel-Crafts reagent.

FIG. 58.—Crude Butyl Rubber.

[*To face page 257.*

It is desirable that the second constituent be soluble in the other, although the process works when ingredients are dissolved in saturated chlorinated solvents such as carbon tetrachloride.

The Friedel-Crafts catalyst may be boron trifluoride, which is bubbled through, or aluminium chloride which is merely added to the mixture.

In many cases interesting fluid products were obtained. In others rubber-like materials were produced.

As an example 90 parts isobutylene and 10 parts butadiene were cooled to − 78° C. by means of solid carbon dioxide. Boron trifluoride was bubbled through, and after a short time reaction began with the production of a flocculent white solid.

In a later patent [17] The Standard Oil Company modified the type of catalyst, and used a complex of aluminium chloride dissolved in ethyl chloride. By using 10–20 parts butadiene with 90–80 parts isobutylene, they obtained products which had high elasticity and pliability. The reaction was carried out below − 50° C. In this manner they obtained a non-tacky material capable of being vulcanized to give a tough elastic rubber-like product, resistant to oxidation and chemical attack. One point of great interest was that crude mixtures of the reacting compounds may be employed, such as a C_4 refinery cut, which contains a substantial amount of butadiene in addition to isobutylene and normal butylenes.

The limiting proportions are 50 to 5 butadiene, and 50 to 95 isobutylene. The molecular weight can rapidly be brought from 50,000 to 250,000.

When the proportion of butadiene in the reaction mixture is increased, elasticity and pliability are decreased. It is preferred to operate at very low temperature, thus − 95° C. gives better results than − 78° C.

A typical example produced the following results:

	Parts
Isobutylene	120
Butadiene	30
Ethylene (liquid acting as refrigerant and solvent)	300
$Al.Cl_3$–Ethyl chloride (5% in ethyl chloride)	Several

Temperature −95° C.

This gave a white rubber-like material. It was made up into a mixing as follows:

Copolymer	100
Zinc oxide	10
Sulphur	3
Stearic acid	3
Zinc dimethyl dithiocarbamate	1
Mercapto benzthiazole	0·5
Carbon black	25

Vulcanized for 5 hours at 130° C., it gave a product with good elasticity and fair recovery. It had a tensile strength of 1560 lb. per square inch, and an elongation at break of 1100 per cent. It was very resistant to benzene, ethylene dichloride, and strong acids.

In another patent The Standard Oil Company [18] stated that polymers obtained as described above could be readily separated from unpolymerized material and from diluent-refrigerant materials such as ethylene.

The polymer appears to be a linear-branched chain aliphatic hydrocarbon which is substantially a saturated organic material.

TABLE 120. DEGREE OF SATURATION OF ELASTIC MATERIALS

	Iodine number
Rubber	350
Isobutylene	450
Butadiene	900
Copolymer	6 to 15

The original process for butyl rubber cooled raw materials down to nearly − 100° C., obtaining a 20 per cent. conversion to polymer by means of catalyst. The remaining raw materials had to be recirculated. Recent improvements have increased the efficiency threefold.

Production is of three grades, A, B, and C, according to tensile strength, in addition to which there is Flexon which is a lower grade. According to Haworth and Baldwin [5] they are designated according to the kind of diolefine used, while an accompanying figure relates to the amount of diolefine. These may be isoprene, butadiene, or dimethylbutadiene. Thus the best-known types at the present time are Butyl B—1·45 and Butyl B—3.

It is interesting to note that in 1938, the I.G.[8] described rubber-like products obtained by polymerizing isobutylene and butadiene together in the presence of sodium peroxide. The rubbery product could be compounded and vulcanized.

Processing. According to the manufacturers commercial butyl rubber already contains 5 parts zinc oxide and 1·5 parts sulphur to 100 parts of butyl rubber.

The most authentic information about processing of butyl rubber has been given by Haworth and Baldwin.

The actual technique for handling butyl on full-scale factory processing equipment is similar to that for natural rubber with one exception. As a result of an unusually high degree of nerve in the pure gum state, together with a rather low degree of cohesion at elevated temperatures, butyl tends

TABLE 121. EFFECT OF 30-VOLUME PIGMENT LOAD IN BUTYL RUBBER[a] [b]

Pigment	Tensile strength Lb./sq. in.	Modulus at 400% Lb./sq. in.	Elongation %	Tensile, lb./sq. in., after: 48 hr., air oven, 250° F.	Tensile, lb./sq. in., after: 14 days, 02 bomb
Kosmobile 66 [d]	2690	610	880	1670	1970
Wyex [e]	2560	810	830	1350	1910
Statex	2510	880	670	2660	2560
Cabot No. 9 [e]	2420	640	840	1400	1920
Gastex [f]	2180	660	710	1600	1500
Kosmos 20	2010	850	650	1830	1800
Thermax	1960	445	760	1650	1750
P.33	1880	420	720	1570	1740
Kosmos 40	1810	1330	570	1730	1610
Zinc oxide	2080	60	830	1870	2000
Calcene	1970	60	840	1110	1470
Gilders whiting	1550	120	820	880	1380
Celite No. 270	1350	175	780	715	1070
Silene	1030	200	760	805	1080

Pigment	Tear resistance, Lb./in.	A.S.T.M. permanent set %	Compression set [b] %	Temp. rise [c], ° F.	Shore hardness
Kosmobile 66 [d]	475	34·0	27·7	121	55
Wyex [e]	470	28 0	20·0	111	55
Statex	320	16·0	18·3	63	56
Cabot No. 9 [e]	500	28·5	20·1	112	52
Gastex [f]	225	18·4	20·8	58	46
Kosmos 20	290	16·0	22·9	91	50
Thermax	120	19·9	14·1	54	47
P.33	195	17·2	21·3	59	47
Kosmos 40	365	27·4	22·5	97	59
Zinc oxide	205	22·3	—	—	42
Calcene	155	18·8	29·2	177	37
Gilders whiting	80	22·0	27·1	121	40
Celite No. 270	70	36·6	37·9	146	48
Silene	170	23·1	19·6	161	46

[a] Butyl B, 1·45, 100·0; zinc oxide, 5·0; stearic acid, 3·0; tetramethylthiuram disulphide, 1·0; sulphur, 1·5; pigment, 30 vol. All data on cures of 60 min. at 307° F. except compression set and heat build-up which are 120 min. at 307° F.

[b] Constant deflection.

[c] Measured in Goodrich flexometer.

[d] Representative of the standard rubber channel blacks.

[e] Representative of the easy-processing channel blacks.

[f] Representative of the furnace type blacks.

to " lace " and fall from the roll during the early stages of pigment addition when being mixed on a mill. This difficulty may be overcome to a considerable extent by placing a small portion of the batch on a tight cold mill and loading it to a very high degree with the pigment portion of the batch; then the mill may be opened, a normal-sized batch added, and mixing continued in a normal manner. An alternative method is to use a " leader " of a previously mixed batch. The success of these two methods in improving mixing conditions is due to the decrease of nerve and the increase in cohesion at elevated temperature that is brought about by the presence of relatively small amounts of pigments.

Butyl is an ideal material for Banbury mixing since no premastication is necessary before the Banbury operation can be carried out. The condition referred to above which makes for rather difficult handling during the early stages of open mill mixing is not a factor in this operation.

Not only can it be handled in a Banbury mixer, but even in the less robust type of internal mixers used for plastics. The reason is that the material is comparatively plastic to start with, and heat generated in mixing is sufficient to make it process without difficulty. Consequently mastication is unnecessary.

The amount of butyl rubber that can be handled on standard machines is no less than in the case of rubber.

Most of the filling materials used with rubber may be employed with butyl rubber. As in the case of other synthetic rubbers, the most important filler is carbon black. Semi-reinforcing types of carbon black appear to be most suitable. For example, loadings up to 100 parts filler to 100 of butyl rubber do not present undue difficulty. High proportions of carbon black may be easily incorporated, and the material holds its physical properties. Butyl rubber is different, inasmuch as reinforcing carbon blacks do not in general increase the tensile strength. The same applies to other inert fillers.

The use of carbon black does enhance properties other than the tensile strength. It improves abrasion resistance, coating resistance, impact strength and the toughness in a manner comparable to that exerted with natural rubber. Moreover, high loadings do not unduly affect flexing behaviour. Nor do they bring up the hardness beyond a fairly hard rubber, e.g. 70° shore. The tensile strength of products may reach 3600 lb. per square inch, while ultimate elongations can exceed 1000 per cent.

An investigation on the effects of different types of black fillers carried out by Drogin,[3] illustrated these features.

TABLE 122. COMPOUNDS EMPLOYED [3]

	Pure gum		Reinforcing black		Semi-reinforcing black	
	Rubber	Butyl B	Rubber	Butyl B	Rubber	Butyl B
Elastic material	100	100	100	100	100	100
Zinc oxide	5	5	5	5	5	5
Stearic acid	1	3	3·5	3	2	3
Tuads	—	1	—	1	—	1
Altax	1	—	1	—	0·65	—
Sulphur	2	1·5	2·85	1·5	2·85	1·5
Pine tar	—	—	3	—	—	—
Kosmos 20/Dixie 20	—	—	—	—	60	60
Kosmobile 77/ Dixiedensed 77	—	—	50	50	—	—

Cured to maximum tensile properties at 307° F.

SEMI-REINFORCING BLACK

	Smoked sheet	Butyl B
Plasticity (mm.)	153	220
Extrusion (seconds)	1·2	5·2
Modulus, at 200%	1000	335
Tensile strength (maximum)	2840	1850
Elongation at break	420	660
Shore hardness	65	55
Tear resistance	1165	830
Abrasion resistance	175	218
Percentage Rebound	53	12
Heat build-up, average temp. ° F.	130°	172°
Percentage Compression	4·3	4·2
Percentage Set	4·0	6·0
Shrinkage	4·8	10·6
Electrical resistance	23×10^3	164

REINFORCING BLACK

	Smoked sheet	Butyl B
Plasticity (mm.)	245	265
Extrusion (seconds)	2·2	6·5
Modulus at 300%	1450	450
Tensile strength	4075	2800
Elongation	565	805
Hardness	64	55
Tear	1360	832
Rebound	48	12
Abrasion	202	395
Heat build-up ° F.	137°	207°
Shrinkage	2·9	11·5
Electrical resistance	$7·5 \times 10^6$	$3·1 \times 10^6$

TABLE 123. COMPARISON OF MIXES CONTAINING CARBON BLACKS [3]

(Properties of rubber rated at 100 in each case)

	Pure gum		Reinforcing black		Semi-reinforcing black	
	Smoked sheet	Butyl B	Smoked sheet	Butyl B	Smoked sheet	Butyl B
Plasticity	100	65	100	58	100	70
Extension	100	—	100	34	100	23
Modulus	100	—	100	31	100	34
Tensile	100	90	100	69	100	65
Elongation	100	98	100	143	100	157
Hardness	100	86	100	86	100	85
Tear	100	17	100	61	100	71
Abrasion	100	—	100	51	100	80
Rebound	100	22	100	25	100	23
Heat build-up %	—	—	—	70	—	42

Softeners may usefully be employed with butyl rubber. They must not be of low iodine number, which eliminate such softeners as pine tar, rosin, factice, and unsaturated fatty acids, all of which have aliphatic unsaturation.

Vulcanization. Vulcanization is dependent to some extent on the degree of unsaturation. This has been shown by experiments carried out on the rate of vulcanization of different butyl rubbers varying in their degree of unsaturation. Normal vulcanizing ingredients are employed with butyl rubber, e.g. sulphur, zinc oxide, etc., in substantially the normal quantities. It should be remembered that a certain amount of sulphur and zinc oxide are already included.

TABLE 124. EFFECT OF TEMPERATURE ON CURING RATE OF BUTYL RUBBER [21]

Cure Min.	138° C. (280° F.) Cure		145° C. (293° F.) Cure		150° C. (302° F.) Cure		155° C. (311° F.) Cure	
	T_B Lbs./sq. in.	E_B %	T_B Lbs./sq. in.	E_B %	T_B Lbs./sq. in.	E_B %	T_B Lbs./sq. in.	E_B %
15	Undercured		1300	1270	2400	1130	2780	1070
30	1400	1260	1970	1080	3350	1090	3540	1000
60	2720	1180	2640	1000	3360	970	3510	980
120	2930	1030	3360	980	3620	980	3640	970

Accelerators have a profound effect on the vulcanization. The behaviour of accelerators does not parallel what happens with rubber. Certain of the standard types such as tetramethylthiuram disulphide, or this together with mercaptobenzthiazole or zinc dibutyl dithiocarbamate, function just as in the case of rubber stocks. Other common types such as butyraldehyde-aniline, P.P.D. benzthiazyl disulphide, and thiocarbanilide, are quite ineffective. This is bound up to some extent with the extremely low degree of unsaturation of butyl rubber.

A typical mixing consists of:

Butyl rubber	100
Zinc oxide	5
Stearic acid	3
Sulphur	0·5
Tetramethylthiurium disulphide	1

At a temperature of 155° C., the rate of vulcanization of such a mix is comparable with that of a rubber stock being vulcanized with mercaptobenzthiazole. The material is not easily susceptible to overcure.

There is a considerable effort being made to find vulcanizing agents and accelerators which will overcome some of the disadvantages of butyl rubber vulcanizates. These are principally the relatively slow rate of cure and the low modulus, which do limit the applications. Great interest has been roused by the use of materials such as *p*-quinone dioxime together with lead dioxide as activating agents, omitting any addition of sulphur. Quantities of the order of 2 parts quinone dioxime to 6 parts lead dioxide give extremely good results in carbon-black mixes, although the material is very touchy and difficult to process. They also tend to improve the ageing properties. A highly loaded carbon-black mix on this basis will cure in 30 minutes at 140° C.

Ageing Characteristics. Ageing and deterioration of rubber is largely due to the degree of unsaturation. In butyl rubber this is not the case, so that it is intrinsically extremely resistant to ageing, and no antioxidants are necessary.

Long-term ageing tests under conditions of high temperature showed remarkable resistance and maintenance of physical properties. When eventually broken down it only undergoes the softening type of degradation; there is no hardening up. Not only does butyl rubber withstand the effect of oxygen, but it is also almost completely indifferent to attack by ozone. It is affected by sunlight and ultra-violet light, but this is virtually inhibited by addition of a small amount of carbon black.

Butyl rubber possesses a very wide temperature range of elastic properties. Not only is its high temperature behaviour comparable with the elastomers, but in the low temperature range it does not become brittle or lose its rubber-like properties until — 80° F. This is considerably lower than the crack-point of any other elastic material.

Because the original unsaturation is very small, and because even this low unsaturation is greatly reduced (and may even be entirely eliminated) during the curing operation, vulcanized butyl rubber is extremely resistant to chemical attack. This is true, because it has become, after vulcanization, not only a non-thermoplastic, strong elastic material, but also an essentially chemically saturated product as well. This means that, while from a physical standpoint vulcanized butyl rubber resembles soft vulcanized natural rubber, chemically it may be considered more similar to ebonite.

TABLE 125. EFFECT OF METALLIC SALTS ON DETERIORATION OF BUTYL RUBBER BY OXYGEN.[21]

Metal salt added %	Type of ageing	T_B Lbs./sq. in.		E_B %	
		Original	After ageing	Original	After ageing
—	7 days Geer oven 95° C. (203° F.)	2110	1880	1000	1000
1 Cu oleate	Same	2070	2380	1000	1000
0·5 Mn phenol sulphide	Same	2250	2000	950	1020
Same	92 hrs. Bierer bomb, 70° C. (158° F.)	2250	2140	1050	1070

As a result butyl rubber is chemically the most resistant of all elastic materials. It withstands virtually all corrosive influences. Its resistance towards concentrated nitric acid and concentrated sulphuric acid is unequalled. In the same way it is not in the least affected by those metals which have such devastating corrosive influence on rubber. It has been conclusively shown that butyl rubber which has been mixed with copper, manganese, or cobalt salts, has approximately the same tensile strength after ageing as before. Rubber treated in the same manner is completely broken down.

It is apparent that the acceleration of ageing by these metal catalysts is related to the presence of an excessive amount of unsaturation in the rubber molecule.

Tensile Relationships. The stress-strain curve of butyl rubber is different from that of natural rubber. Until an elongation of about 500–700 per cent. is reached the stress is very low, or, put another way, it has a low modulus. This is of great importance because it means that for many purposes the yield of the material under small stresses may be very considerable which is not altogether favourable. Most uses of elastic materials involve precisely these small stresses. From this elongation up to the breaking point, the curve is more nearly like that for natural rubber. In effect this means that rubber is more rigid than butyl rubber. Also since more energy will be put into rubber for the same deformation, it will obviously retract more energetically. This is shown by the snap of rubber, in contrast to which butyl rubber is rather flabby.

Abrasion resistance of butyl rubber products are quite good, particularly for carbon black stocks. The order of abrasion resistance is illustrated by the fact that butyl rubber employed as the tread on a tyre is said to give between 40 and 50 per cent. of the wear obtained with rubber.

Butyl rubber does not bounce or rebound to any great extent, a property it shares with polyisobutylene. Incorporation of a plasticizer such as *p*-cymene, has a profound effect in increasing this rebound. Yet at 100° C. the bounce is just as good as that of rubber. This shows that butyl rubber has the normal rebound characteristics at a higher temperature range than rubber and that a knowledge of the mechanics of bouncing may enable the shift down to the ordinary temperature range.

Haworth and Baldwin [5] have described how the rebound characteristics may be profoundly improved by addition of small quantities, e.g. 10 volumes, of materials such as benzyl ether, *p*-cymene, chlorinated diphenyl, and trichlorodiphenyl ether. These properties are profoundly affected by the use of quinone accelerators with oxidizing agents such as lead dioxide. Their use improves the modulus, the degree of resilience and lessens hysteresis, without detracting from the tensile strength.

Butyl rubber has excellent flexing and impact characteristics. Comprehensive tests on the resistance to flex cracking shows conclusively its great superiority over rubber. This superiority is maintained after long periods of ageing during which rubber compounds fail completely. The behaviour is illustrated in Table 125 which records comparative results obtained with comparable tyre tread mixes.

A wide range of products may be produced from butyl rubber compositions. Moulded articles present comparatively little difficulty.

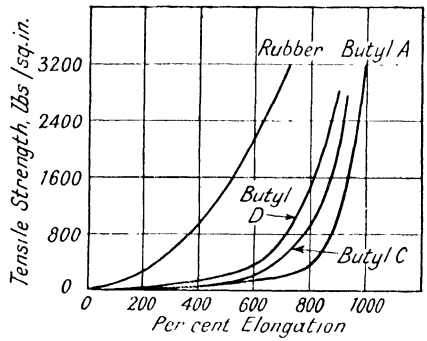

FIG. 59.—Stress–Strain Curves of Butyl Rubbers compared with Natural Rubber.[21]

Tyre treads have been prepared and have been found to give results about 40 per cent. as effective as with rubber. For the production of calendered articles and frictioned articles the prevailing conditions are much the same as with rubber and must be determined by experiment. Loaded mixes process more easily. Softeners and plasticizers are necessary to facilitate the processing. Somewhat similar conditions apply to the production of tubing and to the covering of wire. In these cases, vulcanization by open steam appears to be most effective.

Butyl rubber may be attached to steel. One method uses cements based upon cyclized rubber (e.g. Vulcalock). A film of this is applied to the cleaned steel surface. This is followed by a film of butyl rubber solution heavily loaded with carbon black. The butyl rubber mix is then applied and vulcanization carried through.

TABLE 126. EFFECT OF TEMPERATURE ON THE FLEX RESISTANCE OF RUBBER AND BUTYL RUBBER.[21]

Flexures	Natural rubber tread	Butyl rubber tread
100° C. (212° F.) tests		
To initial cracking	140,000	Test discontinued after 4,500,000 flexures (no cracking)
To complete cracking	2,800,000	
− 22° C. (− 7·6° F.) test		
To initial cracking	90,000	Test discontinued after 1,000,000 flexures (no cracking)
To complete cracking	260,000	

Solvent Resistance. Butyl rubber is not primarily a solvent-resisting material. It has, however, a number of interesting characteristic properties. Untreated butyl rubber disperses in benzene, toluene and other aromatic hydrocarbons to give thick viscous solutions. Such solutions are employed for cements, etc. The best solvent is petroleum naphtha.

Although it is swelled by aliphatic hydrocarbon solvents as readily as natural rubber, when vulcanized it has very good resistance to the simple aromatic hydrocarbons, such as benzene and toluene. It is superior to some materials which now are being used for the construction of petrol hose.

It is unaffected by such nitrogen-containing solvents as nitrobenzene and aniline.

Butyl rubber has very good resistance towards vegetable and animal oils, as may be seen from the comparative table.

TABLE 127. EFFECT OF VEGETABLE AND ANIMAL OILS[4]

(Percentage Swelling)

	Natural rubber	Perbunan	Butyl
Linseed oil	124	172	10
Rape-seed oil	106	0·4	6
Soya bean oil	199	0·0	4
Lard	111	0·7	10
Olive oil	121	2·9	12
Oleic acid	196	35·0	10
Cotton-seed oil	84	0·9	10

Butyl rubber is relatively unaffected by some halogenated solvents, such as ethylene dichloride, but may swell more than natural rubber stocks in others.

