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GLUE AND GELATINE

BY

PAUL I. SMITH

HOLDER OF THE FIRST-CLASS DIPLOMA OF THE WORSHIPFUL COMPANY OF LEATHERSELLERS; AND FIRST-CLASS CERTIFICATES OF THE LONDON CITY AND GUILDS INSTITUTE IN LEATHER MANUFACTURE

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PREFACE

"WHAT is called professional work is, in point of severity, just what you choose to make it, either commonplace, easy, and requiring only extensive industry to be lucrative, or else distinguished, difficult, and exacting the fiercest intensive industry in return after a probation of twenty years or so, for authority, reputation, and an income only sufficient for simple habits and plain living. The whole professional world lies between these two extremes."

George Bernard Shaw.

THE twentieth century is essentially the age of specialists. Whether this state of affairs is really desirable from an economic or sociological standpoint, is a matter of opinion. There is no doubt that specialization, as we understand it to-day, tends towards a restriction of mental development, or perhaps it would be more correct to say, that specialization favours a peculiar type of mental atrophy.

To the industrial worker it is patent that the specialist is generally so immersed in his own little, and frequently elementary, task, that he forgets there are other branches of knowledge and a wider world of industry and science beyond his paltry scope. It seems reasonable and logical to maintain, that if the specialist narrows down or limits his scientific and technological education to the exclusion of everything not directly connected with his own particular work, he fails to do justice to himself, no matter how intensive are his efforts.

A really catholic knowledge and experience are eminently desirable, one might say essential, if the industrial chemist or plant technologist is to make a real success of his work. There are many roads to one town, and it often happens that a wider knowledge eventually leads to a discovery of new methods and the quickening of understanding and initiative.

In this book the author has attempted to treat the subject-matter from a number of totally different angles—the glue manufacturer's, the tanner's, and the chemist's, as well as the general consumer's. By so doing, it has not been possible to go

into abstruse details concerning the less important manufacturing processes, but as the work does not aim to supplant the standard textbooks, only to supplement them, this mode of treatment may prove rather helpful.

There are really very few standard works on "Glue and Gelatine," and even the few on the chemist's bookshelf approach the subject from just one or two standpoints. None of them attempts a general survey, which in the author's opinion is eminently desirable, especially in these days of increased business pressure, when one cannot generally afford the time to read through a weighty treatise practically devoted to colloid chemistry, in order to look up a minor technical point. It would seem preferable to consult a book of less pretentious character, but covering the technology, chemistry, and application of glue and gelatine on fairly broad and comprehensive lines.

The writing of this brief preface has necessitated a considerable amount of care and thought Whilst the author is desirous of thanking all his numerous friends for their generous help in the preparation of this book, he has experienced some difficulty in finding suitable words to express his thoughts.

First thanks are due to Messrs. Turney Bros., Nottingham, for permission to publish much of the material contained in this book, and for the interest they have taken in its compilation.

Acknowledgments must be made to the various Editors who have so kindly allowed the author to reproduce matter which he has contributed to their journals from time to time. Thanks are due also to the numerous firms who have lent him blocks and photographs of plants and chemical apparatus, etc., and supplied him with valuable information concerning the working of the same. In this connection the following names must be mentioned, Messrs. Kestner & Co., the Aluminium Plant & Vessel Co., and Ilford, Ltd.

He is indebted to Mr. E. Richardson, B.A., B.Sc. (Oxon), for information concerning the uses of gelatine in pharmacy

and cosmetics, and for correcting the proofs, and to Miss K. Pearson, S.R.N., for notes on the application of gelatine in the manufacture of foodstuffs.

For reading through the proofs he has also to thank his friend, Mr. S. Mees.

Last, but by no means least, the author must convey his sincere thanks to Miss Ivy E. Norman for her generous help in preparing illustrations and for many suggestions and criticisms which have helped him considerably throughout this book.

PAUL IGNATIUS SMITH.

THORNEYWOOD,
NOTTINGHAM,
March, 1929.

CONTENTS

PAGE

PREFACE v

CHAPTER I

EARLY HISTORY OF GLUE 1

Biblical and classical references—Résumé of primitive methods of manufacture

CHAPTER II

THE RAW MATERIALS FOR GLUE 8

Hide and skin offal—Fish waste—Bones—Leather scrap—Furrier's waste

CHAPTER III

THE CHEMISTRY OF PROTEINS 20

Hydrolysis—Putrefaction and brief survey of the histology of the hide—Preparation of sections of skin for microscopical examination

CHAPTER IV

RAW MATERIALS FOR GELATINE AND ISINGLASS . . 34

Secondary raw materials—Water, air, lime, and salt

CHAPTER V

PRESERVATION OF STOCK BY THE GLUE MANUFACTURER. 52

Washing glue stock—Liming—Washing and deliming—Extraction of skin offal—Notes on extraction of bones and fish waste

CHAPTER VI

FILTRATION ; CLASSIFICATION ; EVAPORATION ; COOLING AND DRYING 74

CHAPTER VII

ANALYSIS OF GLUE AND GELATINE . . . 96

Notes on the different varieties of gelatine

CHAPTER VIII

PAGE

THE APPLICATIONS OF GLUE 107

In veneering, bookbinding—General uses of glue

CHAPTER IX

THE USES OF GELATINE IN THE MANUFACTURE OF FOODS 119

In cookery, pharmacy, bacteriology, chemical analysis, and the use of isinglass in brewing, and gelatine in the leather industry

CHAPTER X

GELATINE IN PHOTOGRAPHY AND PHOTO-LITHOGRAPHY . 142

INDEX 155

GLUE AND GELATINE

CHAPTER I

THE EARLY HISTORY OF GLUE

Biblical and classical references—Résumé of primitive methods of manufacture

THE art of tanning or rendering hides and skins imputrescible by drying in the sun or treating with crude animal oils and fats, infusions of the barks and leaves of certain trees, etc., must have been practised at a fairly early period of man's history.

Professor Arthur Dendy, in his classic *Outline of Evolutionary Biology*, says: "Man is one of the latest products of organic evolution, and his appearance upon the scene apparently does not date further back than Pliocene times."

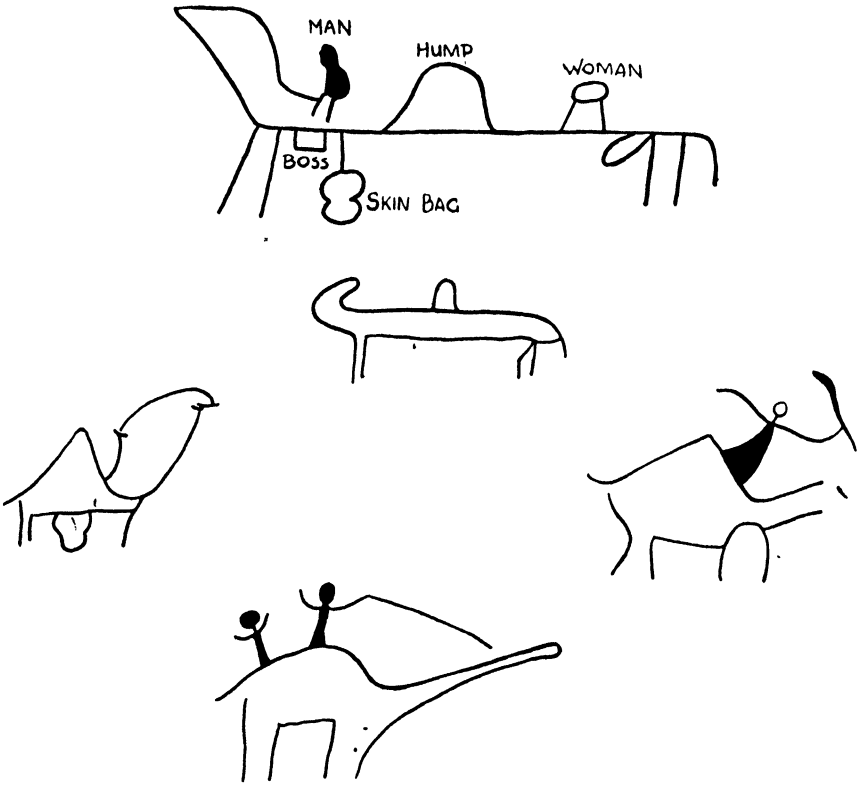
Thirty thousand years or more ago there existed in Spain, and in fact Western Europe generally, a race of primitive human beings now known as "the first true men." For hundreds, probably thousands of years, the Neanderthalers or "ape men" had occupied the cold steppes of Southern Europe. It should be remembered that during the Fourth Glacial Age, Europe was covered with ice, the Mediterranean and Red Sea were great valleys, and a tremendous inland sea spread from the present Black Sea across South Russia and some considerable way into Central Asia. These Neanderthalers whom we now know to have been of the same genus as the "true men," but of a different species, were quickly killed off by the latter, who demonstrated their superior strength and intelligence.

Ethnologists have shown us that these first men, although exceedingly primitive savages, were endowed with sufficient initiative to draw the most wonderful pictures on the walls of some caves in Spain, and also to produce some fine carvings of animal's heads, etc. It is strange to relate that although advanced in one way they had not yet mastered the art of pottery; they knew nothing about cultivation or the weaving of clothing—they had never yet seen a fire.

They were hunters, and chased the bison and reindeer and

other wild animals, occasionally they trapped the mammoth—a gigantic beast.

During the terrible glacial periods, which we are told threatened to exterminate every human creature on the face



(Reproduced by the courtesy of the Editor of "Antiquity")

FIG. 1. ROCK PICTURES AT QALAAT EL WISH, NORTHERN KORDOFAN ("ANTIQUITY," SEPT., 1928)

of the earth, the life of man must indeed have been fearful beyond imagination. At such a time man needed clothes, and it is reasonable to suppose that the only covering he possessed was made up of the skins of animals he had killed. These skins must necessarily have been cured in a very crude manner, probably by drying in the sun or rubbing with certain salt rocks.

As man became more civilized the mere drying of skins intended for clothing was disregarded in place of better methods.

Probably one of the earliest tanning processes was the treatment of the skins with animal fats and oils, followed by drying in the sun. This is said to have been practised by the Azilians, some twelve or fifteen thousand years ago.

It may be said that during the Neolithic or New Stone Age the art of tanning was looked upon as of great importance, and there seems little doubt that the barks and leaves of trees were at this stage used to render skins imputrescible. Twelve to ten thousand B.C., cultivation had begun, and basketwork, weaving, and pottery were all practised; man was definitely on the ascent, and already had shown his unquestionable supremacy over the animals—he began to look upon the world as his own.

We have the first mention of tanning in the carvings of Ancient Egypt. The Egyptians may be said to have educated the world, in fact Egypt is called the "Cradle of Knowledge."

Whilst the savages of the West were intent upon the mere satisfaction of their animal desires, living a nomadic existence not far removed from the animals they hunted, the Egyptians were busy farming their wonderful fertile country; they knew all about the intricate subject of irrigation; they built the most wonderful temples and tombs, and most stupendous of all, they had mastered the art of writing.

Recent excavations in the "Valley of the Kings," by Dr. Howard Carter, have shed some considerable light upon the extent of technical knowledge possessed by the Egyptians. In the tomb of Tut-ankh-Amen a considerable amount of leather was found, in the form of harness, seats of stools, and of sandals. Unfortunately, the damp and heat of the tomb destroyed the leather, in fact rendered it black, brittle, and almost pitch-like. The student with little knowledge of Egyptology, is often puzzled to account for the presence of such weird collections of articles in the tombs of the Pharaohs. The Egyptians believed that no soul could possibly enter the Kingdom of Osiris, the Mighty God, who was Ruler of the Living and Dead, without the possession of the body which it had inhabited on earth. Thus, they took tremendous pains to preserve it by means of embalming and wrapping in specially prepared linen, etc. Finally, the body was placed in a tomb, and in order that the period of waiting might not prove too weary, they placed round it musical instruments, caskets containing food and drink, and all the favourite articles of the

deceased. Thus, if the person had been a great hunter, they would naturally place beside the coffin his harness and bows and arrows.

To pass on to a later civilization, namely, the Roman, which the old chronologies state was founded in 753 B.C., we find that the leather industry was in a flourishing condition. It should be remembered that the eight guilds of the seventh century were those of the flute players, gold-smelters, smiths, dyers, cordwainers, curriers, brassworkers, and potters.

The average Roman was not, as it is popularly imagined, a mere pleasure seeker with no thoughts for anything above the sensual. He was, at least during the Empire's zenith, a simple and straightforward man far less imaginative than his classical neighbour the Greek—he preferred to devote himself to trade or agriculture rather than bother about politics, and was quite content to leave the actual business of running the State in the hands of the two Consuls who were assisted by the Senate.

Paul Louis, in his excellent book, *Ancient Rome at Work*, mentions leather workers—

> The curriers and cordwainers, who from the reign of Numa were organized into a group, seem to have maintained a fairly flourishing industry. Leather was used in making sandals in the Etruscan style, and later for the calcei and other footwear which fashion imposed.

During the great struggle between Rome and Carthage in 264 B.C., there was a great demand for leather equipment for the soldiers, and we are told that the Senate gave every encouragement to the industry, which was held in fairly high esteem.

The fact should not be overlooked that earlier civilizations, such as the people of the Ægean Sea and the great Greek civilization, were all acquainted with the art of leather manufacture, although they can hardly have been so advanced, as regards technical knowledge, as the Egyptians and Romans.

In the classics we find frequent reference to the art of preserving skins, readers of Homer's *Iliad* (XVII, 389–393), will remember the picture the poet draws of the titanic struggle over the body of Patroclus.

The Old Testament contains many allusions to tanning, thus, the Psalmist (Psalm cxix, 83) writes—

> " I am become like a bottle in the smoke." Referring, of course, to a skin bottle made of goatskins, similar to the water bottles seen in the streets of Bagdad and other eastern cities at the present day.

In Kings i, 8, we have the quotation—

. . . an hairy man, girth with a girdle of leather.

While in Matthew iii, 4—

John had a leather girdle about his loins.

It is impossible to state when it was found that a powerful adhesive could be made from pieces of hide and skin by boiling them in water, but like most other discoveries, it was no doubt accidental. In referring to the early history of glue, Bogue, in his excellent treatise, *The Chemistry and Technology of Gelatine and Glue*, writes—

Among the stone carvings of the ancient city of Thebes, of the period of Thothmes III, the Pharaoh of the Exodus, and at least 3,300 years ago, is one representing the gluing of a thin piece of a rare wood of red colour to a yellow plank of sycamore.

Various Egyptologists have shown that glue was in common use in Ancient Egypt. In Dr. Howard Carter's book *Tut-ankh-Amen*, the following useful information is given—

Glue was well known in Ancient Egypt, and a specimen recently examined may be described. This was found some years ago by Dr. Howard Carter in a rock chamber over the mortuary temple of Queen Hat-shep-sut at Deir el Bahari ; it had been cast and was originally rectangular in shape, but now it is shrunken and distorted owing to desiccation: in appearance it cannot be distinguished from modern glue, and it still responds to the usual tests.

In the tomb of Tut-anhk-Amen there is a large cedar-wood casket, inlaid and veneered with ivory and ebony, which shows that glue was used for practically the same purposes as at the present time. It was also mixed with oils and pigments and used as a kind of paint. Gesso was a special form of plaster made up of whiting and glue and used for covering wood before gilding.

Thus it may be taken for granted that the Egyptians were very familiar with the manufacture and properties of glue ; probably their acquaintance with it extended over four or five thousand years. Other ancient civilizations were also alive to the possibilities of a powerful adhesive's being made from hide and skin waste.

The author is informed that in China during the seventh, eighth, and ninth centuries glue was used in the manufacture of furniture, etc. This was during the Suy and Tang Dynasties,

when China was the most secure and civilized country in the world, whilst Europe was rent asunder by guerilla wars.

From the earliest times, as mentioned above, glue has been renowned as a wonderful adhesive, and if we care we can find repeated references to it in the classics, starting from Lucretius and Pliny, and concluding with the great Elizabethan dramatists, Shakespeare and Marlowe.

As far as it is possible to ascertain by referring to numerous works on ancient civilizations, the classics, and that greatest book of all, the Bible, the early method of glue manufacture was extremely crude and simple. Pieces of hide and skin, with the hair removed, were boiled in a large vessel over an open fire, and the cooking continued until the protein matter had all dissolved. When the liquid reached a suitable viscosity the vessel was removed from the source of heat, the grease and hair skimmed from the surface, and the glue stock allowed to cool. The liquor was then strained and poured out into moulds and allowed to dry. Naturally, methods differed enormously, but the principle was the same, and consisted in cooking the skin substance and cooling the resulting product. Even in the time of Lucretius, 50 B.C., it was noticed that glue made from bull hide was superior to other varieties : " Materials are made one from bullish glue."

Glue was manufactured to some considerable extent on the Continent during the seventeenth century, but it was not until the eighteenth, that the industry sprang up in this country. Since that time it has advanced steadily, until at the present time it may rank as an important secondary trade. Even two hundred years ago hide offal was not the only raw material employed. Fish waste, bones, and other scrap were found to make strong glues. Various patents have been taken out since the eighteenth century to cover the manufacture of bone and other glues.

A survey of the industry as it stands at the present day reveals the somewhat astonishing fact that in many ways it has undergone no very radical change for nearly two hundred years. Of course improvements, beneficial in every way, have been introduced, but the method of production is practically the same as that of the Dutch in the days of William III. or that of the ancient Egyptians under the awe-inspiring Pharaohs.

The glue and gelatine industry, like most other time-honoured

trades, is extremely conservative. This is quite natural, if we consider for a moment how the industry was founded. The originators were master craftsmen, who inherited from their fathers the secrets of the craft, and who practised it strictly according to set empirical recipes, and deviated not one iota from the schedule honoured by their ancestors. They viewed innovations with extreme dislike. Thus it should be easy to see that the scientist has found it extremely difficult to introduce improvements.

It is only during the last few years that the services of the technical chemist have been utilized, and even at the present moment, in spite of the widespread knowledge of science, there are only a few large concerns who consider it worth their while to employ a chemist. Everyone who views the subject openly, must admit that the backward state of the industry in this country—for in America and on the Continent the manufacture of glue and gelatine is conducted on definitely scientific lines and under the control of a really skilled worker—is due to the woeful lack of co-operation between the scientist and the self-styled "practical man."

The supreme importance of the chemist and chemical engineer must be recognized by the manufacturer, if he wishes to produce a really high-class product and run his factory on economical lines, so that he may compete with foreign industrialists who, at the moment, practically monopolize the markets.