It is in general unaffected by oxygenated solvents such as ethers, alcohols, and esters.

TABLE 128. ELECTRICAL PROPERTIES MEASURED AT 1000 CYCLES[21]

Dielectric strength (kv./mil.)	Butyl rubber, 0·6		Natural rubber, 0·5	
	Dry	Wet*	Dry	Wet*
Dielectric constant (1000 cycles)	2·11	2·10	2·46	2·76
Power factor, per cent.	0·04	0·05	0·04	0·16

* 88 hours in distilled water; surface wiped dry for measurement.

Butyl rubber products have excellent resistance to moisture. Water absorption of a pure gum butyl rubber stock is only one quarter that of a comparable pure gum rubber stock. This is particularly important in relation to the electrical characteristics which are excellent.

This would be expected from a saturated hydrocarbon free from electrolytes in any form. A comparison between pure gum natural rubber and pure gum butyl rubber also shows that the electrical properties are maintained also after immersion in water.

Gas Permeability. Butyl rubber is much less permeable to gases than is natural rubber, as judged by tests carried out on a variety of gases. In the case of some of these the rate of passage is so low that it has been found difficult to obtain reproducible results.

TABLE 129. APPROXIMATE RELATIVE GAS PERMEABILITIES THROUGH PURE GUM STOCKS

Gas	Ratio of rate of diffusion through natural rubber to rate of diffusion through butyl rubber
Hydrogen	10–12·5
Helium	6 or greater
Nitrogen	10–20
Sulphur dioxide	Very great

Likely applications of butyl rubber include self-sealing tanks, balloons, boats as floats, gas-masks, possibly tyres, inner tubes, mechanical goods, insulation, etc.

The Possibilities of Butyl Rubber for Tyres. Haworth and Baldwin stated that tyres manufactured wholly of butyl B—1·45—gave 20,000 miles' service on passenger cars run at less than 40 miles per hour.

A point of the greatest importance is that two leading companies (U.S. Rubber and Firestone) indicate that, while butyl rubber tyres can be rated as giving only about one-half of the wear of the best natural rubber tyres, and are not capable of standing sustained high speeds, it is nevertheless a fact that tyres suitable for light passenger car service, and giving reasonably good mileages of 10,000 to 12,000 miles, can be made of 100 per cent. butyl rubber, whereas the rubber companies do not yet know how to make the carcase of a tyre from Buna rubber. This means that the tyres for unlimited duty, military service and heavy trucking service, will have to be made of Buna treads and sidewalls and natural rubber carcases, mixed with some percentage of reclaimed rubber.

Haworth and Baldwin have examined the possibilities of different grades of butyl rubber for tyre carcases. They considered that there were distinct prospects for "tailor-made" types of butyl rubber.

TABLE 130. CARCASE STOCKS FROM BUTYL RUBBERS OF INCREASED UNSATURATION [5]

Stock No.	A	B	C	D	E
Formula					
Butyl B—1·45	100·0	—	—	—	—
Butyl B—3·0	—	100·0	100·0	—	—
Butyl B—5·0	—	—	—	100·0	100·0
Zinc oxide	5·0	5·0	5·0	5·0	5·0
Stearic acid	3·0	3·0	3·0	2·0	2·0
Sulphur	1·5	2·0	2·0	2·0	2·0
Gastex	36·0	36·0	36·0	36·0	36·6
Benzyl ether	—	—	10·0	—	10·0
Tetramethylthiuram disulphide	1·0	1·0	1·0	1·0	—
Mercaptobenzothiazole	0·5	0·5	0·5	0·5	1·0
DOTG	—	—	—	—	0·25
Tensile-modulus at 300% elongation					
Cured 15 min. at 307° F.	2000–0–940	2320–210–870	2390–190–860	1370–1310–310	1220–365–640
Cured 30 min. at 307° F.	2540–155–830	2250–460–720	2270–320–760	1180.....200	1060–810–360
Cured 60 min. at 307° F.	2540–235–770	1510–685–560	1670–470–570	1070.....180	1120–845–360
Cured 120 min. at 307° F.	2480–270–740	1290–730–510	1460–475–560	1150.....190	950.....260
Rebound, % (cured 60–120 min. at 307° F.).					
Room temp.	28·6–26·1	37·4–38·6	53·9–53·0	42·8–42·4	50·6–51·5
212° F.	51·0–53·0	77·8–80·7	84·9–79·1	67·9–69·0	65·3–71·8
Heat decompn. (cured 60 min. at 307° F.)	Very badly blown	Slightly porous	Slightly porous	Very slight porosity	Slightly porous

A very interesting product has been obtained from butyl rubbers. They were vulcanized, placed on the mill and mixed with milled natural or synthetic rubber, afterwards vulcanizing the mixture. According to an example, a mixture of isobutylene 70 to 90 parts with butadiene 30 to 10 was polymerized at temperatures ranging from — 50° C. to — 150° C. in the presence of a Friedel-Crafts polymerization catalyst. Polymers of molecular weights 50,000 to 250,000 are obtainable. The following compound was prepared from the copolymer: copolymer 100 parts, sulphur 2, zinc oxide 5, and tetramethylthiuram disulphide 1, to which may be added carbon black 50, stearic acid, and whiting 20. Vulcanization was carried out at 160° C. for 15 to 60 minutes.

The product has the characteristics of a high-grade synthetic rubber, but can be broken down by re-milling. Other materials which may be mixed with the copolymer are: neoprene, Buna-S, Perbunan, Thiokol, etc. The products of the invention have elongations ranging up to 1100 per cent., tensile strengths up to 3500 lbs. per square inch, high abrasion resistance, high flexing resistance, and high resistance to chemical substances such as acids, alkalis and solvents.

Flexon. The preparation of butyl rubber involves the use of very low temperatures, in fact the lower the temperature the better the product.

It has been found that a form of butyl rubber which is inferior to the types already described, yet having many desirable characteristics, can be prepared in an extremely simple manner. This is known as Flexon.

The ingredients are merely mixed in an open vat, low temperature being maintained by addition of solid CO_2. The economies in equipment are astonishing. The great disadvantage is that about half the iso-butylene is lost, and this is a valuable material. Another limiting factor is the amount of solid carbon dioxide which can be made available. Nevertheless, from the point of view of rapid production there are obvious advantages. Flexon may be regarded as an inferior form of butyl rubber. It does not give more than 40 per cent. of the tread wire obtained with rubber.

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CHAPTER 15

THIOPLASTS

THE materials dealt with so far have all been based upon butadiene, and have therefore had reasonably close constitutional affinities with natural rubber. There is a very important group of materials outside this. They are formed in the first place by a condensation process rather than one of polymerization.

The thioplasts form an interesting group of synthetic resins based upon ethylene polysulphide. Although they bear no chemical relationship to elastomers yet they have physical rubber-like properties which bring them into the sphere of elastic materials. When the molecular weight becomes high enough, the materials acquire rubbery characteristics. There is some controversy as to whether these should be regarded as synthetic rubbers. Having much in common with many plastics, they occupy a position between thermoplastics and rubber. As synthetic rubbers they are unique in containing sulphur. They have actually been commercially available in the United States in the form of Thiokol since 1931. About the same time a somewhat similar material known as Ethanite was made by the Belgian Cracking Company. Others have appeared on the market since that time, notably the German materials Perduren.

There has been considerable activity with these ethylene polysulphide synthetic rubbers in Germany. For a number of years Thiokols were produced by the Thiokol Actiengesellschaft, and were selling in large quantities. The I.G. were, of course, very interested at a very early stage. They developed the group of materials known as the Perdurens. Until the war these were available in this country. The properties and behaviour of these materials are very similar to those of the various Thiokol types. Similar materials are also made in other countries, in Great Britain, in the U.S.S.R. and in Japan, but on a smaller scale.

At about the same time as Goodyear was working towards his discovery of the vulcanization of rubber, Loewig and Weidmann [9] first isolated ethylene sulphide.

$$\begin{matrix} CH_2—Cl \\ | \\ CH_2—Cl \end{matrix} + K_2S_5 \longrightarrow —CH_2—CH_2—S_5— + 2KCl$$

In 1861 Crafts [3] purified this and showed the product to be C_2H_4S.

Meyer [13] in 1887 obtained amorphous ethylene sulphide by boiling ethylene dibromide and potassium sulphide. But since scientists were a long way from recognizing the importance of anything that was not crystalline, nothing further came of any of this early work.

Realization of the possibilities came simultaneously in several quarters. In the early 1920's, Patrick [14] in the United States made the discovery which led to the manufacture of Thiokol, while almost at the same time Baer,[1] at Basle University in Switzerland, prepared a similar material. His work formed the basis on which the I.G. subsequently built their production of Perdurens.

Patrick was fortunate. Seeking a new anti-freeze fluid, he mixed ethylene dichloride and sodium polysulphide, and obtained, not a fluid, but a rubber-like material.

Assiduously following up this discovery, a new industry was started. The first commercially available synthetic rubber to appear on the American market was an ethylene polysulphide polymer designated as Thiokol " A ". This product had many shortcomings: it was not nearly so good as natural rubber at high temperatures, nor was it suitable for use at temperatures below zero Fahrenheit, although at that time this was not a critical factor. Its physical strength was not high; tensile strength of about 900 lbs. per square inch was the maximum. However, it had absolutely unique resistance to all classes of solvents, and it was reasonably cheap. It was furthermore completely unaffected by sunlight, even on several years' exposure, and would withstand ozone without cracking. Finally, its water absorption was only a very small fraction of that of the best rubber compound. Such was " Thiokol " in 1931—several years after Dr. J. C. Patrick had discovered it in a Kansas City laboratory.

The thioplasts were found to have quite remarkable resistance to solvents, oils and greases. Since at that time this filled a demand which could not be satisfied, an important commercial field was immediately available.

As a class these polymers possess excellent ageing characteristics and are relatively inert to a large variety of organic solvents. As to solvent resistance, the materials vary somewhat among themselves. Compounds prepared from the ethylene polysulphide are exceedingly resistant to practically all organic solvents. Those prepared from certain other hydrocarbon polysulphides are resistant to the action of petroleum hydrocarbons, but will swell to varying degrees in certain chlorinated and aromatic hydrocarbons. The behaviour of these polymers in organic solvents is influenced by the groups present in the molecules.

Raw Materials. The ultimate raw materials for the production of these synthetic resins are ethylene (obtained from any of the sources earlier described, but notably from natural gas), sulphur, and salt. They are all relatively cheap. Sodium tetrasulphide is obtained by the interaction of sulphur and caustic soda. Organic dihalides are derived from common organic compounds and chlorine. Chlorine comes from salt, while many of the organic compounds are derived from natural gas, or from acetylene via ethylene. While the United States is undoubtedly most favourably placed for these, yet they are freely available in all industrial countries. This fact, coupled with ease of production, has been regarded as offering an excellent source of synthetic rubber in any national emergency.

By virtue of the suitability of a new type—Thiokol N—for re-capping tyres, really large-scale production in the United States is already a fact. No less than 60,000 tons is scheduled in the production scheme.

Manufacture of Thiokol. The manufacture of these synthetic elastic materials is simple by comparison with the process required for the other types of elastics.

A simple laboratory method illustrates the ease with which thioplasts may be obtained:

Dissolve 750 gm. sodium sulphide in water and boil with 300 gm. sulphur. This gives a solution containing chiefly sodium tetrasulphide. It is diluted, 500 c.c. ethylene dichloride added, and refluxed at 70° C. for a few hours. At the end of this time a yellow rubbery solid results, which is ethylene polysulphide.

As now produced by the Dow Company,[23] vast storage tanks of sodium polysulphide and of liquid ethylene dichloride stand side by side. Sulphur and sodium sulphide are caused to react in large tanks which form sodium polysulphide. This is filtered and led to the storage tanks. One of the great features of the process is to have a considerable polysulphide supply since large volumes are required. A suitable quantity of sodium polysulphide is pumped into a reactor tank. The requisite quantity of ethylene dichloride is then pumped in and heat is applied with vigorous stirring. After a comparatively short time—a couple of hours or so—a white watery fluid results, which is a synthetic latex. This contains about 80 per cent. water. The Thiokol latex is then successively transferred to other tanks where it is thoroughly washed in order to remove impurities. It is then transferred to coagulating tanks where an acid catalyst is introduced to bring about coagulation. Acid is introduced at a definite rate in order to control the particle size of the product. The coagulated latex is discharged

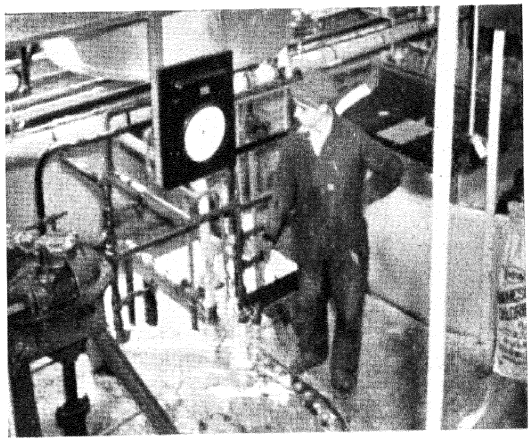

FIG. 60.—Ethylene Dichloride is Measured into the Reaction Tank where a Synthetic Latex of Thiokol is Formed.[24]

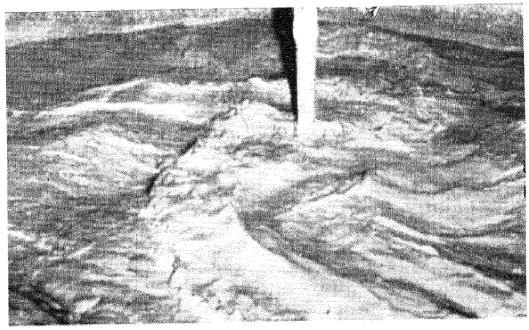

FIG. 61.—Thiokol Latex containing 80% Water and 20% Thioplast.[24]

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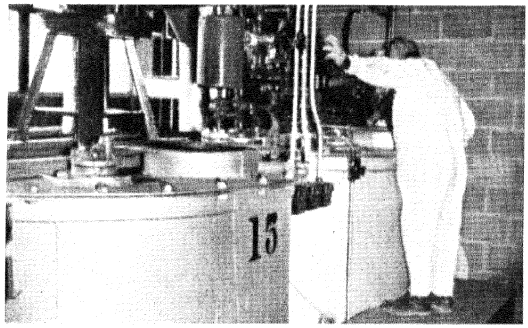

FIG. 62.—Definite Amount of Acid Catalyst added to Give Controlled Coagulation.[24]

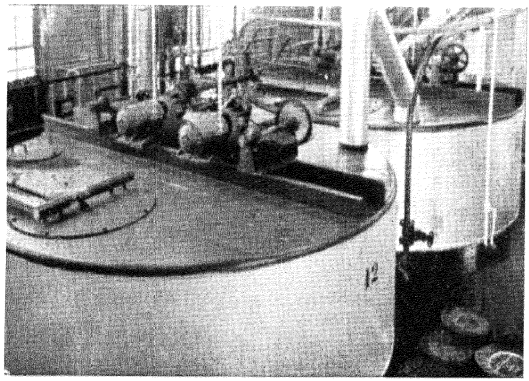

FIG. 63.—Tanks in which Thiokol Particles are Thoroughly Washed.[24]

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into a filter where it is washed and excess water is drained off. It is fed between squeeze rolls and then passed on to a continuous dryer, from which it comes off in particle form. It is then finally pressed into blocks ready for transport.

In spite of the ease of production the amount of Thiokol produced has not been as large as might be expected. Actual authentic figures are somewhat vague. An annual output of about 2000 tons is said to have been reached, although there has now been very considerable expansion stimulated by current international conditions. The limitation has been due to the conservative policy of manufacturing for commercial requirements, which were modest because of the limitations of the materials. For they have some serious disadvantages.

Production in Germany in the past appears to have been on a larger scale. Not only was Thiokol being made and sold under a licensing arrangement with the American concern, but the I.G. were in large-scale production at Saaru. According to one source,[2] production had reached 10,000 tons per annum, i.e. several times the American output. But of course it must be realized that in this case commercial considerations had little to do with output.

Different Types of Thioplasts. By varying the ingredients, notably by substituting other materials for ethylene dichloride, a range of different commercial materials are obtained. Thus Thiokol A is made from ethylene dichloride and sodium polysulphide. It is a greenish-yellow material with a pungent odour and is lachrymatory when heated, e.g. on hot rolls. It contains free sulphur. Thiokol B is made from dichloroethyl ether and sodium polysulphide. It is a more rubbery, darker material than A, with comparatively little odour. It does not give off fumes during mixing. When desulphurized this gave the type known as Thiokol D. Thiokol F (S.G. 1·39) is essentially a disulphide without any free sulphur. It is an amber-coloured rubbery material with comparatively slight odour. A slightly modified Thiokol FA possesses better processing properties, and even less odour than Thiokol F, while not having any material extractable by aviation petrol. This aspect has been more fully discussed by Stevens.[21]

The Perduren series of materials have been developed from somewhat similar materials. According to Stöcklin—[22]

Perduren G is derived from dichloroethyl ether (S.G. 1·68).

Perduren H is obtained from dichloroethyl formal (S.G. 1·56). Another type is obtained from glycerol dichlorohydrin.

The soft type of material produced in Great Britain, Vulcaplas, is based upon glycerol dichlorohydrin.[6] Another harder white type with comparatively little odour is known as Novoplas A.[14] This is similar to

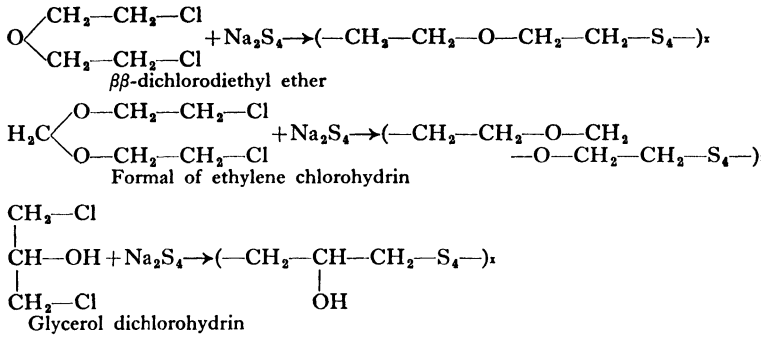

FIG 64.

Perduren G, and intermediate in properties between Thiokol A and Thiokol F, being close to the latter in its processing properties.

The Japanese thioplast known as Thionite is obtained by reacting ethylene diglycoside with sodium tetrasulphide.

Structure of Thioplasts. Patrick [16] has carried out work on the composition of these materials which has brought them into line with other types of plastics. He showed that organic dihalides having a $-CH_2Cl$ group at each terminal, reacted readily with inorganic polysulphides to form long-chain compounds of high molecular weight. When this molecular weight became high enough, rubbery properties were acquired. Molecular growth occurred through elimination of sodium chloride, and in this respect is analogous to the formation of high molecular weight polymers by condensation between dibasic acids and diamines to form long-chain polyamines. So that in effect it is a special case of Carothers condensation. In both cases the reactions involve the interaction of bifunctional molecules to give chain polymers. This reaction can be represented graphically by the empirical equation :

$$\begin{aligned} &X\text{CH}_2\text{—R—CH}_2\text{—}X + \text{MS}_X\text{M} \longrightarrow \\ &2\text{M}X + \text{—CH}_2\text{—R—CH}_2\text{—S}_X \end{aligned}$$

Several examples of this reaction are as follows :

TABLE 131

$$\begin{aligned} \text{ClCH}_2\text{Cl} + \text{NaS}_X\text{Na} &\longrightarrow \text{CH}_2\text{S}_X\text{CH}_2\text{S}_X\text{CH}_2\text{S}_X \ldots \\ \text{ClC}_2\text{H}_4\text{Cl} + \text{NaS}_X\text{Na} &\longrightarrow \text{C}_2\text{H}_4\text{S}_X\text{C}_2\text{H}_4\text{S}_X\text{C}_2\text{H}_4\text{S}_X \ldots \\ \text{ClC}_5\text{H}_{10}\text{Cl} + \text{NaS}_X\text{Na} &\longrightarrow \text{C}_5\text{H}_{10}\text{S}_X\text{C}_5\text{H}_{10}\text{S}_X\text{C}_5\text{H}_{10}\text{S}_X \ldots \\ \text{ClC}_2\text{H}_4\text{OC}_2\text{H}_4\text{Cl} + \text{NaS}_X\text{Na} &\longrightarrow \text{C}_2\text{H}_4\text{OC}_2\text{H}_4\text{S}_X\text{C}_2\text{H}_4\text{OC}_2\text{H}_4\text{S}_X \end{aligned}$$

This conception would bring Thiokol into line with that other great development—nylon.

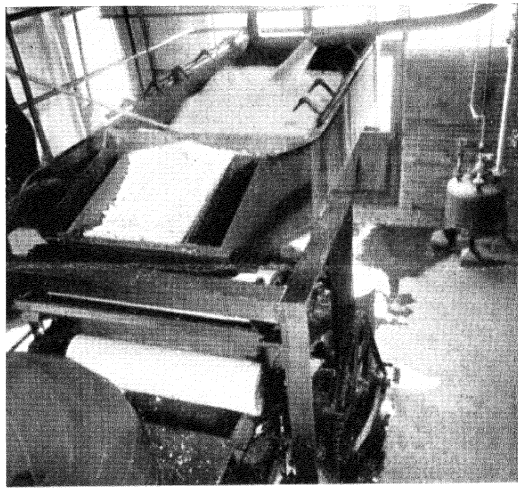

FIG. 65.—Washed Particles is Fed into a Filter Box for Further Washing, then through Squeeze Rolls on to a Continuous Drier.[24]

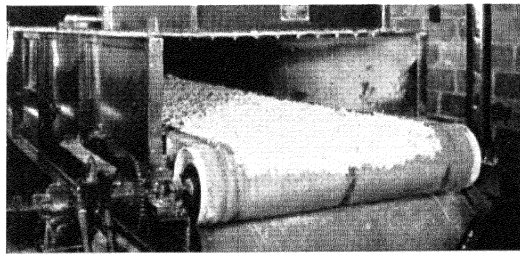

FIG. 66.—Dry Thiokol Particles coming off the Continuous Belt being either Pressed into Blocks or Sheeted.[24]

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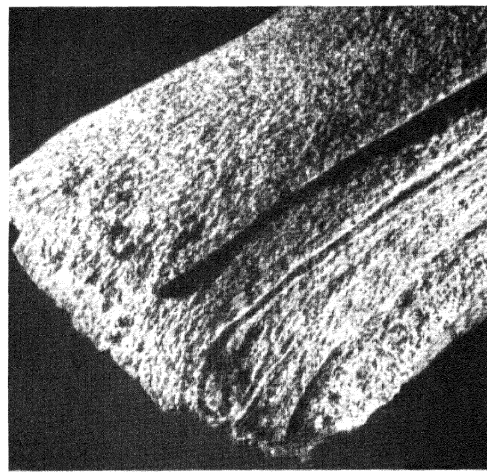

FIG. 67.—Commercial Thiokol Sheet.

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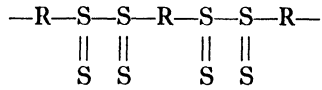
Martin and Patrick [11] suggested that the structure of the polysulphide resins is that of long-chain polymers in which the radicals are connected through disulphide linkages and represented as —R.S.S.R.S.S.R—. According to their hypothesis, any additional sulphur in the material in excess of that required to provide the disulphide linkages is believed to be co-ordinately linked to the sulphur comprising the disulphide linkages. The structure is represented as



with the added possibility that the co-ordinately linked sulphur may be in a trans- rather than a cis- arrangement. The radical may be derived from ethylene or one of its homologues, or it may be obtained from a reactant containing an ether group, a sulphide group, or an unsaturated group. It is of interest that certain of these products exhibit elasticity both when the amount of sulphur is confined to that representing the disulphide linkages as when the primary molecule contains sulphur in excess of these linkages.

In Thiokol and Perduren two sulphur atoms are part of the main chain while two others are attached to them and are not part of the main chain. According to Patrick, if the latter two sulphur atoms are removed Thiokol A gives an inextensible material. On the other hand, Thiokol B yields an extensible elastic material which has been sold as Thiokol D. This is an amber-coloured material with a very slight odour.

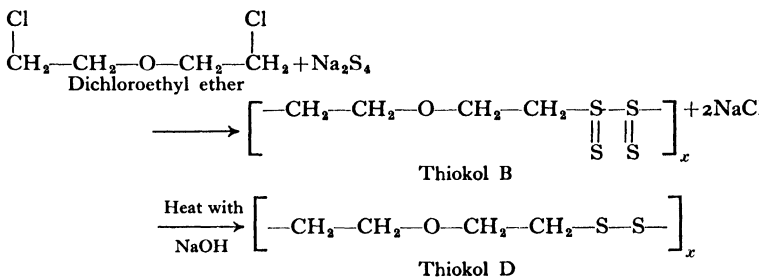


FIG. 68.

The Germans claimed that distinctly improved products were obtained by treating the crude resins with 40 per cent. alkali. According to Spielberger [20] this improved particularly the elasticity and the solvent resistance (as described in an I.G.[8] patent the procedure involved

heating with 40 per cent. caustic soda). Spielberger considered that these thioplasts were made up of " mixed chains " of carbon and sulphur atoms. The great resistance towards solvents was due to sulphur bonds. He thought the vulcanization was caused by a net formation of polysulphide groups.

Commercial Thioplasts. This class of material reaches the consumer in several forms. Most is in the form of sheets and slabs, to conform with normal rubber practice. They are, however, available as suspensions, so that they can be employed in a similar manner to rubber latex. This is a great convenience since thioplasts are so resistant to solvents that the production of solutions is difficult.

Thiokol is also available as moulding powder which greatly increases its scope.

Thioplasts in rubber-like form are handled by the same methods and on the same equipment as are customary for rubber. They are very rubbery, and not particularly thermoplastic, and do not readily form a plastic mass, neither on the mixing mill nor in the Banbury mixer. It is consequently essential to add plasticizers to facilitate the working, the most suitable having been found to be of small amounts of materials such as diphenylguanidine, dibenzthiazyl disulphide, thiuram disulphides, and basic materials generally. Once these have been added, the thioplast works quite easily and the remaining ingredients may be incorporated.

The effectiveness of chemical plasticizers varies with different types of Thiokol. With Thiokol A the most effective are diphenyl guanidine and tetramethyl thiuram disulphide. Diphenylguanidine has the greatest effects, but results in after-hardening, whereas the thiuram is slower working, but does not give after-hardening. For electrical insulation diphenylguanidine is not suitable, and here recourse may be had to thiuram and dibenzthiazyl disulphide.

It is found in the case of Thiokol FA, for example, that the plasticity is controlled by the amount of benzthiazyl disulphide. The softening action exerted is also profoundly accelerated by the presence of 0·2 per cent. of diphenyl guanidine. Depending on the application so the amount of benzthiazyl disulphide is varied, and it is very critical. Thus 0·25 per cent. may give a stiff mix, while at 0·35 per cent. it is likely to be too soft.

The outstanding disadvantages of earlier types of thioplasts, such as Thiokol A, included the dark colour and the pungent odour. In the processing they were distinctly lachrymatory, giving off gas which was most unpleasant. Also when these materials were vulcanized they tended to be porous owing to the trapping of this gas. However, later

materials such as Thiokol F, and FA, are very much better in all these respects, not only the colour and odour being minimized, but there is also a notable decrease of lachrymatory gas. Novoplas A does not smell too badly and is not lachrymatory.

It is essential to add carbon black in order to bring out the optimum physical properties. This exerts a definite reinforcing action, the tensile strength being brought up to the highest value obtainable with these materials—1500 lbs. per square inch breaking value, which of course is materials for Thiokol are semi-hard blacks such as Gastex and soft blacks, notably thermatomic carbon. High proportions of this can be added, up to 200 parts of Thiokol, although a customary loading is 100 parts to 100. It is usual to add up to 1 per cent. of stearic acid to help the dispersion of these blacks. Although these large quantities of black may be added, exceeding even the amount of thioplast, the effect above 60 per cent. is merely to increase the hardness. Other fillers act merely as diluents and cheapeners, and the usual range applied in rubber manufacture may be used for light-coloured articles. Apart from the use of a little stearic acid as lubricant, other ingredients such as rubber softeners, plasticizers, etc., have little effect, and are not used. Coumarone resins appear to be the most suitable. Materials such as Thiokol are lacking in tackiness, and most softeners do little to augment this.

TABLE 132. TYPICAL THIOKOL A COMPOSITIONS

	Parts by weight		
Thiokol A	100	100	100
Rubber	5	5	5
Diphenyl guanidine	0·25	0·25	0·25
Tetramethyl thiuram disulphide	0·10	0·10	0·10
Zinc oxide	10	10	10
Channel black	10	25	45
Stearic acid	0·5	0·5	0·5
Cured for 50 minutes at 141° C.			
T_B lb. in.^{2}	720	750	950
E_B %	435	305	200
H	64	75	84
% Swelling after 72 hours at 50° C in.			
Petrol	nil	nil	nil
Benzene	4	2·2	1·4

Once compounded, the plastic material formed may be processed in the usual manner, i.e. it may be extruded, calendered, moulded, etc. Those processes involving adhesion present difficulty, owing to the lack of tackiness in Thiokol compounds. Thus impregnation and plying up of these materials are not straightforward processes.

TABLE 133. INFLUENCE OF SEMI-REINFORCING BLACK ON THIOKOL FA [10]

	Part by weight					
Thiokol "FA"	100·00	100·00	100·00	100·00	100·00	100·00
Zinc oxide	10·00	10·00	10·00	10·00	10·00	10·00
Semi-reinforcing carbon black	—	10·00	20·00	40·00	60·00	80·00
Stearic acid	0·50	0·50	0·50	0·50	0·50	0·50
Diphenylguanidine	0·10	0·10	0·10	0·10	0·10	0·10
Benzothiazyl disulphide	0·30	0·30	0·30	0·30	0·30	0·30

Data from sheets cured 40 minutes at 298° F.

Parts black 100 Parts FA	M_{300}	T_B	E_B	Set %	H
0	165	165	310	4	41
10	290	415	430	5	48
20	365	665	520	8	52
40	730	1,200	570	19	63
60	1,110	1,265	420	14	71
80	—	1,375	250	6	80

Heat causes materials of this class to vulcanize. In order that the change may come about two things are necessary. There must be a little moisture present, while a certain quantity of zinc oxide is also necessary. Without either of these there is no vulcanization.

According to Patrick[17] the vulcanization that occurs with zinc oxide is an oxidation-condensation with elimination of water, which is thought to explain the change from the plastic to the elastic state.

In the ordinary way about 10 per cent. of zinc oxide is added. With Thiokol A the time required for vulcanization is 60 minutes at 140° C. The change brought about in this way is an improvement in almost every physical property. Tensile strength increases to the maximum possible, the modulus and hardness both increase. The tendency for cold flow decreases. The resistance to solvents, oils, etc., is further enhanced.

Actually Thiokol compositions can be cured satisfactorily without any accelerator. 1·5 per cent. of sulphur does, however, help to speed the cure, without introducing risk of scorching.

One of the most interesting features about compounding these materials, notably Thiokol A, is that in spite of its usual detrimental effect on oil resistance, rubber is one of the most usual additions. It mixes in readily, and facilitates the processing, adds to the tack, and singularly enough does not detract from the oil resistance to any appreciable extent. Additions of the order of 5 to 10 per cent. are usual.

Novoplas A is extensively employed to improve the resistance of Neoprene GN towards oils and solvents. It is also mixed with rubber

and elastomers of the buna class. For addition to neoprene and rubber the following procedure is effective.[14]

(1) The Novoplas A is passed through the mill a few times to soften it, roll temperature being 40–50° C.
(2) The nip is closed and masticated rubber is allowed to form a continuous band on the front roll.
(3) The softened Novoplas A is then added in small amounts at a time until all is incorporated into the rubber, the nip being opened as required to give a rolling bank.
(4) The stearic acid and accelerator are next added and the stock is cut back ten times across the mill.
(5) The carbon black is then added in small quantities at a time, followed by the zinc oxide.
(6) When the fillers are well dispersed, the mix is cut back ten times, then rolled and passed end-wise through a fairly tight nip three times.
(7) After storage, the compounded material should be passed through a mill (roll temperature 40–50° C.) immediately before curing. It is recommended that the material be sheeted to the correct gauge for moulding and that plying up be avoided as far as possible.

Properties of Thioplasts. Thiokol compares favourably with rubber in many of its properties under ordinary conditions, although it is far superior under conditions where oil is present. Its tensile strength does not approach that of rubber compounds, even when reinforced to the maximum, but they retain most of their strength in contact with oils or solvents, these having values which are much higher than those of rubber in the same circumstances. About 1500 lbs. is the top value that can be reached. Thioplasts lack the resilience of rubber at ordinary temperatures. They are much deader. They are little affected by ozone, sunlight, or by oxygen. Although ordinarily the flexing resistance and abrasion resistance are not quite as good as that of rubber or other synthetics, they become far superior in the presence of oils. Under conditions of heat, Thiokol compositions tend to harden up after long periods of exposure. On the other hand, they remain flexible at very low temperatures, Thiokol F, for example, down to — 40° F.

The outstanding advantage of these thioplasts is the unequalled resistance to solvents of every kind. They withstand most effectively precisely those solvents which attack other synthetic rubbers. They are incomparable with respect to petrol, kerosene, fuel oils, and lubricating oils. Thioplasts are very resistant to benzene, toluene, xylene, etc., and

also to the chlorinated solvents. Right from the time when Thiokol A was first brought on to the market it found wide application for all forms of hose, dealing with petrol, oils, and solvents generally, and in accessories for industries concerned with these. It is still the leading material for such applications.

Thiokols are unaffected by water, alcohols, and dilute acids. Strong acids such as nitric and concentrated hydrochloric attack them, as do strong alkalis such as sodium hydroxide.

TABLE 134. SOLVENT RESISTANCE OF THIOKOL AT ROOM TEMPERATURE

(Percentage swelling)

Solvent	Thiokol A after 2 years' immersion [a]	Thiokol F after 1 year's immersion [b]	Thiokol FA after 6 months' immersion [c]
Motor gasoline	0	1	1·5
80/20 Gasoline-benzol	—	3	3·8
50/50 Gasoline-benzol	—	6·3	8
Benzol	1·5	25	26
Kerosene	0	0·8	—
Motor oil	0	0·5	0
Drip oil	0	13·8	13·8
Linseed oil	—	1·3	0
Cotton-seed oil	—	0	0
Ethyl acetate	—	—	6·3
Duco thinner	0	5	—
Acetone	—	2·5	6·8
Methyl alcohol	—	1·3	4
Carbon tetrachloride	0	8·8	12·3

[a] The Thiokol A mix contained 5 parts natural rubber.[4]

[b] Thiokol F 100 parts; Gastex 60 parts; zinc oxide 8 parts, 60 minutes at 100° C.[4]

[c] Thiokol FA 100 parts; zinc oxide 10 parts; soft black 60 parts. D.P.G. 0·10; benzthiazyl disulphide 0·30 part, 40 minutes at 150°.[10]

Thiokol Moulding Powders. One type of Thiokol is available as a prevulcanized moulding power which has found a number of important applications.

At present there are several grades of black powder, differing from each other only in physical hardness. The material is a thermoplastic, occupying in its raw state a greater volume than the solid material (3·30 to 1 approx.). It forms at a moulding temperature of about 300° F., under pressure of 700 lbs. per square inch. It has been found that it shrinks in moulding, but that as the shrinkage is always uni-

form it can be allowed for. The moulding powder is supplied fully compounded and vulcanized. Moulding it is solely a forming operation.

The material may be used in a flash or positive mould with equally good results. It takes about three minutes for the powder to flow and knit together into a smooth, uniformly strong, and highly polished product. More time is needed, however, for pieces larger than 5 or 6 inches in depth and 2 or 3 inches in diameter. Since all trapped air escapes from the material during the moulding operation, it is not necessary to cool the press before opening the mould. Extensive tests on this point have shown that moulded products can be taken from hot moulds without pock-marking or causing porosity. Any flash is reground and used over again.

The most widely used type of Thiokol in the United States has been Thiokol DX (which was actually plasticized Thiokol F). It has now been superseded by Thiokol FA. This has extraordinarily good resistance to petrol, oil, and solvents generally. The most effective softener is found to be benzthiazyl disulphide. Very small proportions, less than 0·15 per cent. effectively soften the material on the mill, and greatly facilitate its processing qualities. The vulcanizing agent is zinc oxide, and an addition of between 5 and 10 per cent. is necessary. The setting is accelerated by additions of benzoic acid or sulphur. 0·75 per cent. of benzoic acid reduces the time of cure from 50 minutes to 30 minutes at 50 lbs. per square inch. Further, it increases the tendency for setting up during the processing.

Thioplasts and Cold Flow. As already indicated the great snag which has checked the progress of this class of synthetic rubbers is the cold flow. Under any degrees of temperature and pressure for any length of time these materials become distorted. Yet under conditions of instantaneous release they are quite as resilient as rubber. The cold flow is of considerable importance, since it means that the products cannot be used under conditions of tension or compression. It also necessitates the cooling of many types of mouldings before extraction, so that there should be no permanent distortion.

The electrical properties are moderate but are comparable with some other synthetic elastic materials. Thus Thiokol A has characteristics which are not as good as those of raw rubber, but can be compounded to give values comparable with some commercial rubber insulations. According to McPherson,[12] Thiokol A had a dielectric constant of 4–4·5 and a power factor of 0·005 to 0·01, while a compounded sample showed values of 4·5 to 5·5 and 0·015 to 0·035 respectively. Having excellent resistance to ozone, sunlight, oxygen, oils, and corrosive influence, it is

extensively employed for cable sheathing, particularly in the United States.

TABLE 135. ELECTRICAL PROPERTIES OF THIOKOL

	Dielectric constant	Power factor	Resistivity ohms/cm.
Raw Thiokol A . .	4·0–4·5	0·005–0·010	—
Compounded Thiokol A .	4·5–5·5	0·015–0·035	$1·6 \times 10^{15}$

Impermeability to Gases. These materials are remarkably impermeable not only to solvents but to gases. This is obviously a matter of great importance in these days. Thus Thiokols find wide application for balloon fabrics and other uses where impermeability is undesirable. This property also has some bearing on moulding behaviour since any air that may be trapped cannot get out in the manner in which air gets out of rubber. This shows up as a tendency for porosity to develop.

According to Sagar,[19] films made from this type of synthetic rubber are as much as twenty times less permeable to air, hydrogen, and other

TABLE 136. PERMEABILITIES TO HYDROGEN OF UNSUPPORTED FILMS

	Average thickness		Permeability		Specific Permeability
	Cm.	In.	L/sq. m./24 hrs.	Cu. ft./sq. yd./24 hrs.	
Disulphide derivative .	0·030	0·012	0·6	0·018	12·5
	0·025	0·010	0·8	0·024	13·8
	0·017	0·007	1·4	0·041	16·2
	0·015	0·006	1·5	0·044	14·6
	0·011	0·004	2·2	0·065	16·8
Tetrasulphide derivative	0·033	0·013	0·2	0·006	4·5
	0·024	0·010	0·4	0·012	6·6
	0·019	0·008	0·6	0·018	7·9
	0·016	0·006	0·8	0·024	8·8
	0·009	0·004	1·2	0·036	7·5
Rubber	0·030	0·012	10·0	0·295	208
	0·025	0·010	14·2	0·419	246
	0·018	0·007	20·0	0·590	250

gases than comparable rubber films; the same superiority also existed in impregnated fabrics.

The table shows the permeabilities to hydrogen obtained with unsupported films of different thicknesses. The organic polysulphide products represent the disulphide and tetrasulphide derivatives obtained

from the reaction between 2,2′-dichloroethyl ether and sodium polysulphide. Values obtained with rubber films of approximately corresponding thicknesses are included for comparison.

TABLE 137. PERMEABILITY OF SYNTHETIC ELASTICS TO HYDROGEN [18]

	Permeabilities to hydrogen at 25° C.
Rubber	22·8
Perbunan	14·4
Neoprene G	5·4
Vistanex	2·6
Thiokol DX	1·9
Pliofilm	0·4

Applications of Thioplasts. In spite of the limitations, thioplasts have found extensive use for a wide variety of applications in the United States. The resistance of Thiokol towards petroleum derivatives automatically gives it pride of place in the manufacture of hose of every description for handling petrol and oils. It is used for transferring petrol and oil to and from tankers, for petrol hose, and for the nozzles of such hose. It also features in hose used for paint-spraying, and other uses where solvents are encountered. They are also extensively used for sheathing cables. For similar reasons it is widely used for printers' rollers, for the actual blocks, and for many other printing accessories. From its first appearance the car industry has utilized it for petrol hose, for tank connections, for many types of gaskets, packings and seals. These applications have been a noticeable feature of the United States' activities. Similar activities have occurred in aircraft production, in which another interesting use is in the production of fuel tanks. Resistant beltings and protective clothings are other important outlets. They are in widespread employment for sealing storage tanks of petrol, oils, solvents, etc.

Recent Developments. Apart from the types which have already been mentioned and which are commercially available, there is information concerning new materials in which existing disadvantages have been overcome. These have recently become available. For example, one type, Thiokol RD, appears to have comparatively little in common with other Thiokol products, except that it has a very pronounced odour, which is quite different from the characteristic pungent smell. Thus its density of 1·03 is far less than that of any of the other thioplasts. It is much closer in behaviour to the butadiene elastomers and to natural rubber. While not possessing quite such good oil- and solvent-resisting properties as the other Thiokol types, yet the mechanical properties are far superior.[5]

TABLE 138. TYPICAL NOVOPLAS A COMPOUNDS [14]

SPREADING MIXES

	Parts	Parts
Novoplas A	90	85
Neoprene GN.	10	15
Stearic Acid	1	1
Magnesia	2	3
Mineral Oil	1	1·5
Kosmos 20	30	30
China Clay	—	100
Zinc Oxide	10	10
Vulcafor M.B.T.	0·2	0·2

Cure: 120 minutes at 120° C. in hot air.