CHAPTER II

THE RAW MATERIALS FOR GLUE

Hide and skin offal—Fish waste—Bones—Leather scrap—Furrier's waste

Hide and Skin Offal. The bulk of the glue manufacturer's raw material consists of hide proteins, which are purchased direct from the tanner. Unfortunately, the latter regards the glue stock only as a mere waste product, and very little effort is made to keep it in a fresh condition. This is due to the ignorance which generally prevails regarding the whole intricate process of glue-making, the common idea seeming to be that providing you boil the right kind of material in a vat or some suitable receptacle, you obtain glue—the condition and age of the raw material being supposed to have little influence on the finished product.

The tanner should remember that although his main object is the manufacture of leather, it is to his advantage to make his by-products contribute largely towards the maintenance of the factory. As glue stock is one of the most important of these products, he would do well to study at some length the whole subject of preservation with a view to obtaining the best possible price for his material. By keeping his hide and skin offal in a sweet condition, the tanner not only ensures a better market, but also eliminates some of the bad smells with which a tanyard is usually associated, as well as facilitating the entire process of glue production.

Many tanners simply " dump " their hide and skin waste in a convenient spot and leave it until the glue-maker sends his compliments, and desires to know when the next delivery can be expected.

When a large heap of hide and skin pieces is left exposed to the weather for any considerable time, those pieces on the top become bone-dry and assume an objectionable bluish colour, which gives the buyer a bad impression ; there is also a considerable loss in weight due to the continual draining of the stock. As the material is sold by the ton, this diminution represents a serious pecuniary loss to the tanner. In view of these facts, it is a good practice to have the " spetches," as they

are called, turned over with a fork about once a day, so that the weight may be kept more or less constant and risk of discoloration considerably diminished.

The tanner is sometimes confronted with the fact that the glue manufacturer, through bad trade or other causes, cannot deal with the whole of the former's stock, with the result that he is left with a considerable stock of putrescible material, likely to diminish in value if kept for any long period. In this case, it is advisable to make up a fresh lime liquor in a pit—half a barrowful of lime should be used, and the pit half filled with water. The author has found by experiment that hide and skin pieces will keep in excellent condition in the above solution for six months, at the end of which time the pieces have a tendency to become " mealy," that is, they seem to lose their characteristic " fleshy " nature owing, no doubt, to intensive hydrolysis, and can easily be broken up into a powder or meal by rubbing.

There is no doubt that when hide proteins have to be kept for any period up to six months, liming is by far the cheapest and best means of preservation for the tanner. The author does not advise the use of either phenolic antiseptics such as phenol, cresylic acid, napthols and salicylic acid, or formaldehyde, as all these compounds have a definite tanning action upon the proteins, which, although slight owing to dilution, nevertheless interferes with the successful extraction of glue during the boiling operation. If the tanner contemplates using an antiseptic solution other than lime water for preserving the " spetches," boric acid is recommended. A solution containing 5 lb. of boric acid per 1,000 gal. of water is one suitable for the purpose. Some tanners use a dilute solution of mercuric chloride, but this is not advisable for reasons which will be explained later.

It must not be supposed that the many varieties of hide and skin wastes all possess the same value from the glue manufacturer's standpoint. There is, in fact, an appreciable difference in the various prices, corresponding to the quality of glue which can be made from the product.

Calfskin. From this source the glue manufacturer obtains the material for some of the best and clearest gelatine and glue. The skin from " very young animals " contains an appreciable amount of chondrigen, the presence of which is not desirable

in stock for the best quality gelatine, as it yields on boiling a substance named chondrin, which resembles gelatine, but is weaker in gelatinizing and adhesive properties. It is the usual practice to keep the " roundings," " pates," and " fleshings " quite separate, as they are priced differently, the best figure being obtained for " pates."

The majority of tanners keep the " roundings " and " pates " piled in heaps covered with sacking which has been damped with lime liquor. Fleshings are generally preserved in a weak solution of lime. This procedure is to be recommended, especially when the heaps are turned over with a fork once a day, to ensure equal distribution of lime liquor.

The reason why " fleshings " are rated lower than " roundings," etc., is owing to the fact that sub-cutaneous tissue does not yield such good quality glue as collagen and its associated proteins, which are to be found in the roundings and pates in greater proportion.

Calf feet do not yield a large quantity of glue, but are of special importance, as they yield neatsfoot oil when boiled.

It will thus be seen that all the varieties of calfskin waste described above, which are obtained during the early stages of willow and box-calf manufacture, must be kept quite apart.

Hide Offal. Under this heading we have the foot, head, fleshings, tail, tendons, and buttock of the cow, heifer, bull, and horse. The foot is one of the most valuable materials with which the glue manufacturer has to deal, as it yields a very large percentage of glue.

Hide pieces are " green," dry, dry-salted, wet-salted and limed.

Wet-salted stock, such as that obtained from frigorific hides, is best soaked in clean water to remove the dirt and salt, then preserved in a weak solution of lime. This procedure applies equally well to dry-salted stock. Pieces from sun-dried or " flint-dried " hides can be kept indefinitely, provided, of course, that they are stored in a dry warehouse. Roundings, etc., from limed goods are best preserved in the open air in the same manner as calf and sheep stock.

The fleshings are generally stored in a large tub containing a weak solution of lime.

Waste from Sheepskins. Offal from the sheepskin forms the largest portion of the glue manufacturer's raw material, which is

not surprising considering the enormous trade done in sheepskin leathers.

The first waste occurs when the skins are trimmed, i.e. the heads, tails, and " shanks " or legs are cut off. These are known as " roundings," speaking collectively. At a later stage the flesh or sub-cutaneous tissue is removed, either by machine or by means of a special knife worked by a man over an almost perpendicular beam. During the other stages of manufacture small amounts of waste may occur, which are usually added to the " roundings."

Some tanners press the " fleshings " and extract the valuable natural fats which they contain, and this procedure has been found more profitable than selling the material direct for glue. The residue obtained from the large hydraulic presses is quite unsuitable for utilization as glue stock, but it can be sold as a cheap, nitrogenous fertilizer.

Sheepskin offal makes a good glue, but is inferior to either the calf or hide varieties, owing to the large amount of natural fat present in the skin, special precautions having to be taken to eliminate all traces from the glue liquors.

Before leaving the subject of sheepskin offal it should be mentioned that " colty " or stale material is best kept apart from the fresh pieces. Good glue cannot be made from stale and decomposing offal, and as the presence of the latter in a consignment of glue stock may possibly diminish the value, it is quite obvious why the two sorts should be kept separate.

It is interesting to consider for a moment the reasons why a skin goes " colty," that is, becomes covered with white hard patches sometimes $\frac{1}{2}$ to $\frac{3}{4}$ in. in thickness. The explanation as given by the foremost leather experts cannot be regarded as conclusive, as there is some difference of opinion.

Alfred Seymour Jones, in his wonderful little book *Sheep and Its Skin*, says, in referring to " colt " or " dead-fat "—

> This curious phenomenon, well known to everyone engaged in handling sheep pelts, has mystified scientific thinkers for years. It is undoubtedly a species of adipose degeneration of the individual cell, and is intimately connected with the hydrolysis of the protein and glyceride molecules on the death of the cell ; this hydrolysis, of course, resulting in the production of crystalloidal or semi-crystalloidal bodies.

In another part he writes—

> A sheepskin possessing a surplus of fat, as it frequently does along the spinal column, especially in the neck, is liable, while resting among

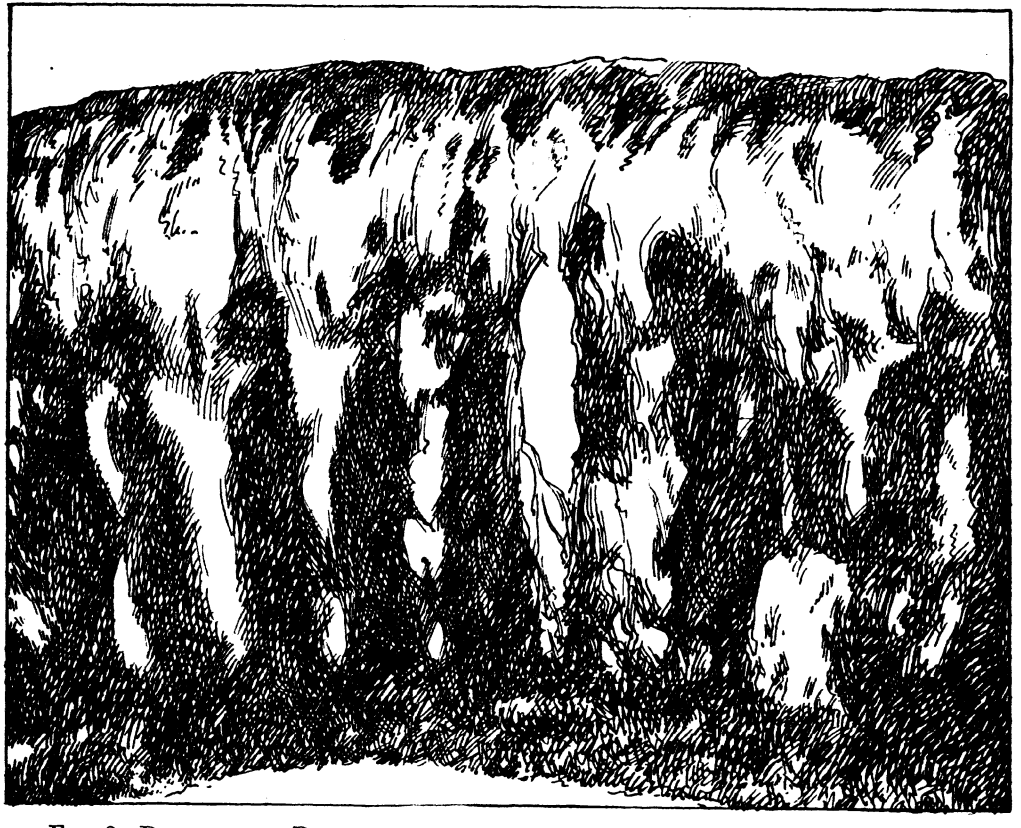


FIG. 2. DRAWING OF PHOTO-MICROGRAPH SHOWING SECTION OF COLTY SHEEPSKIN
I. E. Norman

other woolskins in a pile, to heat and putrefy quicker than if it had been properly cured, rise of temperature, or general atmospheric humidity, of course, facilitating such change. Under such circumstances, cell action will rapidly diminish and ultimately cease, the death of the cell thus taking place, and the large colloidal aggregates can no longer be maintained. Contracting and subsequent subdivision take place, involving the rupture of the cell wall, the fat overflowing between the tissues. During this period, the general molecular forces have been nucleating until the whole mass finally becomes crystalline, a change which is further fixed by the hydrolytic processes of liming.

Possibly enzymatic action facilitates the degeneration of the cells, but as the mechanism of enzyme procedure is still a matter of conjecture, it is difficult to attempt any real explanation. The active enzyme would probably be one of the common fat-splitting species, such as lipase or steapsin.

Goatskins. Although there are very few goatskins available from native sources, an enormous number are imported from the colonies and the East generally. The majority of these are utilized for the manufacture of glacé kid and furniture and bookbinding leathers.

There is really very little waste from the average goatskin, for they are, as a rule, very small in size, the total feetage realizing about 6 sq. ft. per skin.

Most light leather manufacturers use arsenic depilatories during the liming processes, when dealing with goatskins. The presence of arsenic compounds in the final product, namely, glue, is most objectionable. The various processes through which the stock has to pass would appear to eliminate all possibility of contamination, but, unfortunately, this is not so, and samples of glue have frequently been found to contain small quantities of arsenic compounds.

Fish Waste. Waste from large fish canneries, markets, and wet fish shops is utilized to a considerable extent in the manufacture of glue and gelatine.

Fish offal is usually considered *en bloc*, as a rather unwholesome conglomeration of fish scraps, usually in the early stages of putrefaction. In view, however, of the importance of this raw material the author proposes to attempt a description of the various kinds of fish available, that is, the varieties of fish sold, either in the wet, natural state, or preserved by salting, or tinned in oil, etc.

For our present purposes it is convenient to divide the fish

up into two distinct groups—"round" and "flat" fish. Dealing with the former first, the commonest types are—

Hake. A fish indigenous to the south, and forming the major portion of the catch off the south of Ireland and Bay of Biscay.

Whiting. A northern fish, plentiful in the North Sea and round the coast.

Haddock. Found in the North in abundant quantities. Best catches towards the North Sea.

Cod. A northern fish caught in very large quantities towards Iceland.

Ling. Plentiful in northern waters, off Scotland and Iceland.

Another important type of fish belonging to the round fish family includes the herring, sprat, and other smaller members, such as the pilchard. It should be noted that these fish contain a proportionally large amount of natural oil or fat, thus the spawning summer herring may have from 30–40 per cent. A considerable proportion of the fat is present in the skin and flesh, being disseminated in the form of minute globules of oil. Waste from the large curing factories situated on the coast yields, when boiled, a very large quantity of herring oil—a dark, evil-smelling liquid, which no doubt can be utilized in the detergent and other industries after deodorizing, etc.

Dr. James Johnstone's report of analysis of three series of Manx herrings caught in 1917 is interesting.

(1917 : Lancashire Sea-fisheries Laboratory Report)—

	Per Cent
Fat	22
Proteid	21
Ash (+ salt)	9
Water (+ traces)	48

The flat fish, well-known to the people of this country, are, according to Professor W. A. Herdman (University of Liverpool)—

Halibut. A northern fish of large size.

Sole. Commoner in the south down to Morocco ; a shallow-water fish common in the Irish Sea.

Turbot. Found in deeper water ; a North Sea fish, but not very abundant.

Brill. More abundant than the turbot, especially in the south.

Plaice. A northern form, very abundant on the coasts of Iceland and farther north, distributed all around our coast, and important as a food of the people.

Flounder. Of less importance ; especially abundant in estuaries.

(Above particulars quoted from *Animal Life and Human Progress*, edited by Professor Arthur Dendy.)

There are many other kinds of fish, including shark, dogfish, skate and rays, etc., but these rank as only of secondary importance. The skin of the shark is, however, beginning to find an application in the leather and allied industries, and at least one large company has been formed to conduct extensive shark hunting, the entire carcass being used up for a variety of different and somewhat amazing purposes.

The skin of the fish is very similar to that of the average mammal. The horny scales are characteristic structures, the same as hair is to the animal, but the two structures differ enormously, both in their composition and relation to the skin itself.

The scales are outgrowths of the epidermis, whilst the hair of the mammal is an epidermal structure reaching far down into the corium and nurtured by bloodvessels and sensitized by nerves. Chemically, the two substances differ. Hair consists of keratin ; fish scale is a complex mixture of keratin and a related protein—ichthylepidia (Morner).

The glue or gelatine value of fish waste relies upon the amount of collagen present—usually the skin itself is composed almost entirely of this substance. Bogue points out that sebaceous or fatty glands are present in the skin in great abundance.

Histologists point out the interesting fact, that the most significant difference between fish and animal skin consists of the layers of fibres being at right angles to one another in the former and almost horizontal in the latter, thus giving the dermis of the fish skin a definite membranous appearance.

Remembering that the value of fish offal depends upon the amount of collagen present, it can at once be realized that fish heads and bones are unsuitable for glue-making. These two materials are useful as fertilizers, but owing to the large proportion of soluble proteins (mucoids) present, they make a very poor quality glue.

Fish scrap for the glue manufacture should consist only of those materials rich in collagen ; inferior materials known to lower the tensile strength and tenacity of the glue should be abstracted. It is a foolish and definitely unprofitable procedure to use every particle of the fish offal for the production of glue.

Bones: Constitution. As an introduction to the utilization of bones in glue-making, and a discussion of the various kinds and

qualities, it is necessary to devote some space to a brief description of their physiology and chemistry.

Unfortunately, little is known concerning the biological constitution, and structure of bones and most of our knowledge is mere conjecture. It may be said, however, that bones are composed of cells which are enclosed in an intercellular matrix. According to Smith (*Z. Biol.*, 19, 1883), these cells yield no gelatine or keratin, and their composition is unknown. The intercellular substance is always present in great excess over the cellular, and is made up of two important components, an organic substance known as ossein, and an inorganic one composed of a mixture of heavy mineral salts.

As regards the chemical composition of bone, the following analysis by Taggart is of interest—

COMPOSITION OF BONE

	Per Cent		Per Cent
Water	51·0	Ossein	11·4
Fat	15·7	Mineral matter	21·9

Ossein itself is not a definite chemical compound, but consists of three, or possibly more, complex proteins: collagen, asseomucoid, and ossalbuminoid. The inorganic material or mineral matter is given by Matthews (*Physiological Chemistry*) to have the following constitution—

COMPOSITION OF INORGANIC MATERIAL OF BONE

	Per Cent		Per Cent
Calcium phosphate	85	Calcium fluoride	0·3
,, carbonate	10	,, chloride	0·2
Magnesium phosphate	1·5	Alkali salts	2·0

In addition to ossein and the inorganic salts, bones contain what is commonly known as the marrow. This is composed of a mixture of proteins and fats.

The fat from bones is extracted during the process of glue-making or preparatory to it, and is known commercially as "bone fat," large quantities of which are used in the manufacture of coarse lubricants and soap, or bleached for candle making.

Bone oil is also obtained from bones. It is a heavy dark brown liquid, and when redistilled it yields large quantities of ammonia together with an oil. The most important products of fractional distillation are the methyl-pyridines.

The essential part of the bone from the glue manufacturer's standpoint is the ossein, about 11·4 per cent. Fresh bones contain a higher percentage of this protein than dry and aged specimens. From the fertilizer's standpoint the inorganic portion contains the valuable phosphates (di- and tri-calcium phosphate).

Ossein is also an important constituent of horn piths. The piths consist of two portions, one being composed of organic constituents and the other inorganic ; it is the object of the manufacturer to separate the former from the latter, as it is only the organic portion which yields gelatine. This separation is achieved by treatment of the stock with dilute acids, followed by continual washing with cold running water. The remaining organic matter is then treated as described for ordinary hide stock.

All material for the making of ossein is first degreased in the same manner as ordinary bones, using one of the common solvents.

Ossein, if properly prepared, yields a bright strong gelatine of the highest quality.

Leather Scrap. Before discussing the various forms of leather waste available, the author proposes to consider for a moment the constitution of leather. Is it a definite chemical compound, or a mere conglomeration of complex proteins held together by purely physical attractions ?

Professor Meunier, who has carried out a large number of experiments on quinone tannage, favours the chemical theory of tanning. He found that quinone combines with the amino groups of the skin, and concludes that acids and vegetable tannins also attach themselves to these groups. This view of oxidation is held in the case of chamois, aldehyde, and vegetable tannages. Chrome tannage is explained in a different way. The basic chrome salts are first dehydrated by the skin and the insoluble anhydro products deposited in the hide. These react with it in a kind of condensation process, which continues through the neutralization of the chrome leather.

The purely physical theories are important, and need consideration at this stage.

Dealing first with the solid solution theory of Witts, Fahrion first applied this theory to the process of tanning, regarding leather as a solid solution of tanning matter in hide fibre.

The common property of tanning agents is the more or less colloidal character of their aqueous solutions. Colloids are, as a rule, less chemically active than crystalloids. This fact and the many analogies which are found in the behaviour of charcoal and hide powder, with regard to their property of removing dissolved substances from their solution, all seem to favour the view that tanning is a purely physical action.

The important work of Gibbs, Freundlich and others, on the law of adsorption, has led to the adsorption theory of tanning, according to which the tanning agent is taken up by the surface of the hide fibres and subsequently undergoes secondary changes, which render it insoluble and prevent it from being completely washed out. Probably the hide itself favours these secondary changes, the nature of which is little understood, but they may probably be classed as catalytic.

After considering the above résumé of evidence " for " and " against," one must admit that neither the physicists nor the chemists can prove their case. Thus, leather still remains a scientific curiosity. There is no doubt in the author's mind that the tanning reaction will eventually be explained by a theory embracing chemistry and physics—the great mistake is to dogmatize on insufficient evidence.

A considerable amount of leather waste accumulates in the tanner's and boot manufacturer's workshops, and some difficulty is generally experienced in getting rid of it, at least profitably. At the present time there seems little or no demand for leather scrap, and one is often asked by the uninitiated : Can leather scrap be made into glue ?

Vegetable leather wastes are practically valueless to the glue manufacturer, as the removal of the tannin cannot be accomplished with any degree of satisfaction, unless a costly and cumbersome process is resorted to. There have been many patents taken out, which attempt to solve the problem, but the methods advocated are generally too elaborate and the plant too expensive to be economical. There seems little doubt that bark and extract tanned leathers cannot yet be regarded as raw materials for the glue manufacturer.

Chrome tanned leather scrap can, however, be converted into glue, and the process may be worked on fairly profitable lines, providing a sufficient bulk of material is available and at a low enough price. The best form of material is calf shavings, which

are obtained during the manufacture of box and willow calf. Other varieties of chrome leather wastes, such as roundings, fluffings, etc., are quite unsuitable.

Chrome shavings must be kept damp, as once they get really dry it is practically impossible to wet them down again, so that they become quite valueless. The best means of preserving this material is to stock it in large iron tanks, preferably in a cool spot. The surface of the shavings should be watered every two or three days and disturbed by means of a fork. It is a good practice to throw some wet sacks over the tanks during the summer months.

It should be remembered that the price paid for chrome shavings by the glue manufacturer is extremely small, and in some cases the tanner receives no remuneration, only the satisfaction of knowing that a quickly accumulating waste product has been removed.

Alum leather waste can also be utilized by the glue manufacturer, and scrap of this kind should be kept on one side.*

Furrier's Waste. Quite a considerable amount of waste is obtained during the cutting up of furs and in hat-making. It should, however, be realized that the consumption of this material by the glue industry is very small, that is, comparing it with amounts of hide and skin offal utilized.

The small pieces of skin, too insignificant to be of any value to the furrier, are generally sold direct to the waste merchant or glue manufacturer. The latter has generally very little difficulty in converting them into a good-quality glue. Although the hair tankage is rather excessive, it may be sold as a fertilizer.

It seems rather strange that furrier's waste can be utilized quite successfully, whilst vegetable-tanned leather scrap is quite unsuitable. The explanation is simple. The majority of the furs on the market at the present time are not fully tanned, only just pickled in salt and sulphuric acid, tanned in alum liquor, or preserved by means of naphthalene, etc. Thus it is an easy task to convert them into the raw skin. Furriers do not tan furs in the same way as do tanners, simply because the usual processes of tanning are long, expensive, and apt to discolour the hair, or take away their characteristic sheen.

* For the above notes the author is indebted to the editor of *The Waste Trade World.*

CHAPTER III

THE CHEMISTRY OF PROTEINS

Hydrolysis—Putrefaction and brief survey of the histology of the hide—Preparation of sections of skin for microscopical examination

> "To find the truth is a matter of luck, the full value of which is only realized when we can prove that what we have found is true. Unfortunately, the certainty of our knowledge is at so low a level that all we can do is to follow along the lines of greatest probability."
>
> J. J. BERZELIUS.

UNFORTUNATELY, hide cannot be regarded as a definite chemical entity, like sugar or salt, that is, possessing certain known and fixed properties; it must be looked upon rather as a most wonderful natural combination of several unstable organic compounds, known as proteins.

Before attempting to describe the various hide proteins, the author intends to devote a short space to a consideration of their chemistry.

During the last twenty years or so, some considerable headway has been made in the elucidation of many of the secrets of the living cell, but there is still an enormous amount of work to be done, as Nature guards her secrets very jealously. At the present time we have some valuable data concerning the composition and properties of the more important proteins, of which there are between forty and fifty distributed throughout the animal kingdom.

The investigation of proteins represents one of the most difficult and exhausting tasks yet undertaken by the chemist. This is easy to appreciate, when we consider the instability of the product dealt with, and this means the impossibility, at present, of preparing the proteins in a pure state. When the chemist wishes to study the properties and constitution of a particular substance his first task is to prepare that substance in the pure form. This he proceeds to do by means of fractional distillation if a liquid, or fractional crystallization in the case of a solid. In dealing with a protein, it is found that on treatment with even mild acids and alkalis, or subjecting to increased temperature, radical changes take place, and the substance undergoes an almost complete metamorphosis.

For example, in the case of the well-known protein, egg-white, any appreciable increase of temperature results in coagulation. Again, if this substance is boiled with weak acid, a soluble product is produced quite unlike the original in every way, as it consists of a complex mixture of amino acids, the final products of degradation of nearly all proteins. These amino acids are the veritable links in the chain of the complex organic substances under discussion, and an account of their preparation, constitution, and properties is of vital importance at this stage.

First of all an amino acid may be defined as a fatty acid in whose molecule a hydrogen atom is replaced by an amino group, NH_2.

Take any simple monobasic acid such as acetic, $CH_3.COOH$, and by replacing a single H atom of the methyl or CH_3 group, by NH_2 or amino group, we obtain $CH_2.NH_2.COOH$ or glycocoll, the simplest representative of its class. In the case of a higher fatty acid, such as propionic, it is possible to synthesize two forms of the same amino acid, which differ only in the position of the NH_2 group. Thus, it is the practice to designate the respective positions as α and β.

$$\overset{\alpha}{CH_3}.\overset{\beta}{CH_2}.COOH.$$

The first or α-amino-propionic acid has the formula

$$CH_3.NH_2.CH_2.COOH$$

and is known as alanine, whilst the second or β-amino-propionic acid has the formula

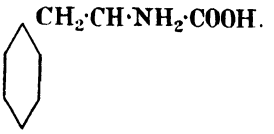
$$CH_3.CH.NH_2.COOH.$$

Alanine is an amino acid of primary importance to the bio-chemist, as it is present in such a large variety of natural proteins. Plimmer, in his book on *Bio-chemistry*, gives the following figures illustrative of the above.

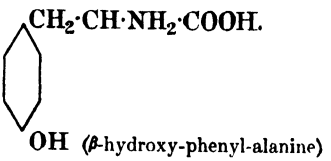
	Per Cent
Gelatine	0·8
Elastin	6·6
Keratin from horse hair	1·5
Keratin from wool	4·4
Casein	0·9
Albumin from blood	2·7

Thus, it should be evident that this amino acid is fairly well distributed throughout the organic world.

Starting from alanine, which is of course a very simple amino acid, it is possible to make more complex acids of the same type. For instance, if the phenyl group is introduced into the molecule in the β position, a very important acid is produced, known as β-phenyl-α-amino-propionic acid.

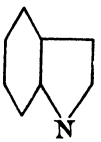


By means of a simple chemical process it is possible to replace the H atom in the para position by the hydroxyl or (OH) group, and obtain the important amino acid, tyrosine.

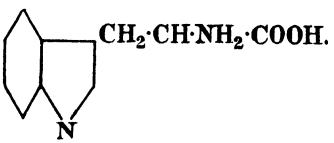


One could go on *ad infinitum* describing the formation of the higher amino and hydroxy-amino acids, but for the present purpose, the author will just mention one other derivative of alanine which is well worth consideration.

If, for the phenyl group, C_6H_5, the indole or



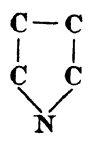
is substituted, then the following compound is obtained—



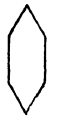
α-amino-β-indol-propionic acid or tryptophane.

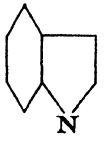
Perhaps it is worth recording that indole, which plays an important part in the synthesis of a large number of complex

amino acids, is formed from the condensation of the five-membered heterocylic ring, pyrrole, with the benzene nucleus.



Pyrrole


Benzene

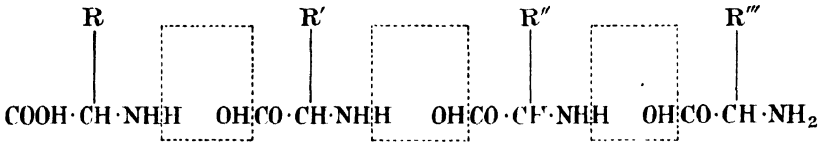


Indole

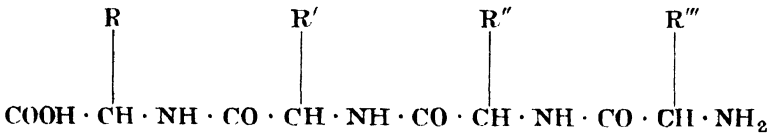
A large number of proteins yield complex amino acids on hydrolysis, although the amounts obtained show no relation proportionally.

Various workers have found that amino acids are the basic constituents of proteins. S. B. Schryver, in his excellent monograph, *Chemistry of the Albumens*, writes—

Hofmeister had already suggested that amino-acids were conjugated together in the albumen molecule by the elimination of H_2O between the carboxyl group and the amino group thus—



to give a body of the general formula



Emil Fischer, one of the greatest of bio-chemists, was the first to synthesize complex chains of amino acids, known as polypeptides, which resembled certain natural proteins very closely. If two amino acids combine by means of this condensation process the product is known as a di-peptide ; if three, then a tri-peptide, etc. Fischer prepared in this way an octadecapeptide.

It was found that a number of the amino-acids set free from the proteins by means of hydrolysis were frequently isolated

in racemic and optically active form, and that as a general rule racemisation takes place during the treatment with hot acid solutions. This caused Fischer considerable trouble in the isolation and identification of the chemically pure acids; furthermore, he was forced to racemize the amino-acids he used in the synthesis of the peptide chains.

The most general method of synthesising the polypeptides is the following—

The chloride of a halogenated fatty acid is condensed with the ester of an amino acid, the ester formed is then hydrolysed, and the halogen replaced by an amino group by treating the product with ammonia. A di-peptide is formed as the result of these reactions, and this, if converted into its acid chloride and condensed with a molecule of an amino acid ester, then hydrolysed, yields a tri-peptide.

$$CH_3.CHBr.COCl + NH_2.CH_2.COOH.C_2H_5.$$
$$\rightarrow CH_3.CHBr.CO.NH.CH_2.CO.C_2H_5.$$
$$\rightarrow CH_3.CH(NH_2).CO.NH.CH_2.COOH.$$
$$\rightarrow CH_3.CH(NH_2).CO.NH.CH_2.CO.NH.CH_2.COO.C_2H_5.$$

The majority of the more important proteins found in the glue and gelatine industry are solids. They are, as a rule, quite insoluble in the majority of common solvents, such as water, alcohol, ether, etc., but on treatment with weak acid or alkaline solutions, they soon hydrolyse, forming products soluble in water. Gelatine is, however, an exception to the general rule, as it is soluble in water after it has been swollen to the required degree, but is thrown out of aqueous solution by alcohol.

In dealing with these solid proteins, the chemist is severely handicapped by the fact that it becomes impossible to apply the common tests, as the majority necessitate a soluble protein. There are two tests, however, which may be applied, although they are of somewhat doubtful value.

Xanthoproteic Reaction. Concentrated nitric acid, when added to a small amount of the protein or its solution in water, gives, on boiling, a yellow precipitate, or the resulting solution may turn a deep orange.

Millon's Reaction. Millon's reagent is made by dissolving one part by weight of mercury in two parts of nitric acid (sp. gr. 1·42), and aiding solution by gentle heat. All proteins containing tyrosine give a whitish precipitate with the solution; the

precipitate may, however, turn a brick-red or pass into a reddish solution.

Summing up, it may be said that natural proteins are built up of complex polypeptides, which themselves are composed of simple and higher amino acids. One might well be amazed to consider the enormous number of possible isomers when building up even the simple polypeptides. The percentage composition of the proteins sheds little light on the subject. Berthensen writes—

The different albumins vary only slightly among themselves in percentage composition : they contain

C = 52·7 to 54·5%
H = 6·9 to 7·3%
N = 15·4 to 17·6%
O = 20·9 to 23·5%
and S = 0·8 to 5·0%.

It is impossible at present to construct a formula from these numbers, and even approximate molecular weights have not been determined.

Von Schroeder and Paessler give the following results of analysis of various skin proteins—

Nature of Material	C	H	N	O
Ox, calf, horse, pig, camel	50·2	6·4	17·8	25·4
Rhinoceros	50·2	6·4	17·8	25·4
Goat and deer	50·3	6·4	17·4	25·9
Sheep and dog	50·2	6·5	17·0	26·3
Cat	51·1	6·5	17·1	25·3

The proteins are divided into groups, according to their origin, solubility, coagulability on heating, and general physical properties.

The most important of the hide proteins come under the heading of scleroproteins, which includes keratin from hair, horns, etc., membrane, collagen, gelatine, elastin, etc. Other proteins found in the hide are the mucins and albumins present in small quantities in the corium.

For the present purpose, a study of collagen, the most important hide protein, will be found sufficient.

Collagen. The white fibres of the corium are composed of this protein, which may in fact be regarded as the most important constituent of the hide.

Collagen is very closely allied to gelatine both in chemical and physical properties, and most of the knowledge of the former has been obtained from a close study of gelatine. It is generally considered that collagen is an anhydride of gelatine, and this would seem to be borne out by the fact that collagen is very similar to gelatine in chemical properties, and can be transformed into that substance by simple hydrolysis. Again, gelatine, when heated up to 100° C. is converted into an insoluble mass which closely resembles collagen.

Collagen gives all the usual colour reactions which can be carried out with solid proteins, such as the Xanthoproteic and Millon tests. Acids and alkalis swell collagen, but no solution takes place providing the concentration of the reagents is not too great. The physical laws affecting the swelling of gelatine are precisely similar to those of collagen. On hydrolysis, collagen is converted into gelatine, the complete process taking several hours. If the hydrolysis is carried a step further, then peptones and amino acids are formed, which means that the gelatine becomes partially destroyed and thus rendered useless for ordinary purposes.

Hofmeister (*Z. Physiol. Chem.*, 2 (1878) 299) is of the opinion that the conversion of collagen into gelatine by the agency of water is a definite hydrolysis which can be illustrated by means of a simple chemical equation.

$$C_{102}H_{149}O_{38}N_{31} + H_2O \rightleftharpoons C_{102}H_{151}O_{39}N_{31}.$$

At first sight the above equation may appear rather helpful, but empirical formulae are seldom reliable, and their scientific value is very small, although, of course, there are times when the chemist can use them to his advantage. Gelatine and collagen cannot be regarded as definite and stable compounds, but rather as unstable modifications of two distinct proteins. Minute quantities of sulphur, phosphorus, etc., are always present in even the purest samples, and although it is simpler and certainly convenient to regard these elements as impurities, this view cannot be supported by scientific evidence. It would appear that both sulphur and phosphorus play a very important part in the make-up of the protein molecule—probably acting as a nucleus in the complex structure.

Hofmeister's equation illustrates the reaction as reversible, but this has been denied by various bio-chemists working on

similar lines. It seems very unlikely that gelatine can be a simple anhydride of collagen, as ammonia is evolved during the hydrolysis of the latter, but this is not indicated in the equation.

Hydrolysis of Hide Proteins. It has previously been pointed out that hide proteins can be broken down into simpler compounds by means of a process known as hydrolysis.

Hydrolysis is a reaction of paramount importance, as gelatine and glue are themselves hydrolytic products of the hide and other proteins.

Boiling in water is not the only means of breaking down the complex structures into simpler ones. Thus, chemical agents, such as mineral and organic acids, caustic alkalis, and enzymes all bring about the same result. Bacteria also break down proteins, as will be discussed when considering the subject of putrefaction.

By various means it is possible to analyse the complex proteins. Hydrolysis is not a perfectly controllable process, and it is difficult, if not impossible, to stop the reaction at a particular stage. Procter gives the following list of hydrolytic products of the hide.

Protein (collagen, casein, albumin, etc.)
↓
Metaprotein (Lieber Kuhn's jelly)
↓
Proteoses (gelatoses, albumoses)
↓
Peptones
↓
Simple polypeptides (Kyrins)
↓
Amino acids.

The best known hydrolytic agents are—

Sulphuric acid (approx. 25%)
Concentrated hydrochloric acid
Baryta water
Hydriodic acid
Lime water (saturated solution)
Caustic soda (decinormal).

Acid hydrolysis proceeds at a slow and normal rate, but alkaline hydrolysis is fairly rapid, although both processes yield practically the same results.

To the leather chemist and technologist enzyme hydrolysis is

a subject of primary importance, but before attempting to describe the actions of these peculiar ferments, a word about their actual constitution must be said.

Enzymes may be looked upon as the secretions of the organisms which bring about fermentation and putrefaction, and these secretions function quite apart from the particular organisms responsible for the reactions—that is, they are unorganized. Chemical analysis has shown that these substances are made up of the following elements—

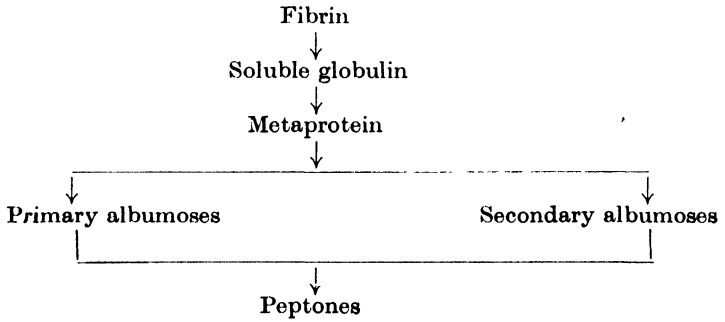
Carbon
Hydrogen
Nitrogen
Oxygen

They are said to be complex proteins, little being known about their composition.