EXTRUSION MIX

	Parts
Novoplas A	95
Rubber.	5
Zinc Oxide	10
Thermatomic Black	25
Stearic Acid	1
Paraffin Wax.	1
Dark Substitute	10
White Substitute	5

Cure: 30 minutes at 60 lb. sq. in. live steam.

Plasticizers and softeners such as are used with neoprene, and with Buna elastomers, are very effective in this instance, for example dibutyl phthalate, tricresyl phosphate, dibutyl sebacate, and the like. Yet on the other hand sulphur and accelerators are used as in rubber compounding, and in similar proportions, while fillers exert comparable reinforcing behaviour. But the most important feature is that cold flow does not occur. For heat resistance sulphur is omitted and a thiuram accelerator is employed.

Processing presents few difficulties. After a few minutes on the mill, which can take almost a full-size batch, all the plasticizers and fillers are added, followed finally by the sulphur. Thereafter calendering, extruding, or any other process may be carried out in the usual manner. Vulcanization requires 50 minutes at 150° C. The tensile strength obtained is of the order of 3000 lbs. per square inch with an elongation of 550 per cent.

There is no tendency for cold flow as exhibited by other thioplasts, the behaviour being nearer to that of the elastomers. Thiokol RD is soluble in acetone and other ketones, in chlorbenzene, ethylene dichloride, etc., and these may be employed for making solutions.

Another type of Thiokol—N, which involves the use of propylene dichloride instead of ethylene dichloride, has aroused great interest and appears to be the type which may feature most prominently in

TABLE 139. PROPERTIES OF THIOKOL RD

Thiokol RD	100
Dibutyl sebacate	20
Zinc oxide	5
Semi-reinforcing black	40
Benzthiazyl disulphide	1
Sulphur	1
Stearic acid	1

Time of Cure Minutes at 298° F	T_B	E_B	M_{300}	Set %	H
15	2970	580	730	12	52
30	3000	530	1025	12	53
50	3050	530	1070	12	53
90	2640	430	1300	8	54

Swelling after 72 hours at room temperature.

	% Linear swell
Petrol	1
Benzene	29
50/50 Benzene/Petrol	13
Carbon tetrachloride	15

the United States production. There is little information available concerning its composition except that it is a " polysulphide " rubber. Some knowledge of its behaviour is shown in the work carried out by Drogin.[6]

Thioplasts Used with Other Elastic Materials. There are a number of soft thioplasts available, such as Vulcaplas, Thiokol S, etc. While these are often unsuitable for the direct manufacture of articles, yet they are extremely valuable ingredients for admixture with other synthetic elastic materials. For example, in one patent Stöcklin [23] made a number of copolymers of butadiene with acrylic nitrile, etc. Al-

TABLE 140. COMPOUNDS EMPLOYED[6]

	Pure gum			Reinforcing black		
	Rubber	Thiokol N	Thiokol RD	Rubber	Thiokol N	Thiokol RD
Elastic	100	100	100	100	100	100
Zinc oxide	5	10	5	5	10	5
Stearic acid	1	0·5	1	3·5	0·5	1
Altax	1	0·35	1	1	0·35	—
D.P.G.	—	0·1	—	—	0·1	—
Sulphur	2	—	1	2·85	—	1
Kosmobile 77/ Dixiedensed 77	—	—	—	50	50	50
Curing temperature	292° F.	287° F.	292° F.	292° F.	287° F.	292° F.

TABLE 141. PROPERTIES OF MIXES WITH REINFORCING BLACK [6]

	Smoked sheet	Thiokol RD	Thiokol N
Plasticity (mm.)	245	457	650
Extrusions (seconds)	2·2	26	36
Modulus at 300%	1450	2200	875
Tensile strength	4075	2925	960
Elongation	565	380	330
Hardness	64	80	70
Tear	1360	385	264
Rebound	48	15	25
Abrasion	202	15	222
Heat build-up (° F.)	137°	184°	187°
Shrinkage	2·9	4·3	0
Electrical resistance	$7{\cdot}5 \times 10^6$	$3{\cdot}4 \times 10^7$	5×10^5

though these had very good resistance to oil, he found this was considerably enhanced by the addition of condensation polysulphide thioplasts which were added on the mixing mill. This procedure is now common practice. For example, the excellent oil-resisting characteristics of neoprene are enhanced. Thiokol S is regarded as an excellent plasticizer for Thiokol RD, particularly where the products are

TABLE 142. PROPERTIES OF PURE GUM MIXES [6]

	Smoked sheet	Thiokol RD	Thiokol N
Plasticity (mm.)	121	440	126
Extrusion (seconds)	2·3	90	2·8
Modulus at 300%	210	605	115
Tensile strength	2680	1500	240
Elongation	820	455	700
Hardness	35	50	35
Tear	384	131	41
Rebound	68	—	53
Heat build-up (° F.)	113°	143°	—
Percentage compression	—	3·3	—
Percentage set	4·0	4·0	—

to be in contact with solvents, such as petrol, that might extract ordinary plasticizers.

Ordinary types of thioplasts are also finding extensive application to elastomer compositions. In these cases the elastomers confer the desirable high mechanical properties, while the thioplasts confer the super-solvent resistance. Thus admixtures with Perbunan, Hycar, Neoprene, etc., are widely used.

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CHAPTER 16

ETHENOID ELASTICS

THE ethenoid resins or vinyl resins are a very important group of materials. They are all based fundamentally upon ethylene, each member possessing the common factor of a vinyl grouping.

The outstanding feature of these materials is that they are thermoplastic, but in many cases they also possess rubbery characteristics. For example, many acrylic esters are intrinsically elastic. In many other cases the elastic properties are dormant, and can be brought into action by the addition of suitable plasticizers or elasticizers. The best example of this is the addition of tricresyl phosphate to polyvinyl chloride. In addition to having rubber-like qualities, they also possess many other useful properties.

The monomeric materials are in most cases liquid, which not only tend to polymerize alone, but will also copolymerize very readily, in many cases with each other. In other cases they will polymerize with materials such as diolefines. Some of these materials have already attained considerable commercial importance, and this is a steadily growing trend. The special characteristics which account for the applicability of these thermoplastics may be summarized as :

(1) Stability to chemicals, more particularly oxidation, ageing, and metallic rubber poisons ;
(2) No taste and odour ;
(3) Good electrical properties ;
(4) High resistance to cold ;
(5) Simple processing properties.

Their mechanical properties in most cases are inferior to those of rubber and elastomer composition.

Among those who have gained importance by virtue of their rubber-like properties the following are outstanding :

Polyvinyl chloride,
Copolymers of polyvinyl acetate,
Polyvinylidene chloride,
Polyvinyl alcohol,
Polyvinyl butyral,
Acrylic esters.

It is interesting to note that styrene, or vinyl benzene is also included in this family of materials, but since its elastic properties are not available in the ordinary working range, this is not considered in detail. Many of these materials are made by emulsion polymerization, and are available as latices. The films deposited from these are distinctly elastic in character.

Polymerization of Vinyl Resins. Vinyl resins in general are prepared by polymerization. The resin molecule consists of a linear chain in which the monomers have reacted with one another at the double bond to form high molecular weight polymers. The reaction may be brought about by irradiation with ultra-violet light or by addition of a small amount of peroxide, ozone, or tetraethyl lead.

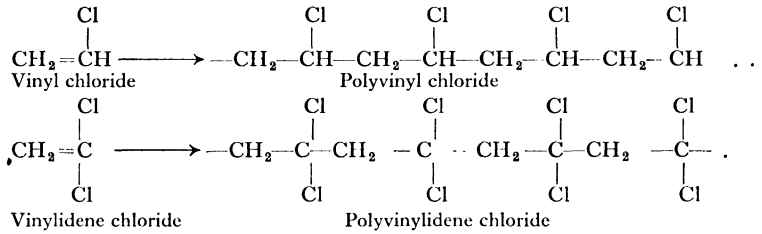

FIG. 69

Vinyl compound polymerization is a chain reaction in which a large number of molecules react in rapid sequence to form one macromolecule. Polymerization is influenced by several factors. For example, traces of certain impurities act as inhibitors and either retard the rate of polymerization or lower the molecular weight of the resin formed, or both.

According to Douglas,[6] the rate of polymerization varies directly as the square root of the catalyst concentration and doubles with every degree of 8° C. rise in temperature. It is also directly proportional to the concentration of the vinyl compounds present. In other words, solvent lowers the rate of polymerization, and the amount of reduction is specific for each solvent. Average molecular weight, or degree of polymerization of the resin produced, is directly proportional to the solvent concentration in the charge. Compounds that are solvents for the monomer but not for the polymer affect the molecular weight in the same way as do solvents for the average molecular weight. The latter decreases with increase in temperature and in catalyst concentration. The properties of the resulting resin are closely associated with its molecular weight and with the relative quantities of the various polymer bands of which the resin is composed.

Certain characteristics vary with the average molecular weight, others are independent of it. Thus tensile and impact strengths, abrasion resistance, and viscosity in solution increase, while water absorption, refractive index, hardness, and electrical properties remain practically constant. Solubility in organic solvents rises with decrease in molecular weight.

Historical Background. Not all of these materials are of recent development. Vinyl chloride was obtained as long ago as 1838 by Regnault,[23] who discovered that it could be obtained by the reaction of dichloroethane with an alcohol solution of caustic potash. He discovered that when this was subjected to the action of sunlight in a sealed glass tube, it polymerized to form a white powder. He also discovered vinylidene chloride. Baumann [1] in 1872 succeeded in polymerizing the vinyl halides to white viscous plastic masses which were unaffected by solvents or acids.

The real background to the present importance of polyvinyl chloride was supplied by the work of Ostromislensky,[21] who aptly enough was trying to make synthetic rubber. His work is of outstanding importance. As far back as 1912 he outlined the conditions for the polymerization of vinyl chloride, vinyl bromide, and other derivatives. He also indicated a method for preparing rubber-like materials from the polymerized products. Ostromislensky was particularly interested in seeking a connection between the polymers of vinyl chloride, which he called cauprene chlorides, and chlorinated rubber. He separated fractions from his polymerized vinyl chloride which he called α, β, γ and δ cauprene chlorides.

He actually found that the composition of a vinyl chloride polymer $C_{32}H_{48}Cl_{16}$ was the same as he obtained for a chlorinated synthetic butadiene rubber, and also it was the same as for the chlorinated isoprene synthetic rubber. The similar solubility behaviour of these materials and their common ability to be transformed into plastic masses suggested to him that vinyl chloride was identical with the chlorination products of butadiene, isoprene, and natural rubber. This work first showed the possibility of the industrial utilization of the vinyl chloride polymers. Ostromislensky also developed suitable technique for achieving polymerization.

About the same time Klatte [16] in 1912 had discovered vinyl acetate. This was subsequently found to polymerize without much difficulty. It is the leading starting material for numerous polymers.

The work on acrylic esters and methacrylic esters was for many years carried out by Röhm,[24] whose researches date from 1901.

The use of catalysts such as benzoyl peroxide in order to bring about

the polymerization of these materials was described by Klatte and Rollett [17] in 1917.

A considerable amount of work was inaugurated about 1925 in line with the work on other synthetic elastics. Ostromislensky was carrying on his work in this field in the United States. Semon of the Goodrich Company had begun his researches which were to result in the production of Koroseal. There was also a considerable amount of work going on in the same direction in Germany, notably by the I.G. chemists. Under the direction of Pavlovitch these materials have been closely studied and widely utilized in the U.S.S.R.

Herrmann and Haenkel [12] discovered in 1928 that polyvinyl acetate could be hydrolyzed to yield polyvinyl alcohol. Subsequently this was found to have latent elastic properties All this work has led up to the numerous important commercial products, many of which have only been developed during recent years, but which are now firmly established for specific industrial purposes. A notable example, of course, is the use of polyvinyl butyral in the manufacture of safety glass for which it was specially designed.

Polyvinyl Chloride. Polyvinyl chloride is one of the most important commercial synthetic materials which is already produced at a rate of many thousands of tons per year. It is widely used in the United States, in Germany, in Great Britain, and in Russia. It is an odourless, tasteless, non-inflammable white powder, having excellent chemical resistance and very low water absorption. It is obtained by the polymerization of vinyl chloride, which is actually a gas at normal temperature, the liquid having a boiling point at -14° C. Vinyl chloride is obtained chiefly from acetylene, by passing it with hydrogen chloride over a contact catalyst. United States production of polyvinyl chloride and its copolymers will be of the order of 3500 tons per month during 1943.

Apart from the method of production based on acetylene, which has already been described, there are two other important methods from dichlorethane which are worth consideration:

First, the manufacture of vinyl chloride by the hydrolysis of dichlorethane. In this process dichlorethane and alcoholic caustic soda are placed in an iron jacketed vessel and dichlorethane is gradually added with continuous stirring. The temperature is regulated by hot water passing through the jacket. The reaction is completed after four hours at a temperature of about 90° C. The procedure is accelerated by increasing the amount of alcohol. The residue left in the vessel at the end of the process may be used over again. The yield of vinyl chloride by this method is between 75 and 85 per cent.

The second method involves the pyrolytic treatment of dichlorethane in the presence of a suitable catalyst. The dichlorethane in the form of gas at high temperature is passed over the catalyst and is cracked. An excellent yield of vinyl chloride is obtained, for example, by passing the vapours over activated carbon between 240° and 350° C. In spite of the advantages this method offers by virtue of the continuity of the process, it is still in the early stages and is being developed.

$$CH_2Cl—CH_2Cl \rightarrow CH_2 = CHCl + HCl.$$

Vinyl chloride polymerizes readily by the action of the usual range of catalytic agents. The process may be carried out in solution or under conditions of emulsion polymerization. It is promoted either by light or by heat. The former has already been described

Heat Polymerization of Vinyl Chloride. Under the influence of heat vinyl chloride readily polymerizes to form resinous substances varying in properties over an extensive range, from rubber-like plastics to hard solids. One method is to add the vinyl chloride together with an acetone solution of the catalyst to alcohol. At 50° C. the reaction may take 80 hours.

Many reagents have been proposed for the use as catalysts in thermo-polymerization of vinyl chloride. It has been suggested, for instance, in Germany to catalyse the reaction with the aid of salts of uranium, cobalt, and lead.[13]

The Carbide and Carbon Chemical Corp.[5] employed tetraethyl lead. Du Pont de Nemours polymerized vinyl chloride by heating it in conjunction with ozonized 90 per cent. methyl alcohol. Lawson [18] recommended the application of small amounts of benzoyl peroxide for polymerization in a chlorbenzol medium conducted in a tin-lined vessel under pressure of 15 atmospheres at 118° C.; the polymer is insoluble in toluol.

Alpha-polymer may be obtained by polymerizing vinyl chloride at 90° C.–120° C. in the following solvents: methyl alcohol, dichloroethane, chlorbenzol, ethyl acetate, benzol, acetone, toluol, in presence of benzoyl or barium peroxides, or ozone, as catalysts.

The polymerization may be accomplished in a solution of methanol, ethanol, pentane, hexane, acetone, aromatic hydrocarbons such as toluol, xylol, in presence of oxidizing catalysts at 40° C.

The polymerization when carried out in alcohol or benzene results in finely dispersed polymeric products.

Properties of Polyvinyl Chloride. Polyvinyl chloride is odourless, tasteless, chemically inert, and non-inflammable except when held in direct contact with flame. It shows thermoplastic properties. It is

almost insoluble in all cold solvents, although readily soluble in hot chlorinated hydrocarbons, such as ethylene dichloride or monochlorobenzene. Heat and light stability are poor. The high softening temperature of this resin makes milling and moulding difficult because inadequate heat stability prevents the use of temperatures high enough to relieve strains. Tensile and impact strength and other mechanical properties of the pure resin are therefore unsatisfactory. As in the case of other vinyl resins, the average molecular weight of polyvinyl chloride can be varied over a wide range, with corresponding variations in physical properties. For industrial use polyvinyl chloride is always plasticized.

This is the raw material for the preparation of commercial plastics. Leading products include Vinylite QYNA made by Carbon and Carbide Corporation, Koron made by the Goodrich Co., and Corvic made here by Imperial Chemical Industries Ltd. It does not find many uses in the straight unplasticized form owing to its comparative lack of flow and the fact that it decomposes very readily at moulding temperatures. The best known materials based on straight polyvinyl chloride are Koroseal and Flamenol [10] in the United States. Leading British materials include Welvic made by Imperial Chemical Industries Ltd., Chlorovene made by Cellomold Ltd., and E.25 made by B.X. Plastics Ltd.

TABLE 143. EFFECT OF SIX PLASTICIZERS ON PHYSICAL PROPERTIES OF "KOROSEAL" [27]

Plasticizer	Hardness	Tensile strength		Elongation	Tear resistance	Heat loss	Flexibility limit
		Kg./sq. cm.	Lbs./sq. in.	%	Kg./cm.	%	°C.
A . .	73	156	2220	350	61·2	2·8	−3
B . .	76	146	2070	365	63·0	6·3	−1
C . .	84	160	2280	325	77·6	26·3	+9
D . .	68	94	1340	380	42·1	32·3	−24
E . .	69	112	1590	395	42·0	6·6	−22
F . .	71	112	1590	340	52·3	8·0	−17

Koroseal was developed by Semon,[28] who started work on the problem in 1927, working upon the principles laid down by Ostromislensky. Semon found that polyvinyl chloride was insoluble at ordinary temperatures in practically every known solvent. On the other hand, he found that at high temperatures it was swelled and dissolved by tricresyl phosphate. On the basis of this he was able to develop a method for plasticizing the material with tricresyl phosphate. This can be done by mixing polyvinyl chloride with tricresyl phosphate

at high temperature either in an internal mixer or on open rolls. It is necessary to add stabilizers in order to protect the material from decomposition, and in general lead salts are used for this purpose. Typical stabilizers include lead carbonate, lead chromate, litharge, etc., being used in quantities of the order of 5 per cent. of the weight of polymer. Small amounts of lubricant material are added, typical ones being calcium stearate or ethyl palmitate.

When this procedure is carried out, a tough rubber-like elastic mass is obtained, which, however, is thermoplastic, and which can be processed or fabricated by all the methods normally used with rubber. It can be extruded, moulded, or sheeted. Its properties are almost entirely dependent upon the amount and nature of the plasticizer which is added. Among materials employed esters are generally the best, while many ketones and sulphur compounds are satisfactory. The outstanding types of plasticizers for this purpose are tricresyl phosphate, dibutyl phthalate, diethyl phthalate, etc. Brous and Semon [4] showed how variation in the amount of a single plasticizer gave a remarkably comprehensive range of properties from hard material down to the consistency of the softest of soft vulcanized rubber. Variation between 10 and 60 per cent. of tricresyl phosphate in a polyvinyl chloride mix gave tensile strength varying from 9000 to 1000 lbs. per square inch, elongation from 2 to 500 per cent., and hardness from 100 down to 15.

TABLE 144. EFFECT OF AMOUNT OF PLASTICIZER ON PHYSICAL PROPERTIES OF "KOROSEAL" [27]

Vol Tricresyl phosphate [a]	Hardness [b]	Tensile strength [c]		Elongation [d]	Tear resistance [e]	Oil extract [f]	Gasoline extracts [g]	Heat Loss [h]	Flexibility limit [i]
		Kg / sq cm	Lbs./ sq in.	%	Kg /cm.	%	%	%	° C.
50	96	233	3320	190	142·8	0·3	−4·8	1·0	20
75	80	211	3000	270	78·5	2·5	8·8	1·3	7
100	68	147	2100	330	53·6	6·3	15·9	1·3	−5
150	49	98	1400	490	28·6	17·9	19·7	1·4	−22

[a] Per 100 volumes of polyvinyl chloride. [b] Shore Durometer, type A, 30° C.
[c] Force required to break standard dumb-bell at 30° C.
[d] Ultimate elongation at 30° C.
[e] Force (in kg. per cm. thickness) required to tear standard sample at room temperature.
[f] Percentage loss in weight after immersion in oil for 14 days at 50° C.
[g] Percentage loss in weight after immersion in motor gasoline for 14 days at room temperature.
[h] Percentage loss in weight after heating in an air-circulating oven for 14 days at 105° C.
[i] Temperature at which a standard strip under a constant weight will bend through an angle of 30° in 2 minutes.

Schoenfeld, Browne, and Brous [27] have shown the different properties obtained for Koroseal prepared with a number of different plasticizers.

Recent technical requirements have made it essential that polyvinyl chloride compositions should retain flexibility at very low temperatures. As a result the standard types of plasticizers have to some extent been replaced by materials such as dibutyl sebacate, dihexyl phthalate, butyl acetyl sicinoleate, etc. Added in suitable quantities they give compounds which will not crack even at temperatures of $-70°$ C.

The material may be further compounded by the addition of a wide variety of filling materials. These tend to make the material shorter and reduce the rubber-like properties. They can confer other advantageous properties such as tensile strength, etc. The quantities used are not very great, up to 25 per cent., for beyond a certain limit the rubber-like properties disappear. The effect of heavy loading is to make the material hard and short; the valuable flexibility at low temperature is adversely affected. Different fillers naturally have different effects. Channel black and silica improve the tensile strength. Softer blacks improve tearing resistance, while other fillers such as clay, whiting, etc., improve oil resistance

TABLE 145. EFFECT OF HIGH PIGMENT LOADINGS [27]

Polyvinyl chloride . . . . . 100 vol.
Tricresyl phosphate . . . . . 89 vol.
Pigment . . . . . As specified

Vol. of Pigment	Thermax					Whiting				
	Hardness	Tensile strength		Elongation	Tear resistance	Hardness	Tensile strength		Elongation	Tear resistance
		Kg./sq. cm.	Lbs./sq. in.	%	Kg./cm		Kg./sq cm.	Lbs / sq. in.	%	Kg./cm
0	74	169	2400	335	62·5	74	169	2400	335	62·5
50	84	155	2200	200	94·6	85	122	1730	225	58·9
100	92	169	2410	95	67·9	92	92	1310	120	46·4
150	95	156	2230	45	30 4	95	70	1000	85	26·8
200	96	151	2140	25	8·9	96	67	960	50	19·6

Polyvinyl chloride is not very compatible with many gums, waxes and oils. Compatible materials include chlorinated diphenyls, coumarone resins, rosin, tung oil, coal tar, and asphalt.

The products prepared in this manner have many useful properties. They are elastic, have high tensile strength and elongation, and excellent flex resistance; they are highly resistant to the effect of oils and solvents, they take up only small quantities of water, and they are very resistant to ageing.

TABLE 146. ACCELERATED AGEING TESTS ON "KOROSEAL"

	Period of ageing	100% modulus		Tensile strength		Elongation
		Kg /sq. cm.	Lbs./sq. in.	Kg./sq. cm.	Lbs./sq. in.	
Bierer bomb	0	98	1390	185	2630	348
	96 hours	105	1490	174	2470	315
	2 weeks	100	1430	172	2440	315
Geer oven .	0	98	1390	185	2630	348
	2 weeks	116	1650	170	2420	275
	2 months	102	1450	174	2470	330

At ordinary temperatures the plasticized material will return to its original shape after any distortion up to the breaking point. When distorted, however, it does not snap back to its original shape as does rubber. Its recovery from either elongation or indentation is slow. When slightly distorted, it recovers in a second or so. More severe distortion may require several seconds before recovery, and if it is stretched to a point just below its elastic limit, it may not recover its original size for several minutes. But eventually it always comes back.

These compositions of polyvinyl chloride are unaffected by ozone and oxygen, and by virtue of their chlorine content they do not support combustion. They have some disadvantage, the chief being that they soften at comparatively low temperatures, about 80° C., when plastic flow becomes evident. However, if applied with due appreciation of the temperature limitations, they are excellent materials.

These materials are very inert chemically, and are consequently highly resistant to chemical corrosion. In this connection the nature of the plasticizer must always be considered in case it should be affected by the chemicals concerned. They withstand strong acids such as sulphuric acid, and nitric acid for long periods, and they also withstand the effect of strong alkalis. For example, they are used for making transparent connections in chemical equipment.

Polyvinyl chloride compositions have excellent resistance towards oils, solvents and greases. They are unaffected by mineral oils, petrol and so on. The only point about these is the tendency for the extraction of plasticizers, so that in contact with such solvents a suitable plasticizer should be employed. They are not affected by alcohol, glycerine, glycols, etc. They are swelled by chlorinated solvents, by nitro solvents, and by ketones.

Polyvinyl chloride compositions are admirably suited for many uses in the cable industry. At the present time the cable industry is the

eading user of polyvinyl chloride. Many profound contributions to the echnique of handling the material have come from the cable industry. A suitably compounded composition has high dielectric strength, it is esistant to ozone, and it can be compounded to give low power factor. The electrical properties have been exhaustively studied by Fuoss.[9] Its use for every form of wire and cable covering is spreading rapidly. Coated wire is fabricated simply by extruding the plasticized material ound the wire to the desired dimension. It offers certain advantages ver rubber e.g. no vulcanization process is required. There is a large ange of bright colours available, either opaque or transparent. Small ores and thin wall thicknesses may be obtained.

TABLE 147. ELECTRICAL CHARACTERISTICS

	Polyvinyl chloride	Polyvinyl chloride-acetate	Polyvinylidene chloride
Resistivity (ohms. cm.) . . .	10^{14}	10^{15}	10^{15}
Breakdown voltage (volts per mil.)	750	450	1000
Power factor (60 cycles) . . .	0·1	0·01	0·02
Dielectric constant	6	3·4	4

Polyvinyl chloride is used for flexible tubings and conduits of every escription and every degree of flexibility. It is employed to make iaphragms, packings, seals, and gaskets. By virtue of its corrosion esistance it is employed for lining metal tanks. It is used to make ransparent tubes for factory and laboratory applications. A notable pplication is in the brewing industry. It is extensively used for nachine parts in the textile industry, where its flexibility coupled with il resistance make it highly valued.

Polyvinyl chloride compositions are used for impregnating cloth. Such fabric is used for raincoats, for shower curtains, and for washable abrics generally. It is used for car fabrics, conveyor belts, printing lankets, diaphragms for motors, etc. It can be taken up into solution which is used for coating metals. Another soft form of material can e cast and is used for moulding purposes

Fairweather has described a most interesting application of polyvinyl hloride to modify the properties of other materials, notably neoprene. Neoprene alone slowly absorbs oil, and polyvinyl chloride slowly loses n oils the plasticizers necessary to maintain its flexibility and firmness f shape. It is therefore proposed to obtain better results by using eoprene in conjunction with plasticized polyvinyl chloride. Simple ixing technique consists in plasticizing the vinyl chloride, e.g. with

tricresyl phosphate, and adding to the mass a preformed mixture of neoprene and vulcanizing ingredients. A typical composition may be: polyvinyl chloride 100, powdered lead silicate $3\frac{1}{2}$, tricresyl phosphate 75, with 30 parts of neoprene 100, litharge 20, rosin 5, magnesia 3, phenyl beta-naphthylamine 2, maleic acid 2. Such a composition is not appreciably affected by oils over prolonged periods.

According to Brous, polyvinyl chloride compositions may be bonded to metals by covering the metal with a coating of chlorinated rubber solution, applying a solution of polyvinyl chloride to this and then attaching the plastic.

Copolymer of Vinyl Chloride and Vinyl Acetate. Polyvinyl chloride has a very high softening temperature, and at this softening temperature the material is somewhat critical, tending to decompose. For many purposes this was a great disadvantage. Just when this fact had become apparent, vinyl acetate and its polymers became available.

Vinyl acetate is a clear liquid with a boiling point of 73° C. It can easily be polymerized to give resinous products which have become commercially important, chiefly for adhesive and coating purposes. It softens at 40° C. but is extremely stable. Efforts were made to use this to plasticize polyvinyl chloride, but physical mixtures were in every case found to be unsatisfactory. On the other hand, when the monomeric materials were polymerized together there was a chemical combination with the formation of a copolymer. In this both vinyl acetate and vinyl chloride formed part of the same molecule chain. The ratio of the two materials can be varied over a wide range. From the point of view of rubber-like properties, these are only apparent when a very high proportion of vinyl chloride is present. In fact, the leading product at the present time (Vinylite VYNW) contains 95 per cent. of vinyl chloride being internally plasticized with the remaining 5 per cent. of acetate. The product has a molecular weight of from 20,000 to 22,000.

The copolymers are obtained as white, tasteless, odourless powders, which are non-inflammable. When the proportion of acetate is high, there is a greater solubility decreasing as the acetate decreases. The material is resistant to oils, solvents, and corrosive influences, and in general shares most of the properties of polyvinyl chloride.

The rubber-like properties are brought out by the addition of plasticizers, similar materials as used with the straight polymer, e.g. tricresyl phosphate, dibutyl phthalate, but a rather wider range is effective in this case.

It is easier to mix and to process than the straight polymer. Mixing

presents little difficulty ; smaller amounts of plasticizers are required, and lower temperatures may be used.

Compounding and Fabricating. The temperature range in which both polymer and copolymer can be handled is more critical than with rubber compounds, and it must be controlled more accurately throughout the compounding and fabricating processes as the characteristics and the quality of the final product as well as its ease of fabrication are thus influenced.

The actual compounding is done by first blending all of the dry ingredients and preferably the lubricant and plasticizer without heat before feeding to the Banbury mixer. This assures that all of the resin comes in contact with the stabilizer before it is fluxed or heated.

Overheating must be avoided. Mechanical working of large masses generates considerable internal heat which, if excessive, may bring about undesirable physical and chemical changes in the resin. Even moderate overheating causes a certain loss of plasticity with consequent difficulty in fabricating. Further overheating may cause decomposition with liberation of traces of hydrochloric acid. For the same reason care must be exercised to avoid storing the stock hot for long periods of time.

The same precautions are necessary when transferring the material from the mill to the calender or extruder. Calendering is done with heated rolls with the stock at a temperature of 120° to 130° C. The sheeted stock can be cooled either in air or by immersion in water.

The same defects as are found in the polyvinyl chloride, also exist here. The material is rather more heat stable, although it is sensitive to traces of iron and zinc which tend to make it decompose.

The copolymer has had a very wide application. It can be prepared as a highly polished transparent sheet, or in any colour. It is used for many articles of attire such as belts, garters, and suspenders, shoe fabrics, raincoats and so on. It has also been fabricated into such things as umbrellas, handbags, tobacco pouches, trunks, flooring, and numerous other diverse articles. It is employed for the coating of fabrics and so on.

In the extruded form the use for covering wires and cables takes pride of place. It is also extruded as tubings of every type. It is utilized as thread in fabrics (e.g. Vinyon) for industrial purposes and as tape and strip for a variety of uses. The type of copolymer used for these applications is made up of 89 per cent. vinyl chloride and 11 per cent. vinyl acetate.

Most polyvinyl chloride and high chloride content copolymers are being used for insulation purposes at the present time both in Britain

and in the United States. The lower chloride-containing copolymers such as VYHH are being used for proofings and general coating production.

Mipolam. The chief material employed in Germany is known as Mipolam. This is a plasticized copolymer of polyvinyl chloride and acrylic ester. The raw material is actually the copolymer known as Igelite. The properties and behaviour of Mipolam in general resemble those of the products already described. Plasticizers and fillers are added in the same manner and approximately the same proportions as in the case of the other polyvinyl chloride derivatives.

Various forms of the material under names such as astralon, guttasyn, vinidur, etc., are used for covering cables, making tubings for numerous industrial applications, transparent sheets, etc. The Germans employ it for hose, for stoppers, acid-resisting linings, filters, packings, gaskets, and so on. They also apply it for protective garments, and in combination with fabric for the whole field open to such products.

Vinidur is the polyvinyl chloride material most widely employed for anti-corrosion purposes, and to replace rubber and metals.

Vinidur has a specific gravity of 1·38. It has a comparatively low softening point (80° C.), is non-inflammable, odourless, tasteless; has a tensile strength of 600 kgs./cm.^{2}, bending strength of 1000 kgs./cm.^{2}, and impact bending strength of over 150 kgs./cm.^{2}. Up to 40° C., Vinidur is resistant to water, alkalis, hydrochloric acid at all concentrations, sulphuric acid up to 85 per cent., nitric acid up to 55 per cent., formic and acetic acid, mineral oil, benzine, alcohol, and carbon tetrachloride. It is not resistant to aromatic hydrocarbons (benzene, toluene, etc.), ether, esters, ketones, and the other chlorinated hydrocarbons.

Vinidur is available as thin sheets 0·2 to 0·6 millimetres thick, 600 to 700 millimetres wide, in rolls; plates up to 40 millimetres thick and in various sizes; tubing from 3 to 150 millimetres in diameter; solid round rods from 5 to 60 millimetres in diameter; and hollow round rods 18 to 60 millimetres in diameter and in lengths of 2 metres. The sheet can usually be employed within a temperature range of − 10° C. to + 60° C., and it can be cut, drilled, turned, sawed, and milled. Because of its low softening point care must be taken to avoid overheating; hence cooling with compressed air during the above operations is recommended. Sheets up to 2 millimetres thick can be cut with shears.

Vinidur sheet can be attached to metal, wood, concrete, and masonry. Metal surfaces are first thoroughly cleaned by sandblasting,

then given three coats of a special cement solution; each coat is allowed to dry thoroughly before the next is applied, a process that takes about 12 hours. Then the metal vessel is carefully heated from the outside to about 130° C., and until the coating takes on a milky appearance. Vinidur sheet at least 0·7 millimetre thick must be used for linings; they are coated with a special cement solution and dried, then carefully placed, so as not to enclose any air, on the pre-heated walls of the container. The edges are allowed to overlap 50 millimetres, and seams and laps receive a final cleaning with methylene chloride and the cement before being stuck together.

Instead of cementing the edges a welding process is frequently preferred. In the welding process developed for synthetics a stream of hot air or gas is directed on the places to be joined; the air is heated in a special heater until it almost reaches the flow temperature of the plastic (usually from 230 to 270° C.), and the burner is held 5 to 20 millimetres away. The edges of the material gradually soften, when a welding wire is inserted into the burner and applied to the softened places. The finished seam may be smoothed down with the tip of the burner. For Vinidur, air is heated to 250° C., while the welding wire is also of Vinidur. Welding offers several advantages over cementing; it is less complicated; the drying period is eliminated; and there is no need of overlapping the edges. The process has proved especially valuable in the production and installation of large-diameter pipes of Vinidur. Before the method was developed all Vinidur pipes and tubes were made on the tubing machines, and the width of the tubing obtainable was thus limited. But welding permits the use of sheets cut by special circular saws to a width corresponding exactly to the required circumference of the pipe. The parts are heated in the tunnel oven, bent to form pipes, and then welded together. The rough shapes are allowed to expand again in the heated chamber and finally given the proper shape with the aid of a divided core.

Large pipes made wholly of Vinidur have given good service where the mechanical demands were not too great; in other cases iron pipes have been lined with the Vinidur. Other uses for anti-corrosive Vinidur are in storage batteries, cooling coils and chemical apparatus.

It has proved satisfactory in coverings for counters and basins.

Vinylidene Chloride. In effect vinyl chloride is an ethylene molecule containing a single chlorine atom. It is possible to introduce another chlorine atom attached to the same carbon, in which case vinylidene chloride is formed. This is a colourless liquid boiling at 31·7° C.

Vinylidene chloride may be polymerized much along the same lines

already described for vinyl chloride. The actual polymer is a white powder, which has no taste, no odour, is non-toxic and does not burn. In actual practice, vinylidene chloride is generally copolymerized, for example with vinyl chloride. In this manner a range of materials becomes available, ranging from the resins which are flexible, and for which there are some solvents, and which soften at about 70° C., up to hard, tough, thermoplastic, for which there are no solvents, and with a high softening point exceeding 180° C.

TABLE 148. RANGE OF PHYSICAL PROPERTIES OF SARAN RESINS [30]

Specific gravity		1·6–1·75
Refractive index	n_d	1·60–1 63
Tensile strength	lbs. per inch^2	Up to 60,000
Elongation	%	25
Modulus of elasticity	lbs. per inch^2 × 10^5	0·4 × 2·4
Flexural strength	lbs. per inch^2	15,000–17,000
Thermal conductivity	10^4 cal. per sec. per sq. cm./° C. per cm.	2·2
Specific heat cal. per	° C. per gm.	0·32
Resistance to heat	° F. (continuous)	160°–200°
Softening point	° F.	200°–325°
Distortion under heat	° F	150°–200°
Tendency to cold flow		Slight
Volume resistivity	ohm-cms. (50% relative humidity and 25° C.)	6 × 10^{13}
Breakdown voltage	60 cycles volts/mil (instantaneous)	500–2500
Dielectric constant	60 cycles	3·0–5·0
,, ,,	10^3 cycles	3·0–5·0
,, ,,	10^6 cycles	3·0–5·0
Power factor	60 cycles	0·03–0·08
,, ,,	10^3 cycles	0·03–0·15
,, ,,	10^6 cycles	0·03–0·05
Water absorption	Immersion—24 hrs.	0·00
Burning rate		None
Effect of age		Becomes stronger
,, ,, weak acids		None
,, ,, strong acids		None
,, ,, weal alkalis		None
,, ,, sunlight		Slight
,, ,, organic solvents		Highly resistant
,, ,, strong alkalis		None
,, on metal inserts		Inert
Clarity		Transparent to opaque
Colour possibilities		Unlimited

These materials have even better resistance to corrosion than has polyvinyl chloride. They have virtually no water absorption, and are practically unaffected by most acids and alkalis in all concentrations. They present certain difficulties in processing owing to the high temper-

atures that have to be used. It is also necessary to have special equipment owing to the fact that iron tends to decompose the material at processing temperatures. The outstanding commercial product is known as Saran, manufactured by the Dow Chemical Company.

Up to the present time the most spectacular application has been in the form of extruded fibres which have been drawn. This procedure enables the production of materials with extraordinary high tensile strength, and with outstanding ability to resist flexing. These materials are being widely used for woven and braided articles. Filaments of the material are being widely applied for the production of textiles, fabrics, fishing lines, and a variety of similar purposes calling for great strength or corrosion resistance. Apart from this, the material is extruded as rod or tubes, or any desired cross section in continuous lengths.

One outstanding application for the material is as transparent tubing for use in chemical industries for the transfer of corrosive liquids. The material is also moulded, either in the ordinary way or by injection, to give a wide range of products. Vinylidene chloride polymers have fairly good electrical characteristics which seem to offer prospects of wide application.

Polyvinyl Alcohol. The monomeric material vinyl alcohol has so far not been isolated. It is, of course, isomeric with ethylene oxide. Nevertheless, the polymer of polyvinyl alcohol is a material of some commercial importance. It is obtained by the hydrolysis of polyvinyl acetate. This was first carried out by Herrmann and Haenkel,[12] who found that they could hydrolyze polyvinyl acetate by means of both acid and alkali.

TABLE 149. PHYSICAL PROPERTIES OF RESISTOFLEX

	Extruded	Moulded
T lb.in^2	5236	2121
E %	213	445
Permanent set %	78	80
Cold flow %	63·2	63·6
Dielectric strength volts per mil	6·1	10·7
Resistivity ohm cm.	$3{\cdot}1 \times 10^7$	$3{\cdot}8 \times 10^7$

In the United States polyvinyl alcohol is the basis of synthetic elastic material known as Resistoflex. It is made by Du Pont de Nemours. The raw materials are available as white powders which are odourless, tasteless, and soluble in water.

For commercial use they are best made as copolymers with a small proportion of polyvinyl acetate. They can be made resistant to water by treatment with various reagents, such as formaldehyde, chromium compounds, dibasic acids, or copper ammonium compounds. They

can be plasticized and then moulded or extruded under moderate conditions of temperature and pressure to give rubber-like articles, or tubes, or coatings. A wide variety of products are now made, including sheets, gloves, gaskets, diaphragms, washers, and tubings.

The outstanding feature of polyvinyl alcohol is the ability to withstand oils, fats, and most organic solvents, including chlorinated hydrocarbons, carbon disulphide, alcohols, esters, ethers, ketones, etc. In fact it is the only flexible material that is completely unaffected by petrol, oils, and most solvents. It is extremely resistant to the action of oxygen and ozone. For example, when subjected to the oxygen bomb test at 300 lbs. pressure of oxygen at 160° F. for ten days it was virtually unchanged. It seems to be almost immune to ageing. Polyvinyl alcohol has high tensile strength and withstands vibration and flexing. Tubing made from it has the singular property of transmitting sound with a minimum distortion and there is no sound absorption by the walls of the tube.

TABLE 150. EFFECT OF SOLVENTS

Tensile strength after 240 hours' immersion at room temperature.

	Lb./sq. in.
Original	5236
Petrol (with lead)	5255
Kerosene	5247
Benzene	5290
Xylene	5351
Acetylene	5340
Trichloroethylene	5140
Carbon tetrachloride	5084
Ethyl alcohol	5779
Ethylene glycol	4335
Acetone	5203
Ether	4980
Butane gas	5332

Polyvinyl alcohol has even better resistance to abrasion than has rubber. It is also only one-twentieth as permeable to gases and liquids.

Polyvinyl Acetals. Polyvinyl alcohol behaves chemically very much like other alcohols, and can be made to undergo a variety of chemical reactions. An outstanding example is the reaction it undergoes with aldehydes when subjected to heat in the presence of a suitable catalyst. Thus in the presence of sulphuric or hydrochloric acid typical acetals are formed. Thus with acetaldehyde, polyvinyl acetal is formed; with formaldehyde polyvinyl formal, and with butyraldehyde polyvinyl butyral is formed.