It has been found by Bayliss (*Journ. Physiol.*, Dec., 1915) that enzymes exist in the colloidal state, and thus may pass through ordinary filters unaltered.

Proteolytic enzymes are those of the greatest significance from our present point of view. Thus trypsin, pepsin, erepin, and enterokinase are the most important. Trypsin is the most drastic in action, hydrolysis in this case taking place in an alkaline medium, $P_H = 8{\cdot}1$, whilst pepsin acts only in the presence of weak acids, $P_H = 1{\cdot}4$. The former enzyme attacks all soluble proteins, but is without action on certain insoluble ones.

The hydrolysis of proteins by means of enzymes is tabulated by Cole in the form of the following diagram, pepsin being employed in this instance—



When tryptic enzymes are used, then the hydrolysis is carried a step further than peptones, amino acids being formed.

Putrefaction of Hide Proteins. The putrefaction of glue stock, which, as previously mentioned, is of a very unstable nature, affects both the tanner and glue manufacturer, as it means rapid deterioration of the raw material, which, of course, entails a serious loss of money. It should thus be apparent that the subject of putrefaction requires some consideration at this stage.

First of all the word putrefaction needs defining. Probably the best and simplest definition is that it is the decomposition of nitrogenous matter by living organisms. As this reaction is generally accompanied by the evolution of malodorous gases, it may be termed a kind of putrid fermentation.

In any putrefying matter, such as hide or gelatine, an enormous number of different species of bacteria may be noticed, as well as monads, infusoria, and moulds.

There are two stages of putrefaction. The first is known as the aerobic, in which the bacteria require the presence of oxygen for their activities, and are known as " aerobic bacteria." They use up all the oxygen present, and form simple organic compounds, such as carbon dioxide, nitrates, and sulphur compounds.

Abt (*Journ. Soc. Chem. Ind.*, 1906, 109) gives the following table illustrative of the action of putrefactive organisms—

- *Aerobic*
  - *Mixed*
    - Proteolytic : Micrococcus flavus liquefaciens, protens vulgaris, white staphylococcus.
    - Peptolytic : B. Coli, B. filiformis, streptococcus pyogenes, diplococcus grisens.
  - *Simple*
    - Proteolytic : B. subtilis, B. mesentericus.
    - Peptolytic : Protens zenkeri.
- *Anaerobic*
  - *Mixed*
    - Proteolytic : B. perfringens, B. bifermentans sporogenes.
    - Peptolytic : B. bifidus, B. lactopropyl-butyricus non-liquefaciens (Tissier).
  - *Simple*
    - Proteolytic : B. putrificus, B. putidus gracilis.
    - Peptolytic : Diplococcus magnus anaerobinus, B. faecalis alkaligenes.

The second stage, the anaerobic, takes place in the absence of oxygen by anaerobic micro-organisms, and whereas the first process was one of oxidation, this one is of reduction.

Organisms, known as proteolytic, decompose the nitrogenous matter into simpler substances, which are also capable of liquefying gelatine. The peptolytic attack the soluble products formed by the proteolytic organisms.

The principal organisms engaged in the liquefaction of hide and gelatine are of the B. liquefaciens magnus type, which are present in dust, and the atmosphere of living rooms, etc. They are said to prepare the way like heralds at the opening of the lists. Of greater importance are B. putrificus and B. putidus gracilis, which are anaerobic, and can live only in alkaline solution.

Nencki, in his classical work *The Chemical Mechanism of Putrefaction*, considers that the processes by which the putrefaction of proteids is brought about by bacteria are analogous to those taking place by melting the respective bodies with potash, and he holds that in the hydration processes brought about by bacteria, the water plays the same part as the potash.

Nencki explains, for example, the metamorphosis of lencin by putrefaction in this way. The bacteria decompose the water into hydrogen and hydroxyl, which act upon the lencin in the following manner—

$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!\rangle CH - CH_2 - CH(NH_2) - COOH + HOH = NH_3 +$$

$$OH - CH_2 (CH_2)_4 COOH \text{ (oxycaproic acid).}$$

The resulting oxycaproic acid is then split up by the second water molecule into methylene-glycol and valerianic acid.

$$\begin{matrix} OH \\ | \\ CH_2 \\ | \\ (CH_2)_4 \\ | \\ COOH \end{matrix} + HOH = CH_2 (OH)_2 + CH_3 (CH_2)_3 COOH$$

The methyleneglycol, which changes into formaldehyde and water, is now split up into carbon dioxide and hydrogen, as it would be by melting with caustic soda.

$$\begin{matrix} H \\ C \Leftarrow\!\!= O \\ H \end{matrix} + \begin{matrix} HOH \\ \\ HOH \end{matrix} = CO\begin{matrix} OH \\ \diagup \\ \diagdown \\ OH \end{matrix} + 2H_2$$

The Anatomical Structure of the Hide. The anatomical structure of the hide needs a little consideration. Academically, the subject bristles with difficulties, but from the technologist's point of view, the main structure of the skin is fairly simple. Hide may, in fact, be divided into two principal, though widely different, layers—the epidermis and dermis, the former being the thin scaly layer on the surface of all skin, and the other, the true skin, with its vast network of capillaries, nerves, and glands, etc.

The enthusiastic student, if he desires to obtain more than a passing acquaintance with this fascinating subject, is advised

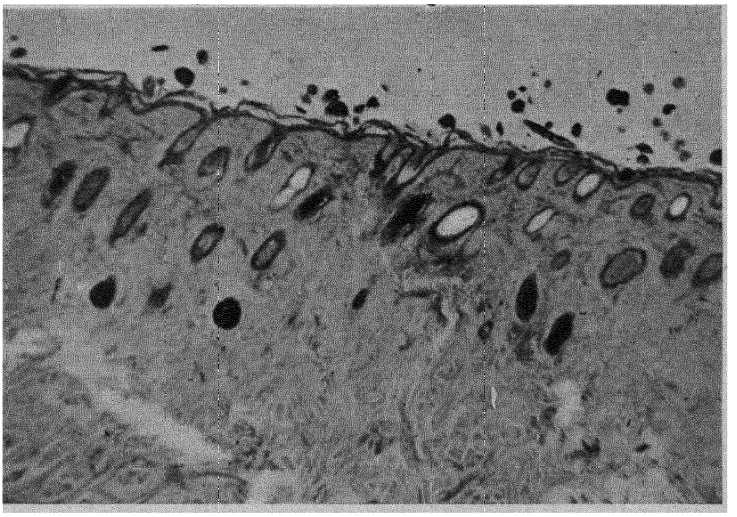


FIG. 3. PHOTO-MICROGRAPH OF TRANSVERSE SECTION OF CALFSKIN

to prepare some sections of skin himself and examine them under a good microscope. In this way a really first-hand knowledge will be obtained.

A knowledge of histology is of some considerable use, both to the work's chemist and technologist. An examination of tissues affords another works control method, and one which in the right hands can prove of very great value.

The Epidermis. The first two layers of the epidermis are known as scarf skin and horny cells, or stratum corneum, and are composed of dry, hard, and horny scales which possess a chemical constitution very similar to horn. The next in importance to these epithelial scales are the stratum lucidum and

granulosum, the former layer lying between the mucous and horny layers. The cells in this case are packed closely together and arranged systematically. The stratum granulosum is the uppermost layer of the rete malpighi, from whence its cells are continually renewed. These cells, although slightly elongated, contain traces of nucleus.

The rete malpighi itself consists of soft mucous and nucleated cells. It is further divided by histologists into two layers, the prickle cells which come directly under the stratum granulosum, and the columnar cells, which rest on the papillary layer of the epidermis. The soft cells of the rete malpighi are transformed as they approach the surface, becoming gradually elongated, until they ultimately evolve into the hard and horny scales of the epidermis.

The cells of the epidermis are composed of what is chemically known as keratin.

The Corium or Dermis. Dealing next with the dermis, we find that it is composed primarily of two important layers ; the papillary layer, which is composed of projections which pass upwards into the rete malpighi which fills in the hollows formed by them ; then there is the true dermis, and this is composed of bundles of connective tissue fibres bound together with a yellow elastic substance known as elastin. These bundles of fibres are interlaced, and the space between the fibres is filled with a gelatinous matrix known as " interfibrillar substance."

The corium is plentifully supplied with bloodvessels and nerve centres, especially in the region of the hair roots.

The glue manufacturer is concerned only with the corium, which, of course, forms the major portion of the hide, the epidermis being merely a very thin layer on the surface.

The Preparation of Sections of Hide for Microscopical Examination: Paraffin Method. Take a small piece of the skin ($\frac{1}{4}$ in. square) and fix with the well-known Zenker's reagent for 24 hr. ; this fixes the tissues. Wash in water and then soak in 50 per cent alcohol for a further 24 hr. Now transfer to 60 per cent alcohol, then to 70, 80, 90 per cent and, finally, absolute. The tissue should be thoroughly dehydrated when it is put into xylol and allowed to remain for some length of time.

A saturated solution of paraffin wax in xylol is made, and the skin placed in it. When thoroughly permeated with paraffin, it

should be placed in melted paraffin in a mould and allowed to cool, when a small paraffin block will be obtained.

The procedure should be as follows—

Zenkers reagent	24 hr.
Washing	3–4 ,,
50% ethyl alcohol	1 ,,
70 ,, ,, ,, ...	1 ,,
90 ,, ,, ,, ...	1 ,,
100 ,, ,, ,, ...	1 ,,

Now put into a solution consisting of half alcohol and half xylol for 2 hr. with one change of solution. Leave in this 2–3 hr., then place in melted paraffin wax alone for 3–4 hr., take out and block. Cool, and then cut on a paraffin microtome. The ribbons of sections obtained in this way should be floated in warm water, transferred to slides previously thinly coated with albumen and glycerine, and then left in the paraffin oven for 2 hr.

The best method of staining these sections is the one recommended by The British Drug House, Ltd., in their excellent little brochure *Clinical Pathology and the Use of Stains*—

For staining these sections, the slides are immersed successively in xylol for 5 min., absolute alcohol for 2 min., 90 per cent alcohol for 2 min., and then transferred to iron haematoxylin solution for 5 to 10 min. They are next washed under a tap and placed in a dish of tap-water to which a few drops of ammonia have been added. They rapidly become blue-black in colour, and can then be counterstained with a 1 per cent aqueous solution of either Eosin or Biebrich Scarlet , the latter being preferable if a standard stain is available. After washing for ½ min. the sections are blotted dry and then dehydrated in a 90 per cent alcohol for 5 to 10 min., followed by absolute alcohol for 10 min., and are then cleared in oil of cloves for ½ hr. and mounted in Canada Balsam.

This method may seem somewhat more complicated than the usual one, but it gives excellent results. The nuclei stain well with the haematoxglin, whilst the rest of the tissues show up very clearly when counterstained with the red.

By means of a microscopical examination of tissues, it is possible to follow the liming, deliming, and washing of the hide and skin offal, and thus gain valuable information as to the completeness of these operations.

CHAPTER IV

RAW MATERIALS FOR GELATINE AND ISINGLASS

Secondary raw materials : water, air, lime, salt

SIMILAR materials are used in the manufacture of gelatine as in glue production—hide and skin offal, bones and fish waste are all utilized. In considering the process of gelatine manufacture, it must be realized that this substance ranks as an important food, and consequently the raw materials employed must conform to certain standards of purity not demanded for ordinary glues. Again, the conditions under which gelatine is made must be strictly hygienic, and every possible attention paid to cleanliness, both as regards containers and the hands of the workmen who convey the product from one part of the factory to the other.

Only the very best hide and skin offal is utilized. The pates and trimmings from calfskins are, perhaps, the most valuable raw materials, although it should be pointed out that the skins from very young animals contain appreciable quantities of water and mucin-like substances, which lower the setting properties of the jelly. Offal from the ox may rank almost as high as calf-waste. The hide proteins obtained from aged animals do not, however, give a really high-grade gelatine, although they make an excellent glue.

The presence of even small quantities of undesirable materials in a boiling of gelatine, will lower the value of the resulting product to a quite appreciable degree. Goat, sheep, and other skin offal are not employed by the majority of gelatine manufacturers, except in small quantities. One of the many disadvantages attached to the use of these materials, is that they contain excessive amounts of animal fats, which are extremely difficult to eliminate from the product during the ordinary processes of purification.

Bones may be considered as an important source of gelatine, but here again there are difficulties in the way of selecting the most suitable materials. The dry and stale varieties, commonly known as junk bones, and the steamed and pickled specimens are totally unsuitable for edible gelatine. Soft bones from very young animals contain excessive proportions of water, and

consist almost entirely of a material practically identical with cartilage—thus they make a rather inferior product and their use is not recommended when a really first-grade gelatine is desired. Briefly, it may be said that the best bones are from mature cattle, but they must, however, be treated or worked as quickly as possible. Long delays in boiling, etc., favour the growth of liquefying organisms, which cause the valuable protein matters to decompose and, consequently, deteriorate in value.

A small amount of fish scrap, composed of the freshest skins of the cod and similar fish is utilized by some gelatine manufacturers, although fish scrap generally is not regarded very favourably. The reasons for this are not hard to find, probably the most important is that the material is generally in the earlier stages of putrefaction. Very little, if any, effort is made to preserve or freshen up the waste by the use of salt or employment of cold storage, the heads, trimmings, and bones being simply dumped into large metal containers and sent to the glue or fertilizer manufacturer. In America, the large canneries have their own gelatine plants to cope with the enormous waste obtained during the tinning of the numerous kinds of fish. It is claimed that a very high-grade gelatine can be manufactured and at a low price.

Ossein from fresh horn piths is a very valuable source of gelatine, but unfortunately the supply is strictly limited. A clear and strong product is made from ossein.

Miscellaneous stock, which includes leather, fur trimmings, etc., is quite unfitted for gelatine.

It should be apparent from the above that the gelatine manufacturer's task is not an easy one, and in no other industry is the operator confronted with such a galaxy of difficulties, some of which can be overcome only by prolonged research. Gelatine is a highly putrescible organic substance of a very complex chemical and physical constitution. It is a colloid about which little as yet is really understood, in spite of years of research by the greatest physicists. Again, gelatine absorbs impurities, such as metallic salts, with avidity, and it is greatly affected by atmospheric conditions. A thunderstorm will sometimes cause the gelatine jelly to liquefy, and hundreds of pounds may be lost in a very short time by this peculiar metamorphosis.

Unfortunately, the gelatine manufacturer has little reliable information to help him. The data at hand is generally so wrapped up in scientific euphuisms, as to be quite unintelligible to anyone below the status of a doctor of philosophy. Consequently, the manufacturer is bound to rely upon his own or his staff's accumulated experiences.

Isinglass. RAW MATERIALS. Isinglass is a much more expensive substance than gelatine and, consequently, the raw materials used for its manufacture are the very best and most suitable for the purpose. In explanation, it may be said that isinglass is a product made from the swimming bladders of the sturgeon, cat-fish, hake, cod, etc. There are in fact a large variety of fish utilized ; the sturgeon, however, is the best known, and for our present purpose, the most important.

STURGEON (Acipenser). The sturgeon family is not particularly large, embracing at the most some twenty odd species, which are to be found in the principal rivers of Europe, Asia, and North America. The most important sources, however, are the rivers of Southern Russia, where the sturgeon are found in enormous quantities. In Asia and America they are not so plentiful.

The sturgeon fisheries of Russia are of immense value, and this can be appreciated when we consider the full utilization of the various parts of the fish. The flesh is most valued as a food, and is salted, smoked, or dried for the purpose. Other valuable portions are the ovaries, which are made into caviare, and the air bladder removed from the carcase and preserved ready for the manufacture of isinglass. Various wastes obtained during the dissection of the body, are boiled for the oil and also treated and made up into fertilizers.

The sturgeon is a large fish. ranging from 8 to 11 ft. in length, and sometimes considerably larger. Unlike a large number of the denizens of lakes and rivers, they live to an exceedingly ripe old age. Prof. Van Baer, who has conducted some considerable zoological research work in Russia, states that the hauser (acipenser huso) attains an age of 300 years or so, which is indeed remarkable. To trace the growth of the sturgeon from the embryo to old age would be a fascinating occupation, but, unfortunately, neither space nor time permits the author to indulge his fancies. Perhaps it is worth mentioning that, although the early growth of the fish proceeds at a rather rapid

rate, when it reaches maturity growth slows down to a very considerable degree.

To the student of evolutionary biology the phenomena of convergence, or the slow metamorphosis of one organ into another, is one of the most interesting and fascinating studies. The air bladder of certain fish is a very important structure, when viewed in the light of evolutionary biology. Dendy states that the hollow outgrowth from the front part of the alimentary canal, which becomes almost completely filled with gas, and is known as the air bladder, was at one time an accessory organ of respiration. He points out that there survive at the present time some remarkable fish which breathe by means of the air bladder and the gills, notable examples being the Australian mud-fish and the African protopterus.

There is no doubt that the air bladder was the forerunner of the lungs, and it was the development of this organ, which completely replaced the gills, then of the lungs, which rendered possible that tremendous step " in the evolutionary history of the vertebrates—the migration from water to land."

Before the air bladder can be said to be of any real practical value its size and origin must be very carefully considered. Very small bladders are generally unsatisfactory. If the bladder is so diminutive as to be very securely attached to the backbone of the fish, then its removal is uneconomical. Bogue points out that—

> The yield and quality of the product varies greatly, however, with the specie of fish. The large, deep-water hake yield from 40 to 50 lb. of dry isinglass per ton of fish, and the product contains about 85 per cent gelatine. The smaller shallow-water hake yield only about 30 lb. of isinglas per ton of fish. The cod yields but 15 to 20 lb., and the squeteague 20 lb. The gelatine content of the product from the latter two species is also low, being only about 50 per cent.

Russia has been for centuries almost the sole manufacturer of isinglass, and has up to the last few years exported it in relatively large quantities. At the present time, however, the amount produced is quite eclipsed by other countries, principally the United States and Germany. Of course, Russian isinglass is generally recognized as the best, and there is always a steady demand for the product made from the sturgeon.

The sounds, or bladders, reach the manufacturer in two conditions—salted or air-dried. Generally, every possible

precaution is taken to ensure excellent preservation, and whether the first or second method is adopted, the skin substance is usually very efficiently preserved. Prior to treating or preserving the bladder, the inner or glutin-containing membrane is removed.

The salting is quite simple, and in the majority of cases is performed by packing the sounds in large barrels and throwing on top of each layer a sprinkling of clean salt. The concentrated brine exercises the well-known salting-out action on the proteins, and owing to its peculiar physical action and its slight antiseptic properties, bacterial activity is extremely small. The salt can soon be removed by washing, leaving the bladders swollen and quite fresh. Very frequently this crude salting is performed on the vessels engaged in sea fishing, that is, unless the fish are dressed ready for immediate sale on landing.