In actual practice the process is carried out direct from polyvinyl acetate, since the hydrolysis, too, may be carried out in the presence

of acid. The resin is finally recovered as a white precipitated powder which can be stabilized, purified, and dried.

The following method describes how they may be made: [2]

One hundred parts of polyvinyl acetate is dissolved in 185 parts of glacial acetic acid. To this is added 83 parts of formalin and a suitable amount of a mineral acid, e.g. 6·8 parts of concentrated sulphuric acid. This is hydrolysed in an enamelled vessel at 70° C. Samples removed from time to time are analysed for the formalin content, which indicate how far the acetate has been converted to formal. When the desired stage has been reached a suitable amount of neutralizing agent, e.g. 13 parts concentrated ammonia, is added. The neutralized mass is poured in a thin stream into water. The thread-like material is washed and dried.

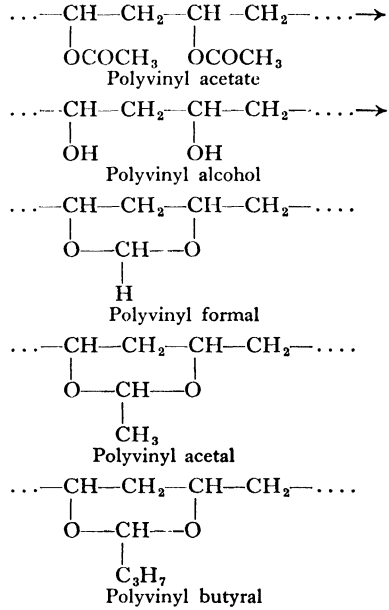

FIG. 70.

While the formal, the acetal, the butyral, etc., are white powders showing no elastic properties, other aldehydes such as furfural give products which are distinctly rubbery. However, when suitably plasticized, the white powders develop marked elastic properties. For example, even the toughest material, high molecular weight polyvinyl formal, when milled with an equal amount of tricresyl phosphate gives

a transparent rubbery plastic which can be stretched 300 per cent. and will recover its original shape when the stress is released, although somewhat slowly.

The materials obtained in this way have already attained profound commercial significance. To some extent this has been a measure of the elastic properties. These are most pronounced in the butyral and least in the formal. Films formed from solutions of these materials illustrate the elastic properties. The acetal and the formal can be compounded with plasticizers to give flexible rubbery materials, which can be moulded, extruded, calendered, etc.

The properties of the acetals, or formals, will depend on the extent to which acetaldehyde or formaldehyde respectively have combined and also the state of polymerization. The latter factor will be measured by the viscosity of a standard solution, and will be directly related to the viscosity of the polyvinyl acetate from which the production commences. These features are best illustrated by the characteristics of some of the best-known materials.

TABLE 151. POLYVINYL ACETALS

	Polyvinyl acetate	3 centipoise	7 centipoise	15 centipoise
	Degree of hydrolysis	Softening points		
Polyvinyl	90%	161° C.	191° C.	220° C.
Formal (Formvar)	90%	170° C.	206° C.	250° C.
Polyvinyl	80%	134° C.	170° C.	188° C.
Acetal (Alvar)	90%	143° C.	180° C.	208° C.
Polyvinyl	80%	114° C.	137° C.	149° C.
Butyral (Butvar)	97%	124° C.	146° C.	163° C.

These figures relate to products of the Shawinigan Company.

Polyvinyl formals are soluble in chlorinated hydrocarbons, dioxan, acetic acid and mixtures of benzene and alcohol. They are insoluble in water alcohols, benzene, toluene, petroleum fractions, vegetable oils and so on.

They may be plasticized by the usual materials such as tricresyl phosphate, dibutyl phthalate, benzyl benzoate, with which they are compatible up to 60 per cent.

Polyvinyl acetals are soluble in most organic solvents such as alcohol, benzene, toluene, acetone and chlorinated hydrocarbons. They are insoluble in petroleum hydrocarbons, oils, and so on.

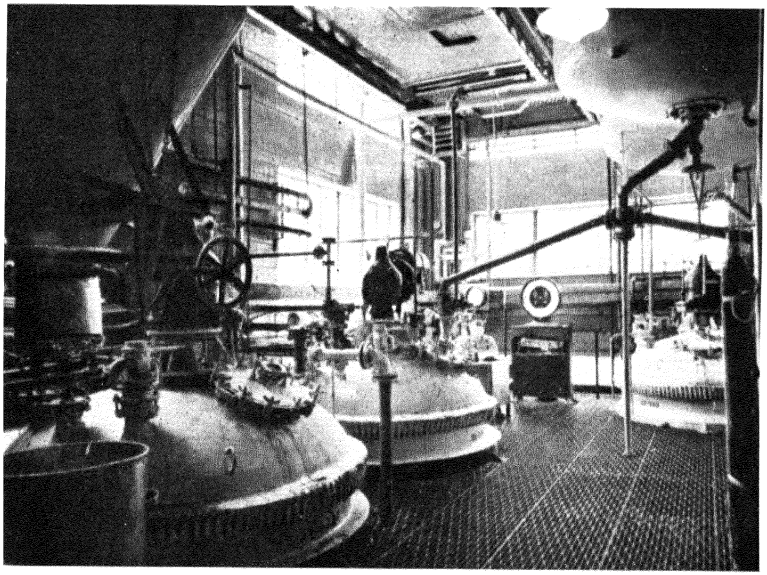

FIG. 71.—Digesters Used in the Preparation of Polyvinyl Butyral.

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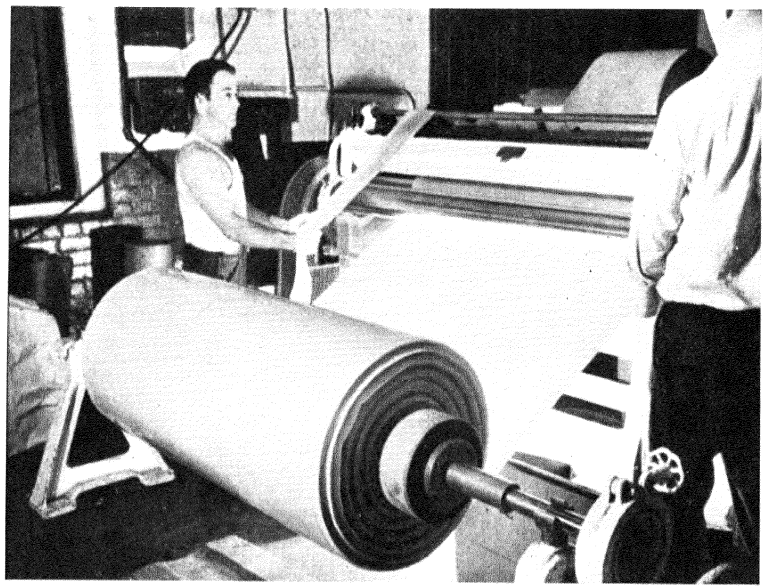

FIG. 72.—Polyvinyl Butyral Formed as a Continuous Rubbery Sheet for Use in Safety Glass.

[*To face page* 309.

The physical properties are summarized in the following table:

TABLE 152. PHYSICAL PROPERTIES OF POLYVINYL ACETALS

	Formal	Acetal	Butyral
Density at 20° C	1·23	1·14	1·107
Refractive index at 20° C.	1·50	1·446	1·488
Dielectric strength (volts/mil.)	1000	1000	—
Dielectric constant	3·7	2·8	—
Power factor	0 007	—	—
Water absorption (%)	1·3	2·0	4·0

Fillers and colouring matter may be incorporated in the usual manner. These materials have a limited range of application owing to a tendency for cold flow. However, they have found a wide application for a variety of purposes. Polyvinyl butyral was specially designed with the object of providing the interlayer in safety glass. For this purpose it contains a little polyvinyl acetate and polyvinyl alcohol.

Polyvinyl butyral was developed for the interlayer of safety glass as the result of a long, comprehensive, and expensive joint research undertaken by a number of United States concerns. It is already employed for the greater portion of safety glass manufactured in the United States.

Polyvinyl butyral is soluble in alcohols, esters, ethylene dichloride, dioxan, etc. It is insoluble in hydrocarbons, oils, and so on. It may be plasticized by addition of the usual types of materials, e.g. tricresyl phosphate, dibutyl phosphate, dibutyl sebacate, etc. In this manner pronounced elastic properties are developed. Thus the elongation possible may reach 400 per cent. The yield under pressure is very easy and the recovery is slow but nevertheless effective. The softening temperature of the plastic is between 60° and 70° C. The tensile strength attainable is also quite high, being 2500 lbs. per square inch when elongation is 400 per cent., and 8000 lbs. when elongation is only 20 per cent. The flexibility is retained at low temperatures.

It ages well, is unaffected by sunlight, and takes up little moisture. The refractive index, obviously of great importance for application in safety glass, is 1·488, while the light transmission is about 90 per cent.

An interesting development in this field is the application of a vinyl acetal as a substitute for rubber in preparing waterproof fabrics. Haas has been able to transform the thermoplastic material into a thermosetting one. He employed Saflex,[26] made by Monsanto Chemical

Co. The material is applied to fabric by conventional methods used for rubber, by spreading or by calendering. The manipulation and processing of the material is said to present no difficulties. Curing is carried out under the same conditions as apply for rubber.

Polyvinyl butyral has been extensively employed for the manufacture of raincoats, water-bags, pontoon boats, food packs and so on, for the use of the United States armed forces. It has also been used as a substitute for rubber in hose-pipes.

Polyacrylic Esters. Acrylic acid has been known for a considerable time. As far back as 1843 Redtenbacher [22] prepared the ethyl ester of acrylic acid. Kahlbaum [15] made the transparent polymer of methyl acrylate in 1880. The methyl, ethyl and propyl esters of acrylic acid were obtained by Weger [31] in 1883. The preparation of numerous other derivatives including acrylic acid amide, the chloride, and the nitrile was carried out by Moureu.[19]

Present-day production is based on the work of Röhm [24] who, in 1901, systematically prepared the solid transparent polymers of the acrylic acid derivatives.[27] Commercial production had to wait until 1931 when successful methods for preparing acrylic esters were developed by Bauer, collaborating with Röhm.[25]

Acrylic ester polymers are chiefly prepared by emulsion polymerization. The liquid monomers are emulsified in water and polymerized by heat or light. The process may be kept under strict control by the addition of cold water. The polymers may be obtained in the form of a stable latex. These emulsions were first described in an I.G. patent in 1931.[14]

Acrylic acid can be esterified with numerous alcohols to give a wide variety of monomers. As the molecular length of the alcohol increases so do the properties of the ultimate polymers become more elastic, the softness, flexibility, heat resistance and water resistance also improving. The properties depend upon the chemical constitution of the monomer and the method employed for polymerization.

The polymerizing conditions largely control the nature of the final product. These may range from hard, tough, thermoplastic materials to rubbery products, down to semi-fluids. Thus the polymer of methyl acrylate is a tough, pliable, rubber-like substance, films of which may be stretched more than 1000 per cent. The polymers of ethyl acrylate are softer and more elastic. Many of the butyl acrylate polymers are rubbery, but much softer and inclined to be tacky. Methacrylic acid derivatives yield polymers which are much harder, only becoming soft when the amyl esters are formed. They all share certain common properties, they are all thermoplastic, very transparent, resistant to

ageing, sunlight or oxygen, and very resistant to chemical attack. They have excellent adhesive properties and are not affected by oils, petrols, or solvents.

In the field of elastic materials the synthetic latex products which give an elastic film have found some application. They dry out to adhesive flexible films, which require no plasticizer. They are widely used for impregnating fabrics, for waterproofing, and for artificial leather. One well-known product is known as Acronal.

One interesting application of dispersions of ethenoid resins has been recently discussed by Nazzaro.[20] This is their use in the preparation of treated paper, which is quite an important commercial commodity. Rubber latex-treated paper was widely used chiefly for making all types of shoes, artificial leather, and for numerous novelty articles. The main applications in shoes were for inner solings, midsolings, quarter linings, sock linings, etc. Latex, being tough, elastic, and giving a continuous film, was an ideal binder. With the virtual disappearance of rubber latex, and shortages in the supply of reclaim dispersions, it has been found that vinyl and acrylic resin dispersions are extremely satisfactory substitutes. Their effectiveness depends to a great extent on the nature of the plasticizer employed, just as in ordinary compositions. They are particularly successful in association with dispersions of reclaimed rubber. They are also found suitable when employed with quite small proportions of dispersions of synthetic rubbers. A variation of this field of application is in the production of flexible fibre board. The resin emulsions are mixed with the pulp in the usual manner in a beater, and the normal production conditions are employed to produce sheets. This represents a very considerable advance in the scope for these resins.

Solid rubbery materials include the Acryloid resins made in the United States by the Resinous Products and Chemical Co., and Plexigum and Plextol made by the I.G.

The most important part played by acrylic acid derivatives at the present time is as the secondary monomer in the production of butadiene copolymer elastomers.

The methacrylic polymers have, however, attained great importance by virtue of their transparency and amazing transmission of light, Coupled with their great strength and lightness they are extensively employed in aircraft for cockpit covers, windows, instrument panels, etc. They are also able to conduct light round curves and bends, a unique property finding many uses. The leading materials are Perspex in Great Britain, Lucite and Plexiglas in the United States.

Although at present the harder types are employed by virtue of

making all types of shoes, artificial leather, and for numerous novelty articles. The main applications in shoes were for inner solings, midsolings, quarter linings, sock linings, etc. Latex, being tough, elastic,

these properties, yet more rubber-like materials with the same optical properties may be anticipated. In which case there may be a perfect combination of the properties of glass and rubber vested in one material.

Another interesting application, where acrylic resins already compete successfully with a rubber product, is for dentures.

It is interesting to observe that Röhm and Bauer [25] have described methods for making skid-proof tyres from acrylic ester polymers containing mineral fillers and other organic ingredients.

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CHAPTER 17

ETHYL CELLULOSE

THERE are a number of cellulose plastics which have been widely used chiefly by virtue of their toughness and flexibility. The most important is of course cellulose acetate. However, ethyl cellulose has in recent years attained some importance. There has been a realization that ethyl cellulose compositions could be prepared which were distinctly elastic and rubber-like. This particular aspect has been greatly developed since the rubber shortage became acute and substitutes were necessary. It has attained sufficient importance for this application as to justify inclusion among synthetic elastic materials. In the United States compositions based on ethyl cellulose are already being described as ethyl rubber.

It has been manufactured on quite a large scale for some years both in the United States and in Germany. The leading producers in the United States include the Dow Chemical Co., the Hercules Powder Co., Celanese Corporation, etc. It has long been manufactured in Germany by the I.G. Farbenindustrie. In Great Britain until recently there has not been any notable interest in this material.

Ethyl cellulose is of much more recent derivation than the older better-known cellulose esters such as cellulose nitrate and cellulose acete. Chemically it is rather different, inasmuch as it is a substitution product of cellulose, an ether, whereas the others are essentially esters. Methods for preparing ethers of cellulose were described, almost simultaneously in 1912 by Dreyfus,[2] Leuchs,[4] and Lilienfeld.[5]

It is for this reason that ethyl cellulose possesses greater chemical stability than either of the other materials. By virtue of being based on cellulose, it has a number of outstanding properties. For example, it is extremely flexible, it has great toughness, it has a high degree of thermoplasticity, it does not tend to age, is unaffected by sunlight, and it maintains its strength at very low temperature. These characteristics are favourably affected by the addition of suitable compounding ingredients.

Production of Ethyl Cellulose. Ethyl cellulose is manufactured from cotton linters or from wood cellulose by the action of ethyl chloride or ethyl sulphate. Cellulose itself is now considered to be composed of long-chain molecules composed of units of glucose residues having an empirical formula $C_6H_{10}O_5$. Each unit has three

reactive hydroxyl groups which can be substituted. Ethyl cellulose is the product obtained when an ethyl group has replaced the hydrogen in these hydroxyl groups. This need not be carried to completion, partial substitution taking place. The extent to which substitution has been carried accounts for the ability to obtain derivatives having somewhat different characteristics. In the production of commercial materials ethyl cellulose is never fully substituted, there being only from 2 to 2·5 ethoxyl groups present in each glucose unit.

It is interesting to notice that cellulose derivatives have a long-chain structure of repeating units, in this respect resembling rubber.

The actual preparation of ethyl cellulose involves the treatment of cellulose, in the form of cotton linters, with a strong solution of sodium hydroxide. Alkali cellulose is formed in this manner. The appearance of the cotton linters is not substantially changed. This alkali cellulose is then treated with gaseous ethyl chloride under pressure. In this process the ethyl group replaces the sodium atom and forms ethyl cellulose. The manufacturing conditions are kept under very careful control so that the reaction may proceed without undue degradation of the cellulose, and incidentally with the greatest economy of alkylating agent. When the reaction has been completed the product is washed with large quantities of water so that water-soluble ingredients are completely removed.

Different Grades of Ethyl Cellulose. A number of grades of ethyl cellulose may be obtained according to the degree to which alkylation has been carried. These are differentiated by reference to the ethoxyl content possessed by each type. For example, the Hercules Company markets five types, as follows [3]:

T—48·5—50% ethoxyl content
N—46·8—48·5% ethoxyl content
K—45·5—46–48% ethoxyl content
G—44·5—45·5% ethoxyl content
D—43·5—44·5% ethoxyl content

The Dow Chemical Co. markets the following types:

TABLE 153. SOFTENING POINTS OF ETHOCEL TYPES [1]

Ethoxy type	Ethoxy content		Softening temp. ° C.	Melting temp. ° C.
	Mols per C_6 unit	%		
Low	2·25–2·25	43·5–45·0	180–160	200–210
Medium	2·25–2·46	45·0–48·0	160–140	200–210
Standard	2·46–2·58	48·0–49·5	140–160	200–210

The more completely substituted materials, containing between 48 and 49·5 ethoxyl, are more widely soluble, have a higher water resistance, a lower softening point, and are more compatible with other materials. They are not as tough as the materials containing lower proportions of ethoxyl.

Apart from the ethoxyl content of the material there can be a variation of viscosity in each instance, which has a profound affect on the properties of the material. It must be clearly understood that ethoxyl content refers to chemical composition, while viscosity is quite different, being a function of the structure. In other words, viscosity is primarily a function of molecular weight or the number of glucose units which comprise the average chain length of the particular derivative. The viscosity will vary, therefore, depending upon the mechanical treatment to which the cellulose has been submitted, and the degree of degradation that has been permitted to take place during production. Commercial materials are therefore supplied in a range of different viscosities corresponding to each particular ethoxyl content. Plastics and films made of high-viscosity materials are usually much tougher and stronger than those made from low-viscosity materials.

Properties of Ethyl Cellulose. Ethyl cellulose has the lowest specific gravity of any of the cellulose derivatives available commercially. Its density is 1·14, so that the cost per unit of volume for any product is comparatively low.

Films may be cast from solutions of ethyl cellulose, and in the form of films ethyl cellulose has exceptional toughness. This strength is retained over a wide range of temperatures. What is important is the fact that even at extremely low temperatures, for example, — 40° F., ethyl cellulose films are extensible and resistant to shock.

Ethyl cellulose has exceptionally good electrical characteristics, not only possessing a high insulation strength and low specific inductive capacity, but it also has a relatively low power factor. The significance of these properties is enhanced by its comparatively low water absorption which may be further improved by suitable compounding. It is resistant to acids and alkalis.

Ethyl cellulose is soluble in most organic liquids. In fact, the only solvents which do not appear to affect it are straight-chain petroleum hydrocarbons. The best solvent combination for preparing solutions comprises 70 to 80 parts by weight of an aromatic hydrocarbon such as toluene or solvent naphtha, together with 30 to 20 parts of aliphatic alcohol such as ethyl alcohol. Such solutions are easily made, and may be handled without difficulty.

Plasticizers. In a similar manner ethyl cellulose is compatible

with a very large number of plasticizers and modifying agents. True plasticizers include such materials as esters, and chlorinated diphenyls. Outstanding among these are the following materials: tributyl phosphate, tricresyl phosphate, triphenyl phosphate, diethyl phthalate, dibutyl phthalate, diamyl phthalate, butyl stearate, amyl stearate, amyl oleate, dibutyl sebacate, benzyl benzoate, triacetin, sulphonamide plasticizers, chlorinated diphenyl, etc. In addition, all fatty acids are miscible with it such as castor oil, fatty acids, stearic acid, oleic acid, etc.; and fatty alcohols such as lauryl alcohol, cetyl alcohol, etc.; in addition to these, castor oil, linseed oil, liquid paraffin, etc., and the corresponding blown oils, are all compatible, and act as plasticizers for ethyl cellulose.

Extenders. Ethyl cellulose, by virtue of its compatibility with many types of resins, may be extended by their use. For example, it is miscible with alkyl resins and alcohol-soluble resins, e.g. natural resins and gums, rosin, phenol-formaldehyde, ester gum, etc.

Apart from these characteristics, it is compatible with all proportions of cellulose nitrate, although it does not mix with cellulose acetate, nor with chlorinated rubber. One of its outstanding characteristics is the fact that it dissolves readily in hot resins, oils, waxes, plasticizers, and mixtures of these. By use of this property, thermoplastic compositions may be prepared which can be applied in the molten condition, and form a basis for adhesives, coatings, etc.