Air drying, if carried out on proper scientific lines, leaves nothing to be desired by even the most exacting manufacturer. Unfortunately, however, the air drying as done by the casual fisherman is most unscientific. In some cases the bladders are partially decomposed, and in others so hard and horny from exposure to the sun, that to soften them necessitates the expenditure of considerable time and labour. Sounds dried by exposing them to a cool current of fresh air, and not subjected to the fierce heat of the sun, will be found quite satisfactory—that is, they will keep indefinitely (when dry) and soften fairly easily in warm water.

Water Used in Glue and Gelatine Production. It is essential that the glue and gelatine manufacturer should have his factory so situated that a supply of pure water is available. The importance of a water containing a low percentage of total solubles and the absence of organic matter cannot be sufficiently emphasized.

Generally speaking, the chief impurities of most waters are dissolved salts—temporary hardness (bicarbonate of calcium and magnesium), and permanent hardness (sulphates and chlorides of calcium and magnesium).

Sodium chloride, carbonate, and ammonium carbonate, together with small quantities of iron and zinc salts, etc., may be present. Organic matter, which includes micro-organisms, can be traced in certain waters contaminated with sewage.

The purest natural water is rain-water which is collected in

a country district, the only impurities likely to be present in this case being dissolved air and carbon dioxide. It may be said that rain-water is in reality a very weak solution of carbonic acid. In spite, however, of the low acidity of the solution, it has a very decided action upon limestone, and when the water passes through a strata of limestone the following reaction takes place—

$$H_2CO_3 + CaCO_3 \rightleftharpoons Ca(HCO_3)_2$$

calcium bicarbonate being formed. This salt causes temporary hardness, which may be removed by boiling

$$Ca(HCO_3)_2 \rightleftharpoons CaCO_3 + CO_2 + H_2O$$

In an exactly similar manner the sulphate and chloride of lime and magnesia enter into solution, and cause what is known as " permanent hardness," but unlike the unstable bicarbonate, they cannot be removed by boiling.

Sulphur dioxide, hydrogen sulphide, and oxides of nitrogen are present in varying amounts in the atmosphere of most manufacturing towns, while sometimes chlorine is present in chemical centres, such as Huddersfield. In consequence the rain-water collected in those places contains traces of these impurities.

Iron in water is due to the percolation of the water through a strata of iron-stone, a quantity of iron being dissolved by the weak acid solution. It sometimes happens that the iron is present in suspension as the oxide, if in solution the acid carbonate is usually the principal salt. Sulphates and chlorides of lime cannot exist in the presence of bicarbonate of lime.

In the manufacture of gelatine, distilled water is more or less essential, especially for the boiling of the glue stock. Bogue writes—

> For the actual boiling of the glue, distilled water is to be preferred. Any salts in the water will be concentrated during evaporation and remain in the finished product to the probable detriment of its appearance. If the liquors are drained off at, say, 5 per cent concentration, that means there will be nineteen times as much mineral matter added to each pound of glue as there is in each pound of water.

In conclusion, it may be said that soluble salts should not be present in excessive quantities, so the percentage of total solubles must be as low as possible. Traces of sulphur dioxide, hydrogen sulphide, chlorine, etc., are most undesirable, as they cause

discoloration of the gelatine, or if present in the edible product, are regarded as objectionable and harmful impurities.

Bacteria are very dangerous adulterants, if the term may be stretched to include them. The reason why micro-organisms are viewed with distinct disapproval by the glue manufacturer is not because he fears the presence of pathogenic bacteria, but because of the likelihood of the presence of gelatine liquefying organisms.

Moore and Partridge state that in pure water less than 10 per cent of total organisms is gelatine liquefying. Whilst in the purest upland streams the bacteria in 1 c.c. are less than 100. Compare this with 1000–100,000 in river water and a good comparative idea of purity will be obtained.

The subject of sterilizing impure water is a large and difficult one, and needs the most careful consideration. Unfortunately, the author can only touch upon the fringe.

By far the best method of sterilization is the one in which chlorine is utilized. An extremely minute quantity is necessary to achieve the desired result, and Sims Woodhead found that the proportion of chlorine necessary to kill the whole of the non-sporulating bacilli in Cambridge water is about 1 part per 7,000,000 parts of water. The chlorine may be used in the form of bleaching powder or made on the spot by means of the usual electro-chemical method.

Moore and Partridge mention the sterilization of water by ultra-violet ray treatment by means of special Cooper-Hewitt lamps made from transparent quartz. "A continuous supply of sterile water is available in five minutes."

No matter what method is used for the purification of the water, it should be kept under control by a skilled chemist, or, at least, an intelligent technologist with some knowledge of the bacteriology of water.

Iron and similar metals, such as zinc, discolour the finished product, and for this reason the water used should contain less than 1 part per 1,000,000 of these substances.

Analysis of Water. The following estimations are the simplest and most important, and may be carried out by any one possessing a comparatively limited knowledge of chemistry.

DETERMINATION OF TEMPORARY HARDNESS. 100 c.c. of distilled water is titrated against $N/_{10}$ HCl, using methyl orange as indicator, this titration is a blank, and performed in

order to obtain the figure for the methyl orange. 100 c.c. of the water to be tested is now titrated against the $N/_{10}$ acid, using methyl orange, the figure obtained for the indicator in the first instance is subtracted from the acid figure, and the result worked out as follows—

100 c.c. of distilled water requires ·1 c.c. $N/_{10}$ HCl.
100 ,, ,, sample ,, ,, 3·7 ,, ,, ,,
,, ,, ,, ,, ,, ,, 3·6 ,, ,, ,,
∴ 3·6 − ·5 Degrees temporary hardness.

18·0 degrees T.H. This represents 18 mg. per 100,000 calculated as calcium carbonate.

Determination of Permanent Hardness. 100 c.c. of $N/_{10}$ NaOH is added to 100 c.c. of $N/_{10}$ Na_2CO_3, 50 c.c. of this alkali is added to 200 c.c. of the sample water, and the mixture boiled in a Jena flask having a funnel at the top to prevent spurting. The mixture is boiled until the bulk is reduced to 150 c.c. and then made up to 200 c.c. with distilled water.

The liquid is filtered and the first 50 c.c. of filtrate rejected, the next 100 c.c. titrated against $N/_{10}$ HCl using methyl orange.

100 c.c. of solution requires 45 c.c. of $N/_{10}$ HCl.

Originally present in solution 50 c.c. of alkali, which would require exactly 50 c.c. of $N/_{10}$ HCl.

Difference of 5 c.c. $N/_{10}$ alkali must be accounted for by neutralization of the acids of permanent hardness.

Thus 5 × 5 in milligrams per 100,000, calculated as calcium carbonate, represents the permanent hardness, or expressed as 25 degrees P.H.

Determination of Magnesia Hardness. Take 100 c.c. of the water to be tested and carefully neutralize the temporary hardness with $N/_{10}$ HCl. Boil down to expel carbon dioxide and then add 100 c.c. of saturated lime-water of known strength. Boil, then allow to cool, make up to 200 c.c. and filter. When filtering, throw away the first 50 c.c. which comes through, then take the next 100 c.c. and titrate against $N/_{10}$ HCl.

50 c.c. of lime-water requires 21·0 c.c. of $N/_{10}$ HCl.
100 c.c. of lime-water mixture requires 19·1 c.c. of $N/_{10}$ HCl.

(21 − 19·1) = 1·9 c.c. $N/_{10}$ HCl, which corresponds to magnesia hardness in 50 c.c. of sample.

1·9 × 2 × 5 = 19 mg. $CaCO_3$ per 100 c.c. water.

Actual mg. may be calculated by multiplying by 0·24; or MgO, multiplying by 0·4.

Result 7·6° magnesia hardness.

DETERMINATION OF CHLORIDES. Titrate 100 c.c. of the sample in a porcelain dish with $N/_{10}$ $AgNO_3$, using K_2CrO_4 as indicator—

1 c.c. of $N/_{10}$ $AgNO_3$ = ·00355 grm. Cl_2.
100 c.c. of water = 1·1 c.c. $N/_{10}$ $AgNO_3$
= (1·1 × ·00355) grm. Cl_2.
∴ 100 c.c. of water contains ·00355 grm. chlorine.

COLORIMETRIC METHOD OF ESTIMATING TRACES OF IRON. This reaction is based on the well-known property of ferric salts, giving a red coloration with potassium thiocyanate, KCNS.

A standard iron solution is made up by dissolving ·7 grm. of ferrous ammonium sulphate, $FeSO_4(NH_4)_2$ SO_4. $6H_2O$. This weight of salt is equivalent to ·1 grm. of pure iron.

The ferrous iron is converted into the ferric condition by dissolving it in water and adding 2 to 3 drops of concentrated nitric acid free from iron. Boil for 1 hr., then make up to 1 litre. This is the stock solution, and should be diluted 1 in 10 before use, which means that in 1,000 c.c., 0·01 grm. of iron is present.

Take 100 c.c. of the sample to be tested and evaporate down to dryness with a little H_2SO_4 free from iron, moisten the residue with HNO_3, and add boiling distilled water and transfer to a Nessler glass. Add 5 c.c. of 5 per cent KCNS and 100 c.c. of 10 per cent HNO_3 to two Nessler glasses, one of which contains the sample. Run into the glass containing no water, a little of the standard iron solution until the colours of the two liquors correspond. It is important to note that, when matching, the volumes must be the same. Always make up to the required level with pure distilled water.

100 c.c. of water requires 6·1 c.c. of Fe solution in order to effect a perfect match.

1 c.c. of ferrous ammonium sulphate is equivalent to ·00001 grm. of iron.

∴ (6·1 c.c. × ·00001) = grams of iron per 100 c.c. of water.

·000061 grm. of iron per 100 c.c. of water, or ·061 grm. per 100,000.

Iron is generally expressed in parts per million, thus—

·61 parts per million.

Air. The purity of the air supply is not infrequently overlooked by the technologist and chemist. It cannot be sufficiently emphasised that the purity of the air is of vital importance in the manufacture of such delicate substances as high-grade glues and gelatines.

The following analysis of a sample of pure air will give some idea of the standard desired—

Oxygen	20·35
Nitrogen	78·10
Carbon dioxide	0·03 to 0·04
Water vapour	1·5 variable

The purity of the air supply is generally gauged by the amount of carbon dioxide present—thus, pure air contains 3 to 4 parts of CO_2 per 10,000. Good ventilation may be said to exist when the air contains a total of not more than 6 to 8 parts of CO_2 per 10,000.

The humidity of the air is of great significance to the glue manufacturer. It should be noted that the amount of moisture the air can hold at saturation per unit of volume increases in proportion to rise of temperature. At 70° F. it will hold 8 gr. of moisture per cubic foot, while at 32° the amount drops to 2 gr. per cubic foot, and at 0° F. only 0·5 gr. Normal conditions prevailing, the air has a humidity of 50 to 70 per cent of saturation.

Micro-organisms are frequently present in the air, and as these are sometimes gelatine-liquefying, their presence is not desirable. The works chemist should always carry out a few simple psychrometric experiments to determine the humidity, and follow this up with an ordinary bacteriological examination to estimate the number of micro-organisms present in a known volume. Humidity tests can always be carried out by means of the simple wet and dry bulb thermometer.

The contamination of air is expressed in so many organisms per cubic metre of air. The old method of conducting the quantitative estimation of organisms present in the air was to draw a known volume through some sugar, then dissolve out the sugar and determine the bacteria by plating out on gelatine, then agar.

A modern method is the following—

Draw 10 litres of air through 50 c.c. of pure distilled water. Of the 50 c.c., pipette ½ c.c., and plate out on gelatine incubated at 20° C. for three days, then count all the colonies on the plate and calculate to 50 c.c.

Result should be checked at the end of three to five days by using agar instead of gelatine. The reason for this is that

liquefying organisms, such as B. butyricus, could not be estimated with gelatine, agar being necessary.

The qualitative analysis is simply a step farther, and consists of isolating each organism representative of a colony, staining and examining with $\frac{1}{12}$ in. objective (oil immersion).

It cannot be said that any particular species of bacteria is to be regarded as characteristic of air. Streptococci and staphylococci are often found, and it is likely that they are derived from domestic dust and surface of the skin, from which they may be easily detached by the wind. Spores of moulds, yeasts, and bacterial spores are frequently present in the air of most towns. Air drawn from high altitudes in a country district is fairly pure, whilst in mid-ocean the air contains no micro-organisms, and is in fact practically sterile.

Raw Materials Used in the Preservation of Glue and Gelatine Stock. There are two widely-known chemicals which are employed as preservatives by the tanner and glue manufacturer, etc. They are, lime or calcium oxide in the form of its soluble hydrate, and sodium chloride or common salt. The first is, however, the most important, as not only is it used on a large scale by the tanner, for the ordinary purposes of depilation and plumping of hides and skins, but it is essential to the glue manufacturer, the liming of glue stock being an important preliminary process.

Salt is used to an enormous extent for the preservation of all putrescible materials, and in this connection is invaluable. There are a few disadvantages attached to the wholesale use of this substance as a preservative for glue stock, and they will be enumerated when salt is described.

In view of the very great part which these two chemicals play in the glue and allied industries, the author considers it necessary to devote some space to a consideration of these properties and characteristics.

Lime. This is a most important alkali, and is used in very large quantities, both in the production of glue and also the tanning of leather. Probably the reasons why it is so popular are—

1. Low cost.
2. Limited solubility in water, which renders its use almost foolproof.
3. Regularity of action.

In spite of the large number of new alkalis on the market, the consumption of lime is greater than ever, and although the former may in some cases be of considerable help, they do not supplant lime.

As everyone knows, the universal source of lime is limestone, which is quarried *en masse* in Derbyshire. Limestone consists almost entirely of calcium carbonate, at least the best varieties do—lime from the famous Grin Quarry, Buxton, contains less than 1 per cent silica and 0·20 per cent magnesia, and may be regarded as almost pure calcium oxide, i.e. calcined limestone. The lumps of limestone are removed from the quarry to the kilns, where they are burned, the usual method being to fill the kiln with alternate layers of limestone and fuel, and a fire is, of course, built at the bottom of the stack and the whole fired. When the fire has burned out, then the lime is removed and cooled. The simple chemical reaction is as follows—

$$CaCO_3 + (HEAT) = CaO + CO_2.$$

The carbon dioxide, and sometimes the monoxide, passes off as gases.

It frequently happens that the burning of the limestone has not been carried out efficiently, and in consequence considerable proportions of stone are present. This represents a dead loss to the buyer, and it is always wise to have a sample analysed before purchasing a large consignment. If the original limestone contained seams of clay mixed with alumina, magnesia, and other earthy impurities, then the resulting lime will be very impure, perhaps only containing 30 per cent of available alkali.

Prof. H. R. Procter gives an analysis of a bad lime, which illustrates the point in question.

	Per cent
SiO_2 and insoluble matter	17·70
Fe_2O_3	6·42
CaO	49·86
$CaCO_3$	14·21
$CaSO_4$	3·01
$CaCl_2$	0·33
MgO	2·09
Organic matter	0·80
Moisture by difference	5·58

(Analysis made by Mr. G. W. Flower, B.Sc., in the Leather Industries Laboratory at Leeds University.)

Calcium oxide or quicklime, CaO, reacts with water, forming the hydroxide

$$CaO + H_2O = Ca(OH)_2$$

A considerable evolution of heat accompanies the reaction. The heat of formation of calcium hydroxide is 16·25 calories. It is a mistaken idea to suppose that in hydrating lime all that is necessary is to put the lime into a large receptacle and fill the latter up with cold water. If lime is treated in the above manner the resulting product will be most unsatisfactory. For the really ideal method of slaking, the lumps of lime, which should be of uniform size, must be thrown into a clean, large receptacle or pit and sprayed with cold water intermittently for about 5 hr., then just covered with cold water and left for a further 12 hr., when the reaction should be complete. After thorough mixing the lime liquor may be considered ready for use.

Lime does not slake well in cold water, and even if left for a long time free limestone will always be found to be present. When a small amount of water is used for the hydration, the heat evolved is retained by the solution, and favours the completion of the reaction. Even heavily-burned magnesia hydrates at 100° C. in 6 hr.

It has been mentioned previously that lime is not very soluble in water, and it is interesting to note that the solubility decreases with increase of temperature. Thus, whereas 0·17 grm. of the hydroxide Ca $(OH)_2$ is taken up by 100 c.c. of cold water 10° C., the same amount of water at a temperature of 100° C. can dissolve only 0·077 grm.

Lime-water containing 0·17 grm. per 100 c.c. is practically 1/20 normal. It is found that 1 litre of chemically pure lime-water needs exactly 471·4 c.c. of N/10 HCl for complete neutralization.

Glucose reacts with lime to form a soluble calcium glucosate, thus it has the property of rendering lime more soluble in water. This property is seldom utilized by tanners or glue manufacturers, owing to the numerous side reactions which take place when glucose is added to the lime liquors.

Every tanner and glue manufacturer should test his lime for true "available lime." This requires the attention of the chemist, and although the experiment is very simply carried out, it is a valuable indicator of the purity of the consignment.

The author recommends the following method of determining the available lime in commercial samples—

Estimation of Available Lime. Weigh out accurately about

1 grm. of lime and place in a litre flask. Make up to the mark with previously boiled distilled water. Shake thoroughly at intervals, and then allow to stand for 12 hr. Pipette off 50 c.c. of the clear solution into a conical flask. Add two drops of phenolphthalein and titrate with $N/_{10}$ HCl.

1 c.c. $N/_{10}$ HCl = ·0028 grm. CaO.

Thus, supposing the following data of analysis were obtained—

50 c.c. lime-water = 8·8 c.c. $N/_{10}$ HCl
1000 ,, ,, = 176 ,, ,,
(176 × ·0028) = ·4928 grm. of pure CaO in 1 grm. sample

hence, in 100 grm. of sample the available lime would percentage 49·5.

The above analysis would represent a low-quality lime, evidently containing large percentages of silica and other impurities.

It should be remembered that lime is hygroscopic, and if left exposed to the weather for any considerable period, hydration takes place and the solid lumps crumble down to a fine powder. This is undesirable, as the powdered calcium hydrate is rather apt to carbonize when in the presence of an excess of air. The "lime hole," as it is called, should be a concrete or brick building containing no windows, but having a door, which, when shut, renders the interior airtight.

The Action of Lime on the Hide Proteins. Fresh lime liquor is practically sterile. It is only when hydrolysis of the hide substance takes place that the bacteria present in the air obtain access to the skin, and together with those already in the skin commence the process of decomposition, which results in the production of complex amino acids, such as tyrosin, leucin, and some caproic acid.

The most important putrefactive organisms which take part in the liming process are B. putrificus and B. putidus gracilis, which are anaerobic, and can exist only in an alkaline medium. The so-called mellowness of limes is due to the presence of enormous numbers of micro-organisms, some of which loosen the wool or hair, others decompose the skin substance, whilst the majority have little or no effect on either. Unfortunately, the whole subject of the bacteriology of liming has not yet been tackled with any real degree of thoroughness, and research work so far undertaken has not been taken to completion.

The production of ammonia in the limes is due principally

to bacterial action. Cold sterile limes contain very little ammonia, even after a considerable period.

Dealing now with the histological action of lime, Procter states that--

> It is throughout a solvent one. The hardened cells of the epidermis swell up and soften, the mucous or growing layer and the hair-sheaths are loosened and dissolved, so that, on scraping with a blunt knife, both come away more or less completely with the hair. . . . The fibres swell and absorb water, so that the hides become plump and swollen, and, at the same time, the "cement-substance" of the fibres is dissolved, and they become split up into finer fibrils; the fibrils themselves become first swollen and transparent, and finally corroded and even dissolved.

Lime, by reason of its alkalinity, has the usual action upon the natural fat of the skin, causing the formation of a calcium soap, which is, of course, insoluble and remains attached to the surface of the skin, and forms on the surface of the liquor as a scum. The saponifying action of lime is, however, over-emphasized by technical writers who know little about the actual practice of glue manufacture. Lime is, at the best, one of the weakest of the caustic alkalis, and the saponification in the cold of the natural fats is, undoubtedly, a process which only just commences and cannot by any means be said to be completed.

G. D. McLaughlin, G. E. Rockwell and I. H. Blank (*J. Amer. Leather Chem. Assoc.*, 1927, 22, 329–344), give a very useful account of research work undertaken to inquire into the bacteriology of liming. They found that non-spore-forming bacteria were at once killed by fresh lime solution containing excess lime, whilst sporulating micro-organisms were unaffected. The antiseptic value of lime was proved to increase with increasing temperature and alkalinity, and whereas bacteria do not function in lime liquors under normal conditions, they may do so if introduced in large quantities by badly-cured skins, the lime-water being unable to cope with them.

The action of lime may be tabulated thus—

1. Solvent action on epidermic structures.
2. Chemical action on the mucius and albumins present in the soft mucous layer—soluble calcium albuminates being formed.
3. Saponification action between the alkalis and the natural fats in the skin.
4. Swelling action of lime on the fibres.

Salt or Sodium Chloride. Immense quantities of common salt, known chemically as sodium chloride, are used annually in the leather and kindred trades.

In view of the wide use of salt in the preservation of putrescible material, the author intends to preface his remarks with a brief introductory note on the occurrence of salt. When mentioning the use of chemicals in various processes it is a useful practice to give a short description of the properties, etc., of the particular substance in question.

Occurrence of Salt. Rock salt may be said to occur in transparent cubic crystals. In some districts, however, these crystals may be white owing to the presence of calcium salts; or yellow, owing to iron impurities.

Deposits of rock salt occur in numerous parts of the world. The principal deposits are in Wielicza, in the Carpathians, and have been worked from the eleventh century. The deposits are said to be 500 miles long, 20 miles broad, and 1,200 ft. thick.

At Cardona (Spain) there are two hills of very pure rock salt, and it is estimated that the hills measure a mile in circumference.

Extensive deposits of potassium and sodium chlorides occur in the country around Stassfurt, in Prussian Saxony, where the layers are said to exceed 3,000 ft. in thickness, and the salt is mined at a depth of over 800 ft. The richest deposits of rock salt in the world occur near Iletz Zaschtchiti, in the province of Orenberg, South-east Russia.

Rock salt is also found in China, Africa, Asia, Mexico, Colombia, Venezuela, Russia, California, Utah, Kansas, New York, and in England at Nantwich, Droitwich, and Northwich (Cheshire).

Composition of Rock Salt. Although the composition of samples of rock salt from various districts and countries may not differ to any great extent, the presence of only 5 per cent ferric oxide, or the same amount of magnesium chloride, would be of great importance to the glue manufacturer. The presence of the iron salt might possibly result in discoloration of the glue. Magnesium chloride would tend to make the salt hygroscopic and absorb appreciable amounts of moisture, which means that the salt would become more expensive, a considerable proportion of moisture being bought in place of salt.

The best and purest commercial salt comes from Cheshire.

Composition of a representative sample is as follows—

	Cheshire Salt
Sodium chloride	98·30
Calcium sulphate	1·65
Magnesium salts	0·05
Calcium chloride	—
Alumina and ferric oxide	—
Water	—
	100·00

Chemistry of Salt. It has already been mentioned that salt crystallizes in cubes. The specific gravity of the cubes is 2·2, and their hardness 2 (Bohr's scale). The solubility of salt in water is a subject of paramount interest to the chemist and technologist generally. G. Martin, in his excellent little monograph, *Salt and the Alkali Earths*, gives the following table—

Temperature	NaCl in 100 grm.	NaCl taken up by 10 grm. H_2O
0° C.	26·3	35·7
10° C.	26·4	35·8
20° C.	26·4	35·8
50° C.	26·9	36·8
100° C.	28·1	39·1
107·7° C.	28·4	39·7

Antiseptic Action of Salt. There is no doubt that salt has a definite antiseptic action.

J. T. Wood, in his paper "The Bacteriology of the Leather Industry," states that the antiseptic action of salt is due to the dehydration of the fibre of the skin. Other authorities attribute the antiseptic action to the fact that, directly after slaughtering, the skin is in an acid condition owing to the production of sarcolactic acid, and the salt in contact with this acid brings about a pickling action.

Experiments have been carried out by Haenlein, demonstrating the antiseptic action of salt. He took strips of hide and placed some in various salt solutions and others in sterilized water. After one week he counted the bacteria.

Sterilized Water. After one week, too many to count.

Two per cent NaCl Solution. After one week, 0·1 c.c., 871 colonies, mostly micro-cocci, which did not liquefy gelatine.

Ten per cent NaCl. 0·1 c.c., 1 colony.

Saturated Solution. 0·1 c.c., 1 colony.

After Eight Weeks. Saturated solutions, no colonies. Ten per cent solution, no colonies. Two per cent solution, many colonies, but no liquefying bacteria.

Curing Hide and Skin Offal. Although the curing of hides and skins appears very simple, and is on this account woefully neglected, the fact remains that a large proportion of the so-called salted hides and skins are in various stages of advanced putrefaction by gelatine liquefying organisms.

Butchers, farmers, and also the officials at certain hide markets have very strange ideas about curing with salt. They seem to imagine that if they throw a handful or so of salt on the carcase, it can truly be regarded as "salted." Unfortunately, the minimum amount of salt essential for complete curing is 25 per cent of the green weight of the hide. In salting hides and skin offal, great care should be taken to ensure that the brine formed by the salt and natural juices of the skin does not drain away, but is retained and allowed to soak through the fibres, thus ensuring complete saturation.

Stuart B. Foster and Arthur W. Thomas have done some very useful work on "The Destructive and Preservative Effects of Neutral Salts upon Hide Substance" (*American Chemical Society*, April, 1925).

They found that the halides generally, such as LiCl, NaCl, KCl, NaBr, NaI, $MgCl_2$, $CaCl_2$, exerted a definite hydrolytic action. Arranging these chemicals in the order of the most injurious to the least, they appear: I, Br, Cl, Ca, Mg, Li, K, Na. It is interesting to note, however, that magnesium and sodium sulphates were found to be superior to the widely-used chlorides for purposes of preservation. Hide powder, after being suspended in a concentrated solution of these sulphates for 70 days, showed little sign of bacterial contamination or hydrolysis.

CHAPTER V

PRESERVATION OF STOCK BY THE GLUE MANUFACTURER

Washing glue stock - Liming—Washing and deliming—Extraction of skin offal - Notes on extraction of bones and fish waste

> "The very character of colloids seems to consist in the fact that there is a relation of cause and effect between the colloidal equilibrium of those substances and the chemical equilibrium of their constituent parts. With these particular chemical constituents, therefore, under the conditions existing at the temperature of life, slight variations in the colloid state (electrostatic and hydrostatic state, etc.) may intervene to set chemical reactions among those constituents, or even change the direction of reactions. In other words, the chemical constituents of the colloidal substance can be dissociated at a given temperature."
>
> ALFRED SEYMOUR-JONES.

General Methods of Preserving Stock Practised by the Glue Manufacturer. In previous chapters the general methods of preserving stock, such as hide and skin waste, fish and bone, offal, etc., have been outlined. Exactly the same means are employed by the glue technologist as by the tanner and butcher, etc.

Those who have any knowledge of glue production know that a considerable surplus of raw material must be stored, in order to ensure continuity of manufacture. The preservation of this stock requires very careful consideration.

Stock from the tanner, which includes hide and skin pieces and fleshings, are already in a limed condition. In this case all that is necessary is to pile it in heaps and cover the surface with a layer of slaked lime. This is a better method than treating with lime-water. The technologist has to keep in mind the important fact that hydrolysis must be avoided if a good quality glue or gelatine is to be obtained. On no account should limed stock be allowed to remain intact for any lengthy period. If there is no possibility of early consumption, then the heaps should be raked up and more slaked lime added, but even this will not prevent serious loss through hydrolysis, if the material is not put into work as quickly as possible.

Salting has already been dealt with fairly fully. The usual method of carrying out this operation is to spread the stock out on the concrete or brick floor and cover with a layer of salt.

Add another layer of offal, then one of salt, and so on. Green stock is generally treated in this way. Great attention should be paid to this salting, as if the layers are not uniform, putrefaction will start, and the stock be damaged. It should be remembered that, if the raw material is allowed to deteriorate at this stage, it is quite impossible to apply any effective remedy at a later one.

Desiccation of the drying of the glue stock is practised to a certain extent, especially in conjunction with light salting. If carried out on scientific lines this is most efficacious. It should be borne in mind, however, that, if the drying has not been carried out in a truly scientific manner, it becomes extremely difficult to soften the stock at a later process.

Procter points out that, if the hide is dried at a high temperature, then the albumins present will coagulate, and thus be rendered insoluble. Eitner (*Gerber*, 1880, p. 112) gives the following table, which should illustrate the above—

Sample	Temperature of Drying	Remarks	Time of Softening in Water	Remarks	Dissolved by Salt Solution
I	15° C.	In vacuo	24 hours	Without Mechanical work	1·68%
II	22° C.	,, ,,	2 days		1·62%
III	35° C.	In drying closet	5 ,,	Twice worked	0·15%
IV	60° C.	,, ,, ,,	Refused to soften sufficiently for tanning		Traces

The majority of glue manufacturers make use of liming for partially-limed stock, and salting for green or partially-salted material, and these methods should fulfil all requirements if carried out on the lines indicated.

In considering the important subject of preservation, the technologist should keep in mind the essential fact that " delay in working is fatal."

The Washing of Green and Salted Stock. This operation would appear to be exceedingly simple and unimportant, yet, as frequently happens, appearances are deceptive. The washing of the glue stock requires more than ordinary care, and considerable ingenuity has been exercised in designing special machines to effect complete washing.

Throughout the entire production of glue and gelatine one is faced with difficulties, which are in themselves quite original and apparently quite spasmodic. This is not difficult to understand, when we consider that the material dealt with is practically an unknown x, the constitution and properties of which are still a matter of conjecture. It is almost impossible to dogmatize, and say that, because a certain consignment of raw material gave a definite yield of good-quality glue, the following one will do the same, since many important factors have to be taken into consideration.

Green stock may be contaminated with blood and dirt, or it may be in an early or advanced stage of putrefaction, or it may be quite fresh. The object of washing is to remove all extraneous matter, blood, lymph and hydrolytic products produced by the putrefying micro-organisms. In order to achieve these results, cold water should be used and the stock agitated during treatment. If warm water is employed, the washing may be more thorough, but there is grave danger of putrefaction, as gelatine-liquefying micro-organisms flourish at blood-heat. Some glue manufacturers use antiseptics when dealing with putrid or old stock. Even the best antiseptics are apt to cause trouble during later processes, and, if possible, their use should be avoided. In cases where their employment is essential, the author recommends the following—

Borax or boric acid ; beta-naphthol or cresylic acid ; phenol or salicylic acid.

Although borax and its associated salts are mild antiseptics, they are quite safe to use, though their presence in the finished product is undesirable on account of the manner in which they affect the jelly test. Beta-naphthol and other phenolic bodies are more effective than the borates, but greater care has to be taken in using them. Excess of these substances will affect enormously the quality of the glue. The minimum amount of chemical should always be employed.

There are many machines in use by manufacturers, but it may be said that any plant is suitable which permits of free agitation of the stock in running water.

The most popular mechanical device for quickening up the soaking is the tumbler. This is simply a large barrel mounted horizontally on its axis, with baffles on its periphery to keep the stock from sliding. The stock and water are introduced through

an opening in the side of the vessel, which is, of course, closed during rotation.

Paddles, complete with revolving blades and provided with a false bottom, are in common use in this country. By means of a stop cock the wash water is continually drained off, fresh water being added. They are very satisfactory, but the time taken for complete washing is somewhat longer than when the tumbler is used.

Other washing machines in use, both in England and America, are the hollander and cone mill, the latter being the more popular.

Bogue sums up the relative advantages of the various kinds of machines as follows—

> These four representative types (referring to the cone mill, tumbler, hollander, and half-round mill) may, to a certain extent, be used interchangeably. The cone mill, which produces a combination of rubbing, kneading, and washing, can be used on almost any kind of hide stock. In the tumbler the pounding and kneading predominate, and it is, therefore, more suitable for hard or thick stock. In the hollander the rubbing predominates, and it is most serviceable for loosening foreign materials which adhere rather firmly to the fibres, but its construction prohibits use on heavy or non-uniform stock. The half-round mill gives a simple agitation and rapid circulation of water, suitable only for finely-divided and light stock.

Dealing now with salted stock, the washing must be carried a stage farther. The proteins must be softened in just the same way as green material, and besides this, all traces of neutral salts removed, otherwise the liming process will not be carried to successful completion. Chlorides are most undesirable in the glue stock during the later processes. The best method of ensuring the removal of all traces of salt is to test the wash water with silver nitrate. The washing should be continued until a sample of water gives no precipitate with silver nitrate, making due allowance, of course, for the original chlorides present in the water. The test should be carried out with 100 c.c. of water, titrating with $N/_{10}$ $AgNO_3$, using K_2CrO_4 as indicator.

$$1 \text{ c.c. } N/_{10}\ AgNO_3 = \cdot 00355 \text{ grm. } Cl_2.$$

Liming. In Chapter IV an account is given of the action of lime on the hide proteins. It is undoubtedly hydrolytic, and although the technologist cannot dispense with the process, which is of vital importance, the greatest care must be taken to

control the solvent action of the alkalis. Intermediate products of hydrolysis, that is, substances not soluble in water, but on the border-line between true proteins and meta-proteins, give a glue with a low-tenacity figure, and therefore inferior. The solubility of the mucius and albumins present in the hide and skin structures is, of course, essential—it is the partial hydrolysis of collagen and its allied proteins which is to be avoided. That is, the liming must be stopped at exactly the right stage. To determine this stage requires practical experience and chemical experiment.

Some manufacturers mince the raw material prior to liming. This is advantageous if economical, for by shredding the stock uniformity of action is more or less assured.

The liming is generally carried out in wooden or concrete vats, using a saturated solution of calcium hydrate (0·67 grm. of hydroxyl per litre). It should be pointed out that the swelling of the skin proteins relies upon the ionization of the solution and not upon the strength of the respective alkalis, although, of course, one is proportional, up to a certain point, to the other. The hydroxyl, or (OH) ions, are responsible for the swelling.

$$Ca(OH)_2 \rightleftharpoons \overset{+}{Ca} + 2\,OH$$

$$NaOH \rightleftharpoons \overset{+}{Na} + OH$$

Considerable care should be exercised in the making up of lime liquors. The author advises the use of powdered calcium hydrate, as employed in water-softening plants. By employing this chemical in place of the ordinary calcium oxide, the trouble of slaking is eliminated, and one is assured that if a certain quantity is placed in a pit, then a known percentage will pass into solution, whereas if quicklime is used, it becomes necessary to employ an enormous excess, which renders true control difficult, if not altogether impossible.

Bogue recommends 10 per cent lime on the weight of stock, but this is considered somewhat excessive. Five per cent should prove sufficient, taking into consideration the small solubility of this alkali. If caustic soda or sodium carbonate is used, then the amount can be decreased to an appreciable degree. Thus, Fleck recommends 2 parts soda and 3 parts quicklime to 300 to 400 parts of stock. When using pure hydrated lime, about 1½ to 2 per cent generally meets all requirements.

There is no definite time for liming, everything depending upon the condition of the stock. Green material requires a much longer period than limed, or partially limed, offal. The average time may be taken as one month, provided that the stock is agitated during the process. There is no doubt that agitation of the material is beneficial, as it quickens up the process. Again, agitation can be accomplished by bubbling compressed air through the liquor. Paddles are sometimes used for liming, but these are considered unsuitable, as the stock never appears sufficiently swollen when this method is adopted. Wooden cages are sometimes employed for containing the stock. These are lowered into the lime liquor by means of a pulley.

Antiseptics are frequently added to the limes, but their use is not recommended for reasons given in an earlier chapter.

It is a mistaken idea of economy to work lime liquors until they become charged with objectionable organic products and ammonia and contain enormous quantities of bacteria. As far as possible, fresh lime-water should be employed, as in this way hydrolysis, through the agency of liquefying micro-organisms, may be more or less eliminated.

Although pure rule-of-thumb methods are sometimes the only ones at the manufacturer's disposal, scientific tests should be made, even if they entail some slight inconvenience and expense. Science alone affords the only true guide, and in controlling this complex and little understood process of liming, chemistry can be a willing handmaid.

The most valuable control methods are the following: Total Alkalinity Determination, Estimation of Amino Acids, and Dissolved Hide Substance.

Total Alkalinity. Filter the lime liquor. An old lime liquor contains a large quantity of organic matter in very fine suspension—in other words, it is a colloidal solution. The method of filtration has, therefore, to be adjusted to fit the new circumstances. The liquor should be filtered first through glass wool, then through a No. 4 Watman filter paper.

For the determination of total alkalinity, 25 c.c. of the filtered solution is titrated with $N/_{10}$ HCl, using methyl orange as indicator. A *saturated* solution of calcium hydroxide is $N/_{20}$, i.e. 25 c.c. of $N/_{20}$ $Ca(OH)_2$ = 12·5 c.c. $N/_{10}$ HCl. If more than 12·5 c.c. of acid are required, then ammonia or caustic alkalis are present.