One of the outstanding advantages of ethyl cellulose is its exceptional heat stability. This implies that full advantage can be taken of its thermoplastic character, in contrast to the critical behaviour of polyvinyl chloride. This stability is also well shown by the fact that ethyl cellulose may be melted together with many oils and waxes. It has outstanding resistance to all concentrations of alkalis and is resistant to dilute acids. It is odourless and tasteless.

Ethyl cellulose is easily and smoothly converted into a thermoplastic rubber-like material. This is achieved by mixing with plasticizers in a Banbury mixer, or on open rolls. High working temperatures are employed, comparable with those used with polyvinyl chloride. Fairly large proportions of plasticizers, 50 volumes and upwards, are necessary to give useful extrusion compounds.

As is the case with other plastics the addition of plasticizers causes the range of plastic properties to move up and down the temperature scale. In other words, with high plasticizer additions extremely rubbery compounds are attainable which retain their flexibility at very low temperature, but at the cost of low deformation temperatures in the upper range, and vice versa. Although the electrical character-

istics of ethyl cellulose are extremely good, they are considerably affected by the nature of the plasticizer.

Rubbery Materials. Ethyl cellulose compositions may be handled on standard rubber plant, although rather higher temperatures are necessary than with rubber. The material may be calendered, extruded, and generally processed along the lines normally employed with rubber, allowances all the time having to be made for higher temperatures.

The following mixes give typical examples of compositions which have marked elastic characteristics.

TABLE 154. ETHYL CELLULOSE COMPOSITIONS

(*a*)	Ethyl cellulose	100	
	Chlorinated diphenyl	100	
(*b*)	Ethyl cellulose	100	
	Tricresyl phosphate	75	
(*c*)	Ethyl cellulose	100	
	White paraffin oil	40	
(*d*)	Ethyl cellulose	100	
	Raw castor oil	15	
	Dibutyl phthalate	15	
	White paraffin oil	25	
	Titanium dioxide	1	
	Oil soluble red	0·3	

The following table illustrates some typical flexible materials having elastic characteristics :

TABLE 155. PROPERTIES OF ETHYL CELLULOSE

	Pure film	Flexible plastic
Density	1·14	1·05
Refractive index	1·47	—
Resistivity (ohms/cms.)	10^{14}	10^{14}
Dielectric strength (volts/mil.)	1500	750
Dielectric constant—		
25° C. 1000 cycles	3·0	—
60 „	2·6	2·7
Power factor—		
25° C. 1000 cycles	0·0025	—
60 cycles	0·0030	0·006
Tensile strength (lb./in.^{2})	8000	3000
Elongation (%)	15	90
Softening point	150° C.	80° C.
Melting point	200° C.	—
Water absorption (48 hrs. immersion)	4%	5·0%
Crack point	—	− 55° C.

One of the outstanding features of ethyl cellulose compositions is that they are relatively insensitive to high temperatures. That is to say, that although they become plastic and flow the materials are not decomposed at fairly high temperatures up to 200° C. Almost the

outstanding property is the fact that suitably compounded materials retain their flexibility to extremely low temperatures. For example, compositions may be prepared which will still be flexible at $-70°$ C. This has opened up a number of useful applications for the material.

TABLE 156. PROPERTIES OF TYPICAL ETHYL CELLULOSE PLASTICS[6]

	Ethyl cellulose A			Rubber	
	I	II	III	Dipped article	Inner tube
Water Absorption:					
Percentage of original weight after 24 hrs.	105·1	104·9	104·2	112·8	100·9
Percentage of original weight after 48 hrs.	105·3	111·5	104·9	115·3	101·1
Percentage of original weight after 70 hrs.	106·0	112·8	106·3	117·6	101·2
Dimensional Stability in Boiling Water:					
Percentage of original length after 10 mins.	98·0	99·5	—	102·0	100·0
Percentage of original width after 10 mins.	101·0	101·0	—	103·9	100·0
Percentage of original thickness after 10 mins.	104·0	103·6	—	100·0	100·0
Appearance after removal from water	c	vh	—	Opaque initially	Opaque initially
Dimensional Stability in Water at Room Temperature:					
Percentage of original length after one week	102·4	107·6	—	110·0	101·0
Percentage of original width after one week	103·0	107·5	—	109·2	100·0
Percentage of original thickness after one week	106·2	107·3	—	112·5	101·5
Shore Hardness:					
Shore values	31	29	27	Sample too thin	90
Tensile Strength:					
Pounds per cross-sectional sq. in.	1700	1170	2290	4500[a]	3500[a]
Percentage Elongation	103	86	123	760	575
Permanent Set:					
Percentage of total stretch retained from quick tension, 21° C. (Scott tester Dh-2)	9	6	24·2	0	0
Percentage total stretch retained from slow tension, 21° C.	11·5	81	—	0	0
Percentage total stretch retained from slow tension, 50° C.	100	100	—	0	0
Flexibility at $-20°$ C.:					
Number double folds (M.I.T. Flex Tester)	170	No sample	97	65,000+	Sample too thick
Flexibility at Approximately $-78°$ C.:					
(Pinch test)	brittle	flexible	brittle	flexible	brittle
Burning Rate:					
Seconds for 3-in. length	71	28	—	20	66

Identification of materials tested:
A-Ethyl cellulose, Grade "N" used (46·8 to 48·5 ethyl content, 100 centipoise viscosity).
Composition, Col. I: Ethyl cellulose.
Raw castor oil.
Col. II: Ethyl cellulose.
Cotton-seed oil.
Raw castor oil.
Col. III: Ethyl cellulose.
Raw castor oil.
Opal wax.

[a] Author's figures.

The applications of ethyl cellulose have hitherto been mainly confined to the preparation of lacquers, varnishes and adhesives, and as modifying agents for waxes and resins. It has been increasingly utilized for the preparation of plastics which are moulded both by compression and injection. Suitable compounding enhances the flexibility and extensibility of the material to such an extent that it is being widely used to replace rubber. By virtue of the excellent electrical characteristics the high flexibility and toughness, ethyl cellulose compositions are widely employed for wire insulation and similar applications. Fillers, plasticizers, and colouring materials may be added to ethyl cellulose. The best filler is zinc oxide when used up to 30 per cent. loadings. Other fillers may be incorporated, but heavy loadings detract from the performance. Ethyl cellulose compositions are ordinarily transparent, but by the use of suitable pigments a complete range of colours may be obtained, either transparent, translucent, or opaque.

Wiggam [6] has made a comparison of ethyl cellulose compositions with rubber compounds. He pointed out that their handling differs from that used with rubber, in particular vulcanization being unnecessary. Processing is much more rapid with consequent higher production. He found that in some properties they were superior to rubber. Abrasion could be made better, they were resistant to ozone and to oils and petrol. On the other hand they had very little resilience or " bounce ".

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CHAPTER 18

SOME ADDITIONAL COMPARATIVE PROPERTIES OF ELASTICS

IT is obviously a matter of great practical importance to be able to compare the properties of the various synthetic elastics, and also to be able to detect which type is present in any particular product.

Although these are still early days for any really comprehensive assessment and comparison of the merits of the various synthetic elastic materials, yet a certain amount of data has been accumulated.

The analytical side is very different. At the present time no scheme has been developed for the systematic examination and identification of the numerous existing materials and their compositions. The matter is complicated by lack of methods for identifying the various products.

There are, of course, many points of difference. A number of raw materials have some outstanding characteristics which facilitate recognition. For example, thioplasts can generally be readily detected by the typical unpleasant odour, which compounding cannot entirely eliminate. On the other hand, it is also the case that thioplasts are extensively used as modifying agents together with other synthetic elastics, so that a false conclusion could easily be reached.

Obviously the appearance of thermoplastic properties with rise of temperature sharply divides the groups of materials. But the identification of commercial highly compounded products is a very difficult proposition.

When one considers the complications of standard rubber analysis, the enormity of the task of establishing any systematic routine for the testing of highly compounded elastomers becomes apparent. Most commercial products are likely to contain high proportions of carbon black, which further complicates the problem. Furthermore, it must be remembered that no method exists for the direct estimation of natural rubber in a compound, this value invariably being obtained by difference. Consequently, the analytical aspect of synthetic elastics is beset with thorny problems.

Synthetic materials have some fairly obvious chemical differences from natural rubber, thus neoprene contains chlorine which could be readily detected analytically. Perbunan, too, contains a fairly large proportion of nitrogen which might be detected. But by far the most

extensively used synthetic rubber will be Buna-S or GR-S. This is a pure hydrocarbon just like rubber, and behaves very much like it. Analysis will not show up any marked difference.

This is an important point, for, already, various newspapers in this country have quoted categorical statements from anonymous experts about the lack of evidence regarding the use of Buna-S by the Germans, and discounting their actual use of synthetic rubber. It would be very informative to know what methods were employed to form this opinion. Products prepared by the author have certainly baffled experts from whom an opinion was asked.

Comparative Properties of the Pure Materials. There is not a great deal of difficulty in differentiating between the various raw materials. Since they are not used in this condition these comparisons are clearly academic. Nevertheless, aids to identification are useful for routine purposes.

Appearance and odour will distinguish many. The only difficulty might be encountered in the elastomer group comprising Perbunan, Perbunan-Extra, Chemigum, Hycar, Buna-S, and Buna-SS. All, except the latter two, contain large proportions of nitrogen which can be estimated by the standard Kjehldahl method.

In the case of the thioplasts, apart from their odour, hydrogen sulphide will be emitted when they are subjected to the action of heat. The amount of free and bound sulphur can be estimated by the usual technique employed for vulcanized rubber.

The action of heat on neoprene, polyvinyl chloride, and polyvinylidene chloride will cause evolution of gases which will give the typical cloudiness in silver nitrate solutions showing the presence of chlorine. The polyacrylic esters give characteristic odours of the monomers when strongly heated.

Comparison of Physical Properties. Many interesting differences are shown up by comparisons of various physical properties. Thus the densities are shown in the following table. The straight hydrocarbon materials have the lowest densities, while the materials containing high proportions of chlorine and those containing sulphur are the heaviest materials.

TABLE 157. DENSITIES OF UNVULCANIZED MATERIALS

Material	Density gm./c.c.
Natural rubber	0·911
Neoprene	1·25
Perbunan	0·96
Perbunan-Extra	0·97
Buna-S	0·9
Hycar O.R	1·00
Chemigum	1 06
Thiokol RD	1·03
Butyl rubber	0·91
Thiokol A	1·60
Thiokol DX	1·34
Thiokol F	1·38
Perduren G	1·68
Perduren H	1·56
Perduren L	1 17
Vistanex H.M. (25° C.)	0 9125
Vinyl chloride polymer 0% plasticizer	1 42
Vinyl chloride polymer 30% ,,	1·33
Vinyl chloride polymer 60% ,,	1 25
Polyvinyl formal	1·23
Polyvinyl butyral	1·110
Polyacrylic ester	1 200

Wood[14] has recently determined the densities of a number of available synthetic elastics very carefully. His results are shown in the following table.

TABLE 158. DENSITY VALUES AT 25° C

Name	Manufacturer	Density gm /c c
Neoprene GG.	Du Pont Co.	1 2307
Neoprene E	Du Pont Co.	1 2384
Neoprene FR	Du Pont Co.	1·1406
Neoprene GN	Du Pont Co.	1 2290
Buna-S	Firestone Tyre & Rubber Co.	0 9291
Buna-S*	Firestone Tyre & Rubber Co.	0 9358
Buna-S	U.S. Rubber Co.	0 9369
Buna-S	Standard Oil Development Co.	0 9390
Chemigum IV	Goodyear Tyre & Rubber Co.	0 9391
Hycar OS-20	B. F. Goodrich Co.	0 9385
Hycar OS-30	B. F. Goodrich Co	0 9303
Chemigum I	Goodyear Tyre & Rubber Co.	1 0135
Hycar OR	B. F. Goodrich Co.	0 9097
Perbunan	Standard Oil Development Co.	0 9684
Thiokol RD	Thiokol Corp.	1 0564
Thiokol A	Thiokol Corp.	1·5983
Thiokol FA	Thiokol Corp.	1 3298
Butyl B-1 45	Standard Oil Development Co.	0·9175

* GR—S type.

Many of the thermoplastic materials, the ethenoid resins in particular, are valued because of their transparency. Polyvinyl butyral depends entirely on the combination of transparency with rubber-like properties. In this connection the refractive indices of the various materials is of some interest.

TABLE 159. REFRACTIVE INDICES OF UNVULCANIZED MATERIALS

Material	Temperature ° C.	n_D
Natural rubber	25	1·5190
Neoprene	25	1·5580
Neoprene	30	1·5562
Perbunan	25	1·5213
Perbunan	30	1·5562
Vistanex H.M.	25	1·5089
Vistanex L.M.	10	1·5131
Components of plasticized vinyl chloride polymers :—		
Vinyl chloride polymer (unplasticized)	40	1·565
Tricresyl phosphate (plasticizer)	40	1·5494
Polyacrylic ester	20	1·49
Polyvinyl butyral	26	1·488
Polyvinyl formal	20	1·50

Examination of these materials under ultra-violet light does show up certain distinctive features. The behaviour is shown in the following table :

TABLE 160. EFFECT PRODUCED BY ULTRA-VIOLET LIGHT

Material	Colour by Ultra-violet Light
Butadiene polymers and Copolymers	Strong violet
Polyvinyl formal	Strong whitish-blue
Polyacrylic ester	Bright blue with red tint
Polyvinyl chloride	Greenish blue
Polyacrylic nitrile	Light yellow
Polyvinyl alcohol	Bright white
Neoprene GN	Blue white on fresh surface
Neoprene I	Dull blue
Thiokol A	No fluorescence ; dark brown colour
Thiokol B	,, ,, ,, ,,
Thiokol F	Dark purple
Thiokol FA	Pale white fluorescence
Thiokol RD	Brilliant blue-white
Novoplas A	No fluorescence
Polyisobutylene	Light blue

The period length of fibre patterns obtained by X-ray examination of stretched samples supplies another set of values which is of interest from an academic angle as contributing towards a knowledge of the structure of the materials concerned.

TABLE 161. X-RAY DIAGRAM: STRETCHED RUBBER-LIKE SUBSTANCES

Material	Fibre Period in Å after Stretching the Sample
Polyvinyl alcohol [5]	2·52
Thiokol A [3]	4·32
Polyvinylidene chloride [1]	4·71
Neoprene [2]	4·8
Gutta-percha	4·8
Polyvinyl chloride [3]	5·0
Rubber [7]	8·2
Thiokol B	8·8
Polyisobutylene [4]	18·5

Kluckow [6] has described some of the criteria employed in Germany to distinguish between the many and varied types of synthetic elastics. He considered them in relation to natural rubber.

Natural rubber (sp. gr. 0·93, nitrogen content up to 4 per cent.) begins to soften above 120° C., at still higher temperatures turns into a thick brown oil, which with continued heating yields a large number of dissociation products with boiling points from 18° C. to 300° C. Natural rubber easily burns when held in a flame, giving off a great deal of thick smoke. Finely ground rubber swells and becomes jelly-like in benzene. When rubber is masticated on cold rolls for various periods, rubber solutions with rapidly decreasing viscosity result.

The butadiene-styrene copolymers Buna-S and Buna-SS (sp. gr. 0·92, nitrog n content 0·02 per cent.; portion soluble in acetone, 6·2 to 6·9 in the case of Buna-S and 6·9 to 8·1 in the case of Buna-SS) burn with a thick smoky flame; they also swell and become jelly-like in benzene when finely ground, but mastication has considerably less effect than on natural rubber.

Perbunan (butadiene-acrylic-nitrile copolymer) has a specific gravity of 0·92; while the nitrogen content is 6·7 to 7·3 per cent.; unlike the other synthetic rubbers and natural rubber it is soluble in ketones (acetone) and, when burnt, gives off a more aromatic odour than natural rubber, which can easily be distinguishable from the odour of burning Buna-S or Buna-SS.

The chloroprene polymers, Neoprene or Sovprene (sp. gr. 1·25), have a characteristic odour. When heated to 50–60° C. they become softer and stickier than masticated rubber. They do not burn when held in a flame.

Perdurens (Thioplasts) have a peculiar, unpleasant odour; when samples are heated in a test tube, the smell is of sulphide of hydrogen and other sulphur compounds, but when they are burnt, there is an acrid sulphur-dioxide odour. Perdurens are soluble in trichlorethane,

but not in benzene and benzol. Sheets of the materials have a tendency to flow in storage.

The chemical characteristics of Thiokol are the same as of the Perdurens; the specific gravity is 1·62, sulphur content about 83 per cent. It also is soluble in trichlorethane, but insoluble in benzene, benzol, and mixtures of motor oils.

Kluckow extended his comments about vulcanized materials as follows. Vulcanized natural rubber goods are most easily identified by burning, when the well-known burnt rubber odour should be detectable. Another means of identification is testing the extensibility. Buna and Perbunan goods do not give off a rubber odour when burnt. Benzene hardly affects Perbunan goods, but its action on Buna-S and Buna-SS is distinctly noticeable.

Light-coloured Buna and Perbunan vulcanizates and those low in fillers have poorer elasticity and tensile values than natural rubber vulcanizates. The tensile strength of the synthetic rubbers only approaches that of natural rubber when carbon black is present in appreciable quantity.

According to Kluckow, Thiokol and Perduren goods give an acrid sulphur dioxide odour emitted when they are burnt, and are easily recognized. The high sulphur content is also responsible for the high specific gravity. Although very resistant to oils and fats, their mechanical properties are comparatively poor. Furthermore, they have relatively low resistance to heat, and, as a result of the high sulphur content, harden more rapidly around 100° C. than other materials.

Neoprene goods can be distinguished by the fact that in consequence of the high chlorine content, they do not burn when held in a flame; they resist benzene, petroleum, and mineral oils, but swell rapidly in benzol and chlorinated hydrocarbons. Unlike Perduren and Thiokol, they resist heat well and have better mechanical properties.

Non-vulcanizable synthetics are usually employed in combination with softeners, resins, fats, etc., and when so compounded, it is almost impossible to distinguish them. However, when used alone or mixed with inorganic fillers only, the odour when they are burnt is a serviceable guide.

Softened polyvinyl chlorides (Igelites), says Kluckow, compounded or not, give off a strong hydrochloric odour when burnt. Their cold resistance is lower than that of the vulcanizates, and compared with neoprene vulcanizates, they also have less resistance to heat. For whereas the latter remain hard at temperatures of 140–170° C., Igelites soften under these conditions.

Polymerized isobutylene compounds (Oppanols) easily dissolve in benzene. They retain their flexibility at extremely low temperature.

Oppanols and polyacrylic acid esters yield ester-like, odiferous dissociation products when subjected to dry distillation.

Comparison of Properties of Vulcanized Materials and Compounded Materials. In 1940 Wood [15] prepared an excellent summary of existing information on synthetic elastics. Some of his tables have been modified and extended in the light of subsequent experience. For example, it is of considerable practical interest to be able to compare the tensile strength and elongation of synthetic elastic with the values for natural rubber. While the compounds are not strictly comparable, the figures do afford some guide in this respect. The individual characteristics in relation to fillers, etc., have already been commented upon.