This titration gives a general idea of the age of the lime, for the older the liquor the higher the alkalinity figure.

Determination of Amino Acids (Stiasny's). First neutralize the solution of lime by means of N_{10} acid, then add formaldehyde. In detail as follows—

Take 25 c.c. of filtered lime liquor and neutralize with standard $N/_{10}$ HCl, using phenolphthalein as indicator. Add 10 c.c.

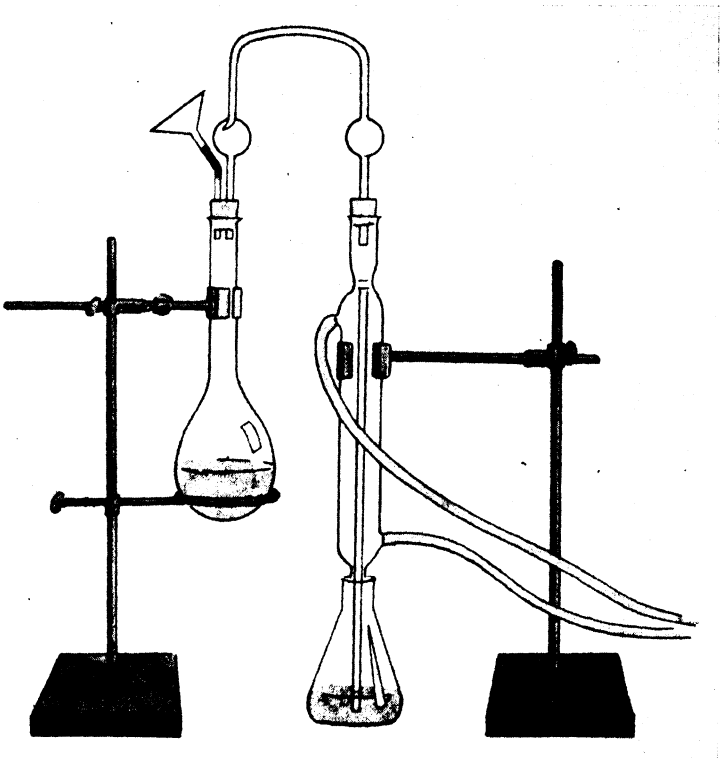


FIG. 4. KJELDAHL APPARATUS FOR DETERMINATION OF NITROGEN AS AMMONIA

of neutral 40 per cent formaldehyde. (To obtain this make up a solution of equal parts of H.CHO and water, add phenolphthalein and titrate with $N/_{10}$ NaOH until just pink.) After adding the formaldehyde titrate with standard $N/_{10}$ NaOH.

The alkali reading will give a rough idea as to the amount of amino acids present in solution.

Unfortunately, formaldehyde does not react with certain anhydrides of amino acid, so that the figure obtained is not strictly accurate.

Estimation of Dissolved Hide Substance. 50 c.c. of the filtered lime liquor is neutralized with dilute sulphuric acid and evaporated to half its bulk, using a Kjeldahl distillation flask. 15 c.c. of concentrated sulphuric acid is then added, and the mixture digested for $\frac{1}{4}$ hr. under a small bunsen flame, 10 grm. of potassium sulphate is added at this stage, and the heating continued until the colour is pale straw. The liquid is cooled and diluted with 200 c.c. of distilled water. The usual Kjeldahl apparatus is fixed up, and the condenser dipped into 50 c.c. of $N/_{10}$ HCl.

Gentle heat is applied to the flask. A concentrated solution of caustic soda (35 grm. of NaOH dissolved in the least possible quantity of water) is added to the mixture very slowly. Zinc dust is sometimes added to the alkali also, and it is claimed that the hydrogen produced acts as a catalyst, and regulates the reaction. After adding the caustic soda, the aperture is closed by means of a screw-tap. The flask is heated for $\frac{3}{4}$ hr., and at the end of that time the apparatus is disconnected, and the acid solution in the receiver titrated with $N/_{10}$ NaOH.

A typical experiment is calculated as follows—

50 c.c. $N/_{10}$ HCl = 31·6 c.c. $N/_{10}$ NaOH

This means that 18·4 c.c. $N/_{10}$ HCl was absorbed by NH_3 liberated by the lime liquor.

As 1 c.c. of absorbed $N/_{10}$ HCl = ·0014 grm. N
= ·007865 grm. hide substance (calculated as containing 17·8% N.)

∴ 18.4 c.c. contains ·2576 grm. of nitrogen or
·1447 „ „ hide substance.

Hence, 50 c.c. of lime liquor contains ·1447 grm. hide substance
25 „ „ „ „ „ ·07235 „ „ „

Analysis of a Mellow Lime Liquor. (18th January, 1922.) 25 c.c. of solution taken. Results in readings of $N/_{10}$ H.Cl or NaOH.

	Phenol Phthalein	Methyl Orange	Difference	Stiasny's Amino-acids
I	13·2	14·3	1·1	2·8
II	13·2	14·3	1·1	2·8

I. ·08374 grm. hide substance in 25 c.c. of liquor.
II. ·08369 „ „ „ „ „ „

Atkins " comparator " method is far superior to the ordinary alkalinity determination. In this case the solution is titrated to an end point of $P_H^+ = 10{\cdot}0$, using thymolphthalein as indicator. By this means the ammonia is neutralized to the extent of 24 per cent, or as he expresses it, using $(a + b)$ as typifying the total alkalinity

$$(a + b + 0{\cdot}24d) \text{ where } d = \text{ammonia.}$$

By means of a series of titrations the following determinations are made—

(*a*) Calcium hydroxide.
(*b*) Sodium hydroxide.
(*c*) Sulphydrates of calcium and sodium.
(*d*) Ammonia of amines.
(*e*) Sodium and calcium salts of weak acids, or hydrolytic products of hide proteins.

For details the reader is referred to the original papers by W. R. Atkin and W. E. Palmer.

Washing and Deliming. When the liming has been brought to a satisfactory conclusion, the next process is washing. The objects are manifold, but may be tabulated as follows—

1. Removal of alkali and its soluble salts.
2. Removal of soluble products of hydrolysis.
3. Swelling of the proteins.

Unfortunately, ordinary washing in cold water cannot accomplish the above, and it is always found necessary to use weak solutions of mineral acids to remove all traces of lime, etc. The stock must first of all be washed in running water, use being made of the paddle, tumbler, or any of the machines mentioned earlier in the chapter. When the water runs quite clear, this is an indication that no more soluble calcium compounds can be removed by water alone. At this stage a small amount of either hydrochloric or sulphurous acid can be added, when the following reactions take place.

$$\left.\begin{aligned} 2HCl + Ca(OH)_2 &= CaCl_2 + 2H_2O. \\ H_2SO_3 + Ca(OH)_2 &= CaSO_3 + 2H_2O. \end{aligned}\right\}$$

It is very unfortunate that there are certain disadvantages attached to the use of these two acids.

1. If hydrochloric acid is employed there is a danger of iron and arsenic contamination.

2. If sulphurous acid is utilized, there is a danger of soluble sulphites creeping into the finished products.

There is no doubt that sulphurous acid has a distinct advantage over hydrochloric acid, as it is endowed with definite antiseptic and bleaching properties. The objectionable sulphites formed can always be removed at a later stage of production.

Perhaps it is unnecessary to state that the smallest possible quantity of acid should be employed. Bogue mentions "that the maximum swelling of gelatine occurs in a solution containing about 0·0025 grm. of hydrogen ion per litre." Procter, in one of his papers on the gelatine equilibrium, gives the following table, showing the swelling of pieces of sheepskin in various concentrations of hydrochloric acid.

SHEEP PELT DRIED AT 80° C. AND HYDROCHLORIC ACID

Series No.	Mgr-mols. HCl per Grm.	Mgr-mols. NaCl per Grm.	Mgr-mols. HCl in Solution	Weight of Solution Absorbed by Skin	Mgr-mols. HCl Absorbed by 1 Grm. of Skin	Acid "Fixed" by 1 Grm. of Skin
			a	*b*	*c*	$c - ab = b$
XXIX 1	0·1466	Nil	0·1386	10·38	2·176	0·737
2	0·0488	Nil	0·0466	10·76	1·236	0·735
3	0·0073	Nil	0·0024	19·31	0·467	0·421
XXX 1	0·1807	3·00	0·1665	5·95	2·389	1·399
2	0·0907	3·01	0·0798	5·70	1·499	1·044
3	0·0378	3·02	0	4·71	0·364	0·364
XXXI 1	0·0692	4·17	0·0580	4·11	1·455	1·217
2	0·0826	1·66	0·0700	4·21	1·315	1·016
3	0·0981	0·48	0·0775	3·93	1·227	0·922

The best means of controlling the acidity or P_H^+ of the deliming liquors is by means of the indicator tests, using the reliable indicators of the B.D.H. This is exceedingly simple, and a wide range is provided for from about $P_H^+ = 4$ to neutral or 7.

Of course, such a low concentration as 0·0025 grm. of hydrogen ion per litre is impossible to achieve on a commercial scale, and the manufacturer must use a concentration of, say, 0·025–0·05 grm. of hydrogen ion per litre.

Very useful data are available concerning the action of dilute acids on gelatine sheets, but, unfortunately, skin is further complicated by delicate structures, which have a tendency to impede the swelling in one direction, whilst accelerating it in another. The inside layer or corium contains a higher percentage of acid than the surface of hyaline layer, and consequently the interior approaches the maximum. There is no doubt that the whole

extent and velocity of the reaction is in ratio to the " active mass " of the acid.

The stock should be worked in the weak acid liquor, until when a piece of skin is tested with phenolphthalein, that is, the cut surface is tested, the " slightest " pink coloration is obtained.

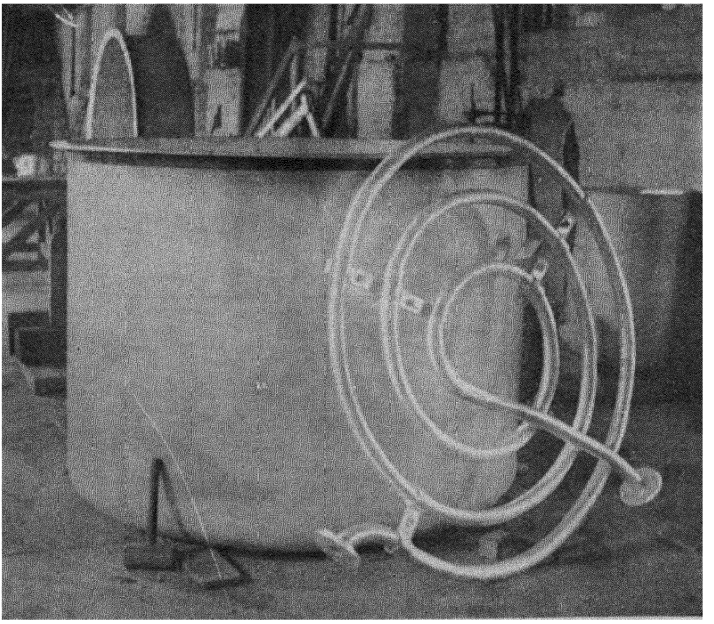


FIG. 5. EXTRACTION PAN COMPLETE WITH STEAM COIL
(By courtesy of the Aluminium Plant and Vessel Co., Ltd.)

Some manufacturers prefer to work until the cut surface shows definitely acid.

After deliming, the stock should be washed very thoroughly in cold running water until the acid content of the protein has been reduced to the minimum.

Extraction or Boiling. In principle, this process is comparatively simple and consists in the first hydrolysis of the collagen, which is, of course, the principal protein dealt with by the technologist. At an earlier stage of this book it was pointed out " that the conversion of collagen into gelatine by the agency of water is a definite hydrolysis which can be illustrated by means of a simple chemical equation

$$C_{102}H_{149}O_{38}N_{31} + H_2O = C_{102}H_{151}O_{39}N_{31}$$"

The hydrolysis must on no account be prolonged beyond the first stage, as undesirable cleavage products of gelatine will be formed, which will affect the foam and viscosity tests, and also give the product a dark and objectionable colour. Again, the extraction must be carried out continuously under almost ideal hygienic conditions, especially when edible gelatine is in the making.

There are two general methods of extraction; the open and the closed.

The open process of boiling is carried out in large pans, preferably made of aluminium, the heat being applied by means of an open fire, a steam jacket, coils, by forcing live steam into the liquid, or by a water jacket. An excellent means of heating is achieved by the use of the steam-jacketed pan, this method allowing of better regulation of temperature than any other. The use of steam coils enjoys a large vogue in this country, but is said by some experts to entail waste of energy by friction of the steam in the coil as well as considerable expenditure for initial outlay and liability of joints leaking. When live steam is used, the temperature is somewhat uncertain, and condensation occurs unless the steam is superheated. Water jackets were once the common means of extraction, but, owing to the difficulty in maintaining one fixed temperature, they have fallen into disfavour.

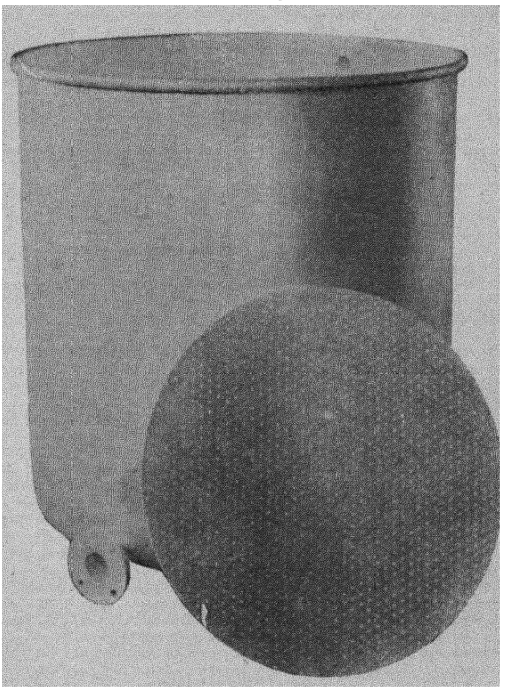


FIG. 6. ALUMINIUM EXTRACTION TANK COMPLETE WITH PERFORATED FALSE BOTTOM

(By courtesy of the Aluminium Plant and Vessel Co., Ltd.)

As regards heating by means of an open fire, the disadvantages of this method are all too obvious, for overheating in certain parts of the boiler causes burning of the stock, while

the impossibility of regulating the temperature causes loss by hydrolysis.

As regards the closed methods of extraction, these are carried out in autoclaves under a pressure of from 10 to 15 lb. Bones, etc., are always extracted by this means, and for this material the closed method is eminently satisfactory. For hide and skin offal, boiling under pressure slows down extraction, as when water is squeezed out of the stock it is replaced only very slowly.

The following conditions are desirable as regards the boiling of hide and skin offal—

High concentration of the glue liquor.

Immediate removal of dissolved glue from zone of highest temperature.

Minimum pressure.

Production of a clear liquid.

The stock is dumped into the boiler until the latter is almost full, then covered with hot water. Heat is then applied and the temperature maintained at 140° F. for several hours or until the liquor has dissolved at least 6 to 7 per cent of its weight of glue. The liquor is drawn off through a valve in the bottom, and fresh water added. The heat is now maintained at 10° or 15° higher, and after about the same time the liquor is drawn off as before. Four or five more such "runs" are generally made, the last being at a temperature of about 210° F.

The greatest care must be taken to remove the "skin" which always forms on the top of the glue liquor. This film will cause the finished product to show up streaky and uneven in colour if not removed at this stage. The usual practice is to ladle it off the surface, then add it to the next batch of stock for boiling.

In order to hasten the extraction, and speed of manufacture is an important consideration in this industry, some technologists agitate the liquor during boiling.

Probably the safest method of speeding-up production is to shred the glue stock, but, as pointed out earlier, this is rather an expensive procedure for small quantities, and needs careful costing before general adoption. The shredding should always be carried out on limed stock, or, better still, prior to liming.

The most popular method of boiling glue stock in this country is the ordinary open-vat process, whereby the liquor is heated

by means of live steam and agitation afforded by simple hand devices, such as small paddles, etc. This procedure, whilst suitable for the production of small amounts of glue and gelatine, is uneconomical and quite unsuitable when the process of manufacture is continuous and on a large scale.

Notes on the Extraction of Bones. Bones are treated on somewhat different lines from those on which the other raw materials used in the manufacture of gelatine and glue are treated.

The object of the glue technologist is to achieve the following results—

1. Removal of dirt and blood, etc.
2. Removal of oleaginous matter.
3. Removal of calciferous and general mineral skeleton.
4. Extraction of remaining ossein.

The green bones on arrival are always crushed, making use of any of the standard machines, most of which have two pairs of heavy rollers with cutters, and a revolving screen for separating the particles into rough, $\frac{1}{2}$ in. or $\frac{1}{4}$ in. and fine dust. The crushed material is then well washed in one of the washing machines described in an earlier chapter. Great stress must be laid upon this preliminary washing, as the presence of blood and extraneous matter will affect the purity of the bone fat to a very appreciable extent. Bogue advises treatment with dilute sulphurous acid, as this would keep the stock sweet and by its bleaching action ensure a good quality glue and fat.

J. C. Kernot and Miss N. E. Speer (Second Report, Adhesives Research Committee, 1926, 17–22) state that maceration of the bones in a dilute alkaline solution, previous to extraction, improves the quality of the glue. The author has attempted some experiments on the manufacture of glue from junk and other inferior quality bones, and he has found that by acting up to the suggestions of the Report a greater yield of glue is obtainable, which is of better colour.

There are two methods of degreasing—

1. The wet process, necessitating the use of water 100° C. and at increased pressure.
2. The utilization of solvents, such as benzine, petroleum, etc. : dry process.

1. The crushed bones are placed in large autoclaves and boiled for a short period. By increasing the pressure, it is possible to cut down the period of treatment. The greatest care

should be taken to ensure that the boiling is not prolonged to the stage of actual extraction of the gelatine. The bone substance is removed after degreasing and laid out on canvas bags to dry. The aqueous liquor containing the fat is run off into shallow vats, where it is allowed to cool and the grease skimmed off and refined. Bone fat from the above process is always of a better colour, and generally superior to samples obtained from the dry or solvent method. It may be reckoned that 90 to 99 per cent of fat can be extracted by this means.

2. A far superior, though costlier, extraction process, is the solvent one. Bogue says that by the use of benzol, carbon disulphide, or any of the well-known solvents, it is possible to remove about 99·90 per cent of fat.

The essential point to bear in mind, when considering this process, is that everything depends upon the percentage of moisture in the crushed bone, 10 per cent being reckoned as the maximum. Various patents have been taken out to protect the manufacture of special degreasing plants. The majority, however, are on the well-known Soxhlet principle, which permits of a continual treatment of the material with hot spirit.