TABLE 162. MAXIMUM TENSILE STRENGTHS AND CORRESPONDING ELONGATIONS

	Unvulcanized		Vulcanized pure gum		Vulcanized carbon black compound	
	T_B kg/cm²	E_B %	T_B kg/cm²	E_B %	T_B kg/cm²	E_B %
Natural rubber [13]	25	1200	290	710	350	650
Neoprene [9]	30	1100	300	820	290	760
Buna 85	—	—	—	—	175	600
Buna 115	—	—	—	—	200	700
Buna S	—	—	—	—	280	650
Perbunan	—	—	150	900	320	600
Hycar OR	—	—	48	540	300	510
Butyl rubber	—	—	250	1000	—	—
Thiokol "A"	—	—	—	—	60	370
Thiokol "D"	7	570	35	750	120	610
Thiokol "RD"	—	—	—	—	220	530
Vistanex M.M.	20	1000	Not vulcanizable		Not vulcanizable	
Vistanex H.M.	60	1000	,,	,,	,,	,,
Koroseal 0% plasticizer	400	2	,,	,,	,,	,,
Koroseal 30% plasticizer	270	170	,,	,,	,,	,,
Koroseal 60% plasticizer	70	500	,,	,,	,,	,,
Polyvinyl chloride 50% Tricresyl phosphate	160	350	,,	,,	,,	,,
Vinylite V. 33% plasticizer	210	300	,,	,,	,,	,,
Polyvinyl formal	250	100	,,	,,	,,	,,
Polyvinyl butyral	175	400	,,	,,	,,	,,
Acrylic ester (66% carbon black)	50	250	,,	,,	,,	,,

The following table gives a useful summary of characteristics of various synthetic materials with emphasis on factors of interest from the engineering viewpoint:

TABLE 163. PHYSICAL PROPERTIES OF SYNTHETIC AND NATURAL RUBBER [10]

	S.G.	T.S.	Shore hardness	Max. temp. use	Dielectric strength v./mm.
Buna-S	0·94	3800	15/90	300	—
Butyl	0·91	500–3000	15/90	250/300	25,000
Chemigum—Oil Res.	1·0 –1·5	800–4000	30/90	300	—
Chemigum-tyres	1·0 –1·15	1000/4000	50/65	450	—
Hycar OS, hard	1·1 –1·3	4000/11,000	—	300	—
Hycar OR, soft	0·99–1·6	1000/4500	15/95	300	—
Hycar OS, soft	0·96–1·20	1000/4000	20/95	250	—
Koroseal,[a] hard	1·3 –1·4	2000/9000	80/100	212	30,000/50,000
Koroseal, soft	1·2 –1·3	500/2500	30/80	190	15,000/30,000
Neoprene	1·25–1·30	1000/4500	15/95	300	—
Perbunan	0·96	500/5000	30/90	300	—
Resistoflex[b]	1·26	2000/5000	—	250	6000/10,000
Thiokol FA	1·34	1400	25/90	200	—
Vistanex,[c] medium	0·9	200	—	—	—
Vistanex, hard	0·9	550	—	—	—
Natural rubber, hard	1·17–1·18	4000/11,000	70/100	220	—
Natural rubber, soft	0·93–1·17	1000/6000	30/80	150/180	—

	Heat effect	Abrasion resistance	Sunlight effect	Ageing effect	Machining qualities
Buna-S	Stiffens	=to rubber	Slight	=rubber	Can be ground
Butyl	Softens sl.	Good	None	Better than rubber	Can be ground
Chemigum—Oil Res.	Stiff.	Excellent	=to rubber	Stiffens	Can be ground
Chemigum-tyres	Stiff	Excellent	Deteriorates	None	—
Hycar OS, hard	Softens 300	Good	V. slight	None	Excellent
Hycar OR, soft	Stiff. sl.	Excellent	Slight	Highly resistant	Can be ground
Hycar OS, soft	Stiff. sl.	Excellent	Slight	Highly resistant	Can be ground
Koroseal,[a] hard	Softens	Good	None	None	Good
Koroseal, soft	Softens	Good	None	None	Can be ground
Neoprene	Softens sl.	Excellent	None	Highly resistant	Can be ground
Perbunan	Softens sl.	Excellent	Slight	Highly resistant	Can be ground
Resistoflex[b]	Softens	Good	None	None	—
Thiokol FA	Hardens sl.	F.G.	None	None	Excellent
Vistanex,[c] medium	—	—	None	Better than rubber	Cannot be machined
Vistanex, hard	—	—	None	Better than rubber	Cannot be machined
Natural rubber, hard	Softens	Good	Discolours	None	Excellent
Natural rubber, soft	Softens and deforms	Excellent	Deteriorates	Highly resistant	Can be ground

[a] Polyvinyl chloride. [b] Polyvinyl alcohol. [c] Polyisobutylene.

The excellent swelling characteristics of most synthetic elastics in contact with solvents and oils are largely responsible for their existence, and certainly constitute the chief justification for the high cost.

Another useful comparison is given by the resistance offered to many corrosive chemicals and solvents. There is little quantitative data on this aspect and only a qualitative indication can be offered.

One of the most useful investigations of comparative properties has been carried out by Sebrell and Dinsmore.[11] They prepared comparable tread mixes and mechanical mixes based on many of the existing commercial synthetic elastics and systematically studied their physical properties. Some of their results are shown in comparative form in Figs. 69–76.

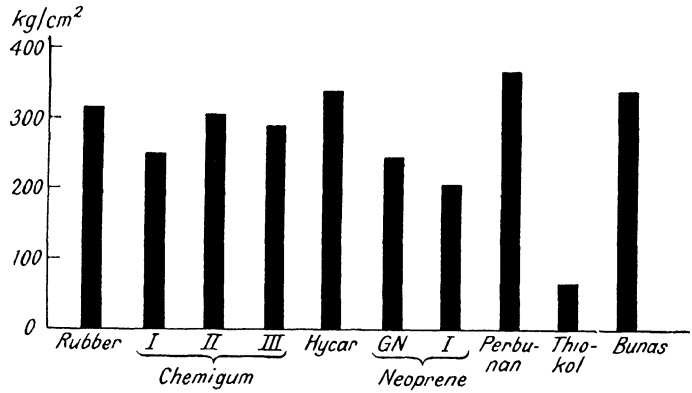

FIG. 73. Tensile strength.

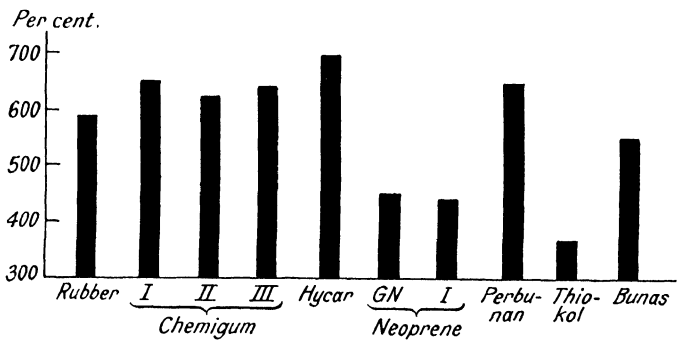

FIG. 74. Elongation. Tread compound.

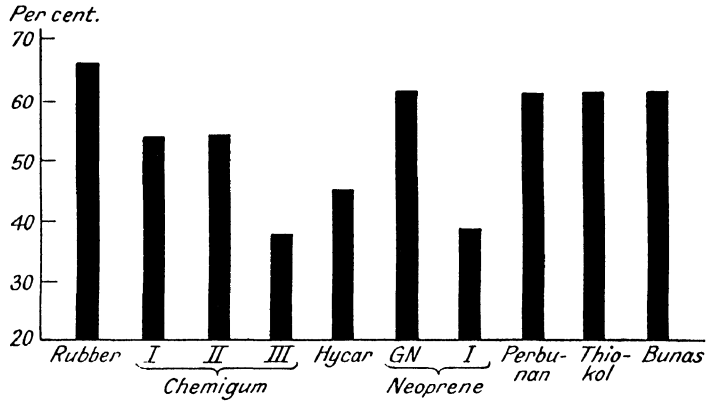

FIG. 75. Rebound resilience. Tread compound.

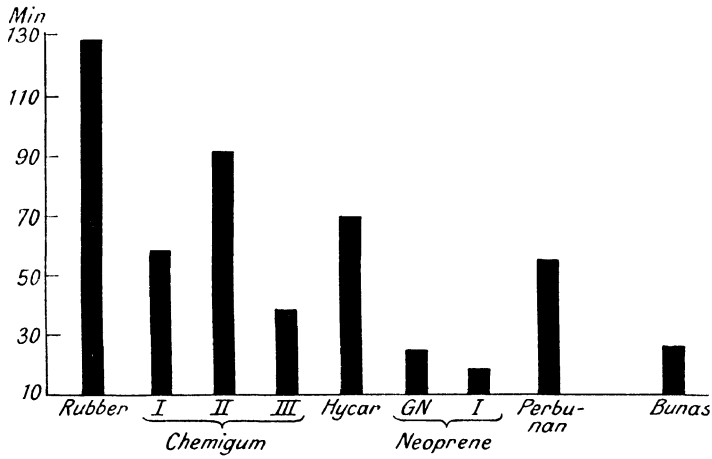

FIG. 76. Flexing. Tread compound.

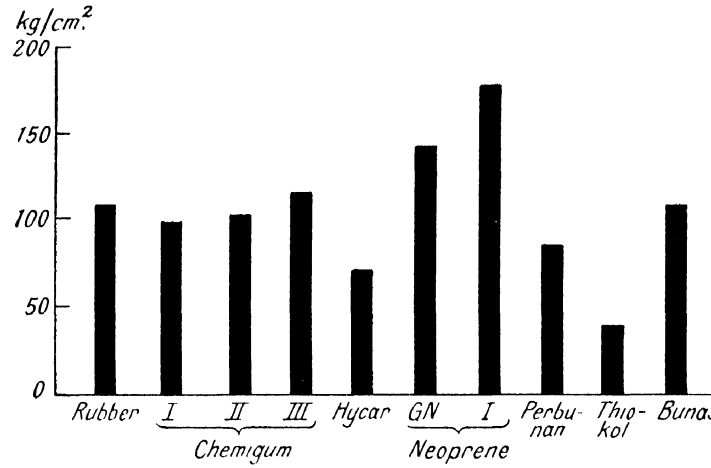

FIG. 77. Modulus at 300% Elongation. Tread compound.

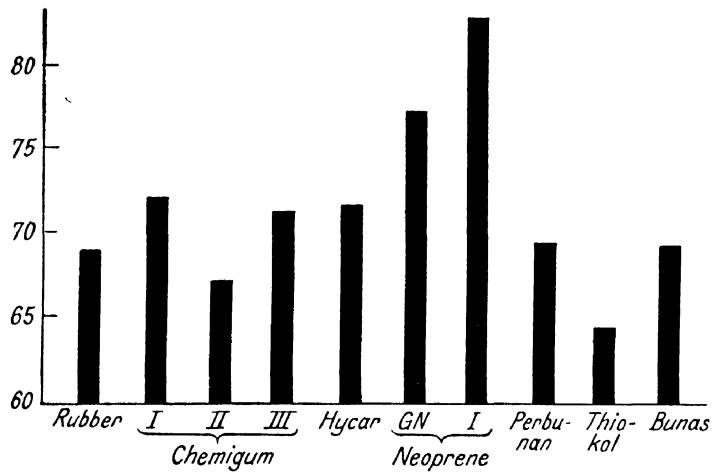

FIG. 78. Durometer Hardness. Tread compound.

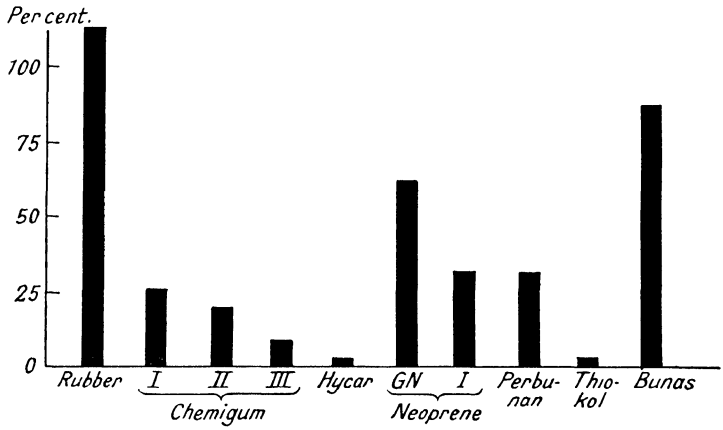

FIG. 79. Volume increase in X-70 Gasoline (12 days). Tread compound.

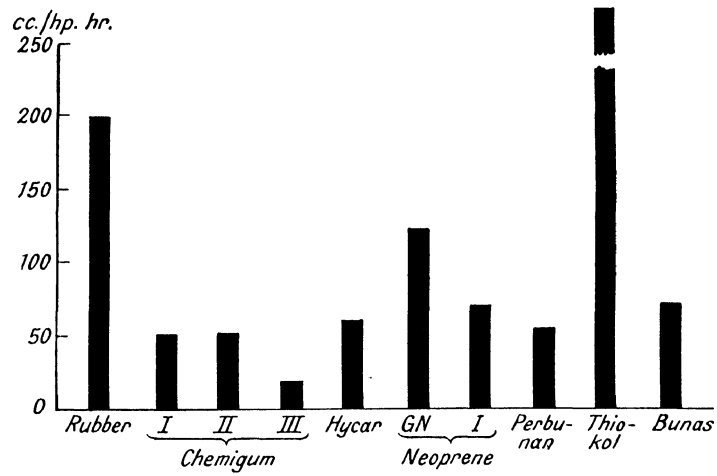

FIG. 80. Grosselli Abrasion Loss. Tread compound.

TABLE 164. SWELLING OF VULCANIZED COMPOUNDS IN LIQUIDS [9]

Volume increase, in percentage, after immersion for 8 weeks at room temperature

	Natural rubber	Neoprene	Perbunan	Perbunan-Extra	"Thiokol" A	"Thiokol" D	"Thiokol" DX and F
Light gasoline (Benzine)	160	—	20	20	0	—	—
Gasoline	230	8	40	—	0	3	3
Kerosene	—	60	—	—	0	2	2
Diesel oil	120	—	15	15	—	—	—
Fuel oil	—	—	—	—	0	10	10
Lubricating oil	—	40	— 4	—	0	1	1
Paraffin oil	140	—	3	—	—	—	—
Transformer oil	150	—	5	—	—	—	—
Acetone	—	25	110	110	—	—	9
Benzene	370	160	210	140	7	150	90
Carbon tetrachloride	670	160	220	120	0	40	30
Ethyl ether	130	50	50	—	—	—	—
Linseed oil	100	—	20	—	—	1	1
Turpentine	300	90	50	30	0	—	—

Perhaps the most important point that they made was that it is extremely unwise to accept the results of any of the tests carried out without considering how far they do apply to actual service conditions.

With synthetic rubbers it is especially important to have tests which evaluate elastic properties in low deformation, rather than to rely on indications furnished from ultimate tensile and elongation entirely. Hysteresis loops, secured in the normal way, indicate that after ten cycles the energy loss of natural rubber tread stock is about six times as great as for Buna-S tread. In actual tests of tyres, however, the Buna-S tread did not run at a lower temperature than the natural rubber tread. Hysteresis, for various ranges of elongation, showed that natural rubber is superior in elasticity and work capacity for tensile stresses below 35 kg. per square centimetre. Only above this stress is Buna-S superior, hence the advantage did not appear when stocks were used in tyre treads. Similarly, other apparently contradictory test results for synthetic rubbers may later find a logical explanation. Where there is interaction of plastic and elastic properties in synthetic rubbers it is necessary, in testing, to closely define variables which might otherwise not be so important. These include the time rate of deformation, character of deformation, etc.

This is another excellent example of the necessity for developing tests for rubber-like materials which are on a more functional basis than existing tests.

The brittle point or crack point at low temperatures is one of the most important characteristics of materials. A comprehensive investigation on this point has been carried out by Selker, Winspear and Kemp.[12]

Table 165. Chemical Resistance at 20° C.

	Rubber	Buna-S	Perbunan	Hycar	Chemigum	Neoprene	Thiokol A	Poly-isobutylene	Butyl rubber	Polyvinyl chloride + tricresyl phosphate	Highly polymerized acrylic acid esters
H_2O	Good	Good	Good	Good	Good	Good	Good	Good	Good	Good	Fairly good
O_2 + Light	Poor	Moderate	Good	Good	Good	Good	Good	Fairly good	Moderate	Good	Good
Ozone	Poor	Moderate	Fairly good	Fairly good	Fairly good	Fairly good	Good	Good	Good	Good	Good
H_2SO_4 conc.	Poor	Poor	Moderate	Moderate	Moderate	Good	Good	Good	Good	Moderate	Moderate
H_2SO_4 dilute	Moderate	Moderate	Good	Good	Good	Good	Good	Good	Good	Good	Moderate
HNO_3 conc.	Poor	Poor	Poor	Poor	Poor	Poor	Poor	Fairly good	Good	Moderate	Moderate
HNO_3 dilute	Good	Poor	Moderate	Moderate	Moderate	Moderate	Poor	Good	Good	Moderate	Moderate
HCl conc.	Moderate	Moderate	Fairly good	Fairly good	Fairly good	Good	Poor	Good	Good	Moderate	Moderate
HCl dilute	Good	Good	Good	Good	Good	Good	Fairly good	Good	Good	Good	Moderate
Acetic acid con.	Moderate	Moderate	Good	Good	Good	Good	Good	Good	Good	Moderate	Poor
,, ,, 10%	Good	Good	Good	Good	Good	Good	Good	Good	Good	Good	Fairly good
KOH conc.	Moderate	Moderate	Good	Good	Good	Moderate	Poor	Good	Good	Fairly good	Poor
KOH dilute	Good	Good	Good	Good	Good	Moderate	Moderate	Good	Good	Good	Moderate
Alcohols	Good	Good	Good	Good	Good	Good	Good	Good	Good	Good	Moderate
Esters	Moderate	Moderate	Moderate	Moderate	Moderate	Moderate	Good	Good	Good	Poor	Poor
Ether	Poor	Poor	Good	Good	Good	Good	Good	Moderate	Good	Fairly good	Poor
Acetone	Good	Good	Moderate	Moderate	Moderate	Good	Good	Good	Good	Poor	Poor
Petrol	Poor	Poor	Good	Good	Good	Good	Good	Poor	Poor	Good	Good
Benzene	Poor	Poor	Poor	Poor	Poor	Poor	Good	Poor	Poor	Poor	Poor
Transformer oil	Poor	Poor	Good	Good	Good	Good	Good	Poor	Poor	Good	Good

TABLE 166. BRITTLE POINT OF SYNTHETIC ELASTICS

Compound	Cure		Brittle point ° C. (±0·5°)
	Temp. ° C.	Time min.	
Polychloroprene [a]—			
Milled 5 min.	109	10	−36·8
Gum stock	142	30	−38·5
+3 parts soft black +8 parts oil	142	20	−40·6
Gum stock +5 parts channel black +20 parts oil	142	30	−42·5
Gum stock +100 parts soft black +8 parts oil	142	30	−36·4
Gum stock +200 parts soft black +10 parts oil	142	30	−32·0
Butadiene polymer—			
Milled 5 minutes	135	10	−67·8
Gum stock [b]	148	60	65·5
Tyre tread stock [c]	148	60	−71 to −69
Butadiene-styrene copolymer—			
Milled 2 minutes	153	30	65·5
Gum stock	148	60	65·5
Tyre tread stock	148	60	−66 to −70
Butadiene-acrylonitrile copolymer—			
American	—	—	−49 to −52
German	148	15	−45·5
Gum stock	142	45	−42 to −45
Tyre tread stock	142	45	46·5
Butadiene-nitrile copolymer, type—			
Milled 5 minutes	148	10	−25·6
Gum stock	153	45	−24·5
Clay loaded stock	153	45	−29·0
Soft stock (d.b.p. 50 parts)	153	45	−42·5
Butadiene-nitrile copolymer, Type II—			
Milled 1 minute	—	—	−29·3
Gum stock	153	45	−29·5
Tyre tread stock	153	30	−26 to −28
Organic polysulphide—			
Type 1	—	—	+ 7·0
Type 1 carbon black stock	142	50	− 3·8
Type 2 carbon black stock	148	30	−22·5
Type 3	—	—	−35·3
Type 3 carbon black stock	148	50	−34·0
Type 4	—	—	−35·5
Type 4 carbon black stock	142	50	39·5

[a] Polychloroprene having improved freeze resistance was recently made commercially available. This material gives products with brittle points 8–12° C. lower than the values given in Table III for regular polychloroprene.

[b] All compounds listed as gum stock in Table III, except 24 (polychloroprene gum stock) had the following composition: 100 synthetic elastomer, 1 benzthiazyl disulphide, 5 zinc oxide, 1 stearic acid, 5 cumar resin, 1 sulphur.

[c] All compounds listed as tyre tread stocks had the same composition as the corresponding gum stock with the addition of 50 parts of channel black.

McCrary [8] and collaborators have prepared some useful comparative data on wire insulation. The electrical characteristics of 40 per cent. wire insulation, using different synthetic rubbers, are shown in the following table:

TABLE 167. ELECTRICAL PROPERTIES OF COMPARABLE ELASTIC MIXES

Type	Dielectric strength (volts per mil.)		Dielectric constant	
	Dry	96% Humidity	Dry	96% Humidity
Natural rubber	498	482	3·35	4·24
25% Vistanex M	442	434	3·53	5·65
50% Vistanex M	442	429	3·51	4·66
Neoprene GN	360	356	7·33	7·74
Neoprene I	330	340	10·2	12·2
Hycar OR	396	241	14·7	20·2
Chemigum I	373	170	11·9	15·1
German Perbunan	342	157	11·6	17·0
Domestic Perbunan	379	243	11·0	14·8
Thiokol RD	403	120	12·0	22·6
Thiokol F	300	132	11·1	48·6
Thiokol FA	287	180	9·05	32·4

Type	Power factor		Insulation resistance (megohms at 180 volts)	
	Dry	96% Humidity	Dry	96% Humidity
Natural rubber	0·0031	0·0446	2,000,000 +	820,000
25% Vistanex M	0·0016	0·0565	2,000,000 +	2,000,000
50% Vistanex M	0·0019	0·0728	2,000,000 +	670,000
Neoprene GN	0·0177	0·0204	1,550	1,100
Neoprene I	0·0368	0·0418	880	400
Hycar OR	0·0233	0·137	200	10·4
Chemigum I	0·0729	0·227	140	7·1
German Perbunan	0·0454	0·155	86	10·5
Domestic Perbunan	0·0527	0·160	85	11·0
Thiokol RD	0·0723	0·130	158	26·5
Thiokol F	0·0081	0·316	580	10·5
Thiokol FA	0·0041	0·234	6,400	80

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