The disadvantages of the method are—

1. The cost of the degreasing plant is rather excessive, and the expense of running appreciable, owing to unavoidable loss of spirit during distillation.

2. A small percentage of gelatine is extracted, especially if the temperature is high. This results in the lowering of the gelatine yield and diminution in the value of the bone fat.

3. The bone fat is usually dark coloured, and, consequently, of lower value than the lighter material obtained during the wet process.

The advantages of the method are—

1. Almost total, that is maximum, speed of extraction, which means that a uniform material is at hand for extraction of the ossein. Again, the method is reliable, and the percentage of fat in different samples of treated bones does not differ more than a decimal point or so.

2. Continuity of the process, which allows for maximum output. This is a very great consideration in these days of speed in industry.

There is no doubt that if large quantities of material are to

be treated, the solvent method will prove more efficient and economical in the long run, but when the manufacture is intermittent and the batches are small, then the author advises the adoption of the wet process.

The degreased material is now ready for treatment with acids to dissolve out the calcium phosphates and other mineral salts. Technologists usually employ large shallow wooden vats or tubs to effect this decalcifying. About 10·5 per cent hydrochloric acid or 15 per cent sulphurous acid gas is usually found to be sufficient. Sulphurous acid is preferable, when the sulphur dioxide can be obtained cheaply by manufacturing it on the spot. The action which takes place is as follows—

$$Ca_3(PO_4)_2 + SO_2 + H_2O = 2CaHPO_4 + CaSO_3.$$

and, in the case of hydrochloric acid,—

$$Ca_3(PO_4)_2 + 2HCl = 2CaHPO_4 + CaCl_2.$$

The skeleton of ossein remaining after treatment should be well washed in running water until neutral. It is always advisable to test the wash water by direct titration, preferably determining the P_H^+ by the electrometric apparatus, or the hydrogen ion concentration by the use of B.D.H. indicators.

The gelatine extraction of bones should always be carried out under increased pressure if the maximum yield is to be obtained. J. C. Kernot and Miss N. E. Speer, in the Report quoted above, state that a short period of treatment under very high pressure is better than an extensive period under low pressure when dealing with undecalcified, degreased bones. They also state that direct air pressure is preferable to steam pressure, as wet steam is said to further hydrolysis of the gelatine.

In extracting bones, it should be remembered that the maximum concentration of the liquor is desired. Thus, the ordinary processes of extraction applicable to skin waste are of little value. An old though still popular plant consists of a large and stout iron cylinder in which the bones are packed. Water is made to trickle down from a shower connected to the lid, whilst steam is forced upwards through a perforated false bottom. By means of pressure gauges and thermometers the process can be controlled very efficiently. The glue liquor should be removed from the source of action as soon as possible

otherwise hydrolysis will commence which will, of course, result in deterioration of the glue.

There has been a large number of patents taken out dealing with extraction of bones, but most of these are not yet commercial propositions. Quite a considerable number embodies centrifugal force as a means of agitation, subjecting the stock to condensing steam. It should be remembered that the quicker the process of extraction, the more difficult the filtration or clarification, as a large amount of insoluble matter will necessarily be in suspension. Recent research has shown that the discoloration and deterioration of bone glue are due in many cases to the presence in the bone material of porous fragments which absorb and retain blood, dirt, etc.

Notes on Extraction of Bones and Tendons. The Research Committee, dealing with adhesives, found that the rate of extraction of ossein from bone particles "increased with the finer division of the bones." A minimum was fixed, namely, $\frac{1}{32}$ in.

The rate of extraction was worked out by means of a mathematical formula, which is true for bones and tendons, but not skin—

$$\frac{1}{a + S_0^2} \log. \frac{a(S_0^2 + x)}{S_0^2(a - x)} = Kt.$$

where a = Total amount of gelatine extractible = 100.
x = Percentage of gelatine extracted in time t
S_0 = Apparent initial surface
K = Reaction constant.

When "K" was calculated from the results of experiments carried out at 90° and 100° C. the ratio $\frac{K100}{K90}$ was found to be 2·1.

The apparent initial surface is determined by counting the average number of particles contained in 1 grm. of material, S_0 being taken as proportional to $\sqrt[3]{n}$ where n is the number indicated. It was found that unit weight, irrespective of relative size of particles, always absorbed the same amount. They state that "Owing to the high porosity of bones, there is always the same surface available, whatever the size of the particles. The different rates of extraction from particles of different sizes are controlled largely by the rates of diffusion of gelatine and water through the pores of the ossein; it is essentially a capillary phenomenon." Regarding the extraction of

gelatine from tendons the same equation holds. Some results worked out are as follows—

Average number of particles = 75 in 1 grain

whence $S_0 = \sqrt[3]{75} = 4{\cdot}22$ and $S_0^2 = 17{\cdot}8$

$$\frac{1}{117{\cdot}8} \log \frac{100\ (17{\cdot}8 + x)}{17{\cdot}8\ (100 - x)} = Kt.$$

t (in Hours)	x (Per cent Extracted)	K
0·5	6·5	0·00279
1·0	17·3	0·00320
2·0	44·2	0·00338
3·0	71·5	0·00352
4·0	87·0	0·00351

Notes on the Extraction of Fish Waste. J. C. Kernot and Miss N. E. Speer (Second Report, Adhesives Research Committee, 1926, 17–22) consider that a glue may be obtained from fish offal which will compare very well with the best bone and hide glue. In order that the process may be a success, they recommend that a preliminary treatment should be given with dilute alkali and acid. This resolves itself into liming and deliming with acid swelling.

In a patent taken out by J. C. Kernot (E.P. 235, 635, 18th Mar., 1924), the offal of fish, whales, seals, etc. is first washed in running water for 3 to 4 hr., then treated several times for 6 to 8 hr. with solutions of 0·5 per cent NaOH until a sample of the filtered liquor will not give a precipitate when neutralized with acid. The stock is next washed in running water for 3 to 4 hr. and treated several times with a weak solution of sulphurous acid, 0·5 per cent strength. After well washing, the product is extracted and treated in the usual way. Kernot recommends that the tankage be dried and ground into meal.

The author considers that the open process of extraction is eminently suitable for marine offal, use being made of the steam coil, which should be at the bottom of the vat and covered over by means of a false lattice bottom. It frequently happens, that if the fish offal is extracted under pressure, a product is obtained with a most objectionable odour, which, of course, lowers the quality of the glue. The question of odour is of supreme importance—fish glue should be odourless, and this is

possible only if the greatest attention be paid to cleanliness and speed of reaction.

In the extraction of fish waste, the following points are of supreme importance—

1. Quick extraction " without pressure if convenient."
2. Removal of extracted gelatine from vessel as soon as possible.
3. Minimum number of runs.

Bogue gives the following account of the extraction of fish waste in America—

> The fish skin and waste stock ordinarily are agitated in running water in large tanks for a period of 12 hr. or so, or until a sample of the wash water on analysis shows a low percentage of chlorides. The stock is then thrown into false-bottomed tanks, called " cookers," which usually have a layer of excelsior on their false-bottoms. The stock is covered with water, and a slow stream of steam is passed into the tanks. The length of the cooking period varies with the nature of the glue stock, fish waste requiring longer cooking than fish skin stock. Usually, two runs are made ; that is, the liquor formed by the cooking of the stock is drawn off when it becomes sufficiently concentrated, more water is added and the cooking is continued. The average concentration of the glue liquors is about 5 per cent. The first run of glue liquor is the better.

Tankage. The tankage after drying and grinding can be used as a fertilizer, either being sold as a simple nitrogenous manure or mixed with basic slag, phosphates, lime, etc., to make compound fertilizers.

In the drying of the material the best method is to spread it out on wire netting and expose it to a high temperature in a sealed stove. It is always advisable to keep turning the tankage, otherwise it may overheat and burst into flame.

When there is a large percentage of wool and hair in the waste matter, the fertilizer value of the product is considerably diminished. It is not a commercial proposition to sell the washed and dried hair and wool to textile manufacturers or plasterers—there is practically no real market for such inferior and almost worthless material.

Bone Fat. Bone fat occurs commercially as a dark brown grease possessing an offensive odour, and containing large quantities of free fatty acids and lime soaps, the latter being formed by the action of fatty acids on the lime salts of the bones. It is used for coarse lubricants and soap, or bleached for candle-making. The manufacture of ordinary commercial bone fat

can be discussed under two headings—" boiling out " and " solvent extraction " processes—each having its advantages and special characteristics, and an outline of the two methods will be given.

In the " boiling out " process, the fresh bones are first placed in a steam-jacketed pan and covered with boiling water, the mass being kept at 100° C. for 5 hr. The mixture is then allowed to cool. While still fluid, the grease which rises to the surface of the liquor is removed and run into a lead-lined tank for refining. This is performed by means of aqua regia, 1·5 per cent on weight of fat being generally the quantity used. (Aqua regia is made by mixing one volume concentrated nitric acid with four volumes concentrated hydrochloric acid.)

The aqua regia should be well mixed with the fat by means of a wooden plunger or pole. After 5 or 6 hr., warm water is added and the acid liquor run off. The fat is then washed repeatedly with warm water until the last trace of acid is removed, and it is then ready for barrelling. When old bones are used, it will be noticed that during the slow cooling of the fat a greyish-white mass separates, upon which floats a brownish-yellow oil. The solid portion is used for soap manufacture, while the liquid oil is refined in the usual way.

Many solvents can be used for the second method. The most commonly used are the following : carbon disulphide, benzine, ether or liquid petroleum. Lewkowitsch gives the following method : " Bones that are no longer fresh are usually extracted with benzene (petroleum ether) in digesters under pressure, or in open apparatus." The method in which pressure is employed is the more dangerous one, and has not infrequently led to explosions. The advantage which this method offers is that practically the total amount of fat contained in the bones can be extracted, the actual yield depending on the nature of the solvent and the time during which the solvent acts on the bones, as also on the construction of the apparatus. That apparatus will be the best in which the volatile solvent is so successfully condensed that only a small amount of it is lost. The fat obtained by the extraction is dark brown, and has a very penetrating, unpleasant smell. Besides a considerable amount of free fatty acids, this fat contains lime soaps, calcium lactate, calcium butyrate, hydrocarbons from the petroleum ether, and colouring substances. This kind of fat cannot be bleached

successfully, and even if some immediate improvement is obtained by bleaching, the colour, as also the unpleasant smell, will " revert a short time after bleaching. Whereas the bone fat obtained by the second process is utterly unsuitable for soap-making and can only be worked up in candle-making." Generally speaking, dry stale bones are extracted by means of volatile solvents, while fresh ones are usually boiled and the grease recovered as explained (boiling-out process).

Some manufacturers remove the oleic acid from bone fat by means of milk of lime. The fat is stirred well in a solution of calcium hydroxide, when the oleic acid is precipitated as calcium oleate and almost wholly removed. The free oleic acid can be recovered by treating the precipitate with sulphuric acid, free oleic acid, and insoluble calcium sulphate being obtained.

Notes on Analysis of Bone Fat. Lewkowitsch gives the following methods of examining bone fat, due to Shukoff and Schestakoff (*Chem. Rev.*, 1898, 6)—

FATTY MATTER. This is determined direct. Weigh off 10 grm. in a small conical flask, add three to five drops of strong hydrochloric acid, and warm on the water bath for about 1 hr., agitating the contents of the flask from time to time, whereby the lime soaps are decomposed. Then add 40 c.c. of petroleum ether, agitate to dissolve the fatty matter, and pour the solution carefully (leaving the few drops of acid at the bottom of the flask) through a tared filter into a second flask ; wash two or three times with petroleum ether, and determine the fatty matter in the ethereal solution as described.

IMPURITIES, ORGANIC AND INORGANIC. The dirt and the acid solution from the first flask are washed on to the tared filter, dried and determined as described.

ASH. This is found by incinerating a fresh portion of the sample. The lime of the organic lime salts is thus converted into calcium carbonate ; the amount of the latter may be ascertained by titrating the ash with standardized acid.

MOISTURE. This is found by difference.

Notes on the Flow of Liquids. In all industries where liquids, viscous and otherwise, are pumped from one container to another, chemical engineers have spent much time in calculating the flow of liquids, and have evolved practical methods for estimating their speeds, viscosities and volumes.

Most industries are now being organized on a basis of continuity instead of the uneconomical intermittent or batch system, and this calls for an accurate and continuous method

of fluid measurement. Up to the last few years our knowledge of the laws regulating the flow of liquids was considerably meagre. It has been left to a mere handful of men, Osborne, Reynolds, Stanton, Pannel and Lees, to show that all liquids, gases and vapours obey the same basic laws of flow which connect up the diverse behaviour of the most varied substances, ranging from the purest oxygen gas to viscid and complex pitch in a precisely similar manner that Boyle's and Charles' laws connected up the behaviour of all gases.

The experiments of Stanton and his collaborators have paved the way for the works chemist and engineer. It is now possible, from a knowledge of the viscosity and density of any particular fluid, to calculate the speed of flow under one set pressure in a tube of known dimensions and the power necessary to effect the desired transfer, and what size of conduits are most suitable and economical.

The glue and gelatine technologist, providing he is equipped with a fair knowledge of mathematics, should be able to work out the approximate speed of flow of the various liquids used in the manufacture, and by this means calculate their respective volumes, thus eliminating the necessity of interrupting the process for accurate measurement.

A recent book by Geoffrey Martin, *A Treatise on Chemical Engineering*, should prove invaluable to the student desirous of applying the laws governing the flow of liquids to the estimation of volumes, viscosity, and speed of the liquids used in glue manufacture.

CHAPTER VI

FILTRATION—CLARIFICATION—EVAPORATION—COOLING AND DRYING

AFTER extraction, the gelatine liquor is run into large shallow vats. A temperature of 60° C. is maintained, when the grease rises and is skimmed off, and the flocculent impurities settle. The common impurities in the liquor are undissolved organic matter, albumin and mucins, lime soaps, grease and hair, as well as mineral and bone particles. This suspended material can be removed by filtration if desired, instead of merely being allowed to settle to the bottom, which takes a considerable time.

Before attempting to describe the best methods of filtering the solution of glue, the author proposes to devote a short space to a consideration of the mechanism of filtration, an extremely important subject, and one which is now occupying the attention of chemical engineers connected with the large-scale production of dyes and fine chemicals.

It should not be imagined that the action of a filter is simply to strain out the particles by reason of the smallness of its capillary passages, which do not allow room for the solids to enter. The action is far more complex than this.

Hatschek (*J.S.C.I.*, 1908, Vol. XXVI, p. 538) approaches the subject of filtration from just one angle, and attempts to cast into mathematical form the results of his research. Taking the case where the particles of precipitate are uniform, solid spheres brought to a standstill by a surface containing the circular opening of tubes of smaller diameter than the spheres, he deduces that the lowest layer of particles would produce a greater resistance to flow than any subsequent layer which would necessarily form over the spaces between the spheres.

It is interesting to note that the interstitial pores in the medium hold back particles very much smaller than the diameter of the pores. In practice, it is always advisable to pass a concentrated solution through the cloth or cake to start with, so that the larger particles may form bridges over the ducts, and thus increase the porosity of the lowest layer, which

every filtration engineer knows, provides superior drainage to that which would otherwise be obtained were dilute solutions used in the first instance, and a fine and compact initial layer formed.

J. A. Pickard (*Industrial Chemist*, page 186, May, 1928), in discussing " The Mechanical Basis of Filtration," writes—

The lowest layer of cake is often deliberately built up of a highly porous material, to which the name of " filter-aid " is usually applied, and favourite materials for this purpose are kieselguhr, paper pulp, or carbon powder.

He gives analysis of three varieties of kieselguhr, which are illustrated with photomicrographs.

1. A cheap variety as mined.
2. A variety which has undergone a process of air levigation.
3. A pure variety.

	I	II	III
Silica	92·48	87·29	89·79
Oxide of iron	·92	1·138	1·50
Alumina	3·02	4·17	4·05
Lime	·47	·328	·35
Magnesia	·24	·197	·07
Loss on ignition	2·87	6·877	4·24

It will be observed that the substance is of an extremely bulky, angular nature, well adapted to form an open interlocked structure with extremely fine pores and with a strong tendency to stick or jar in small channels. Once these channels are partially blocked by the larger particles, the smaller ones are soon arrested, and an extremely fine filtering surface results.

Hatschek (*J.S.C.I.*, 1908, XXVII, page 538) states that variations in pressure are not reflected in the consistency of the filter cake, thus, a high pressure does not necessarily mean a harder or denser cake. Providing the particles suspended in the liquid are inelastic, then Hatschek's contention is borne out. This is quite reasonable if one considers the mechanism of cake building. The particles pack themselves together and support each other, forming shapes relative to their respective sizes. It is a fallacy to think that any unbalanced pressure is applied to any particle in suspension until it settles on others to form an integral part of the cake. When this happens it will support

some pressure dependent on the extent to which it diminishes " the total cross-section available for the flow of liquid."

Four excellent and informative summaries are given by Pickard—

1. With precipitates of hard, non-deformable particles formed on well-defined filtering surfaces, rate of filtration is proportional to the pressure and inversely to the cake thickness, and the formula $R = \frac{KAP}{L\mu}$ applies with fair accuracy.

Note. It should be explained that this formula of Poisenille forms the basis of the mathematics of flow of liquids and filtration generally.

L = thickness of cake
K is a constant for the material
A = the area of filter surface
R is, of course, the rate of flow
P = the pressure
μ = the viscosity of liquid passing through.

2. With precipitates of soft, deformable particles, rate of filtration is not increased proportionately with increase of pressure, and may even be diminished.

3. Cakes of hard non-deformable particles are uniform throughout, and their character is unaffected by pressure of filtration or concentration of solid in the prefilt.

4. Cakes of soft, deformable particles will be drier and more compact at the filter surfaces than at the outer surface, and will be more compact the higher the filtration pressure.

The substances in suspension in the gelatine liquor are extremely difficult to eliminate completely on account of their sticky and colloidal nature. One is not dealing with hard and non-deformable spheres, but colloidal particles carrying practically the same electrical charge as the gelatine particles themselves. Some manufacturers employ fuller's earth to aid filtration. Fuller's earth is mined in Surrey, and has the following composition—

SiO_2, 51–67% ; Al_2O_3, 2–6% ; Fe_2O_3, 2–6% ; CaO, 2–7% ; MgO, 1–5% ; H_2O, 5–15% ; together with small amounts of Na_2O, K_2O, NaCl, carbonaceous matter.

Bogue points out that—

The substances to be filtered out appear all to be negative, and the use of fuller's earth, which is strongly negative, does not appreciably improve the appearance of the glue.

One of the best substances which can be used is " neutral " charcoal.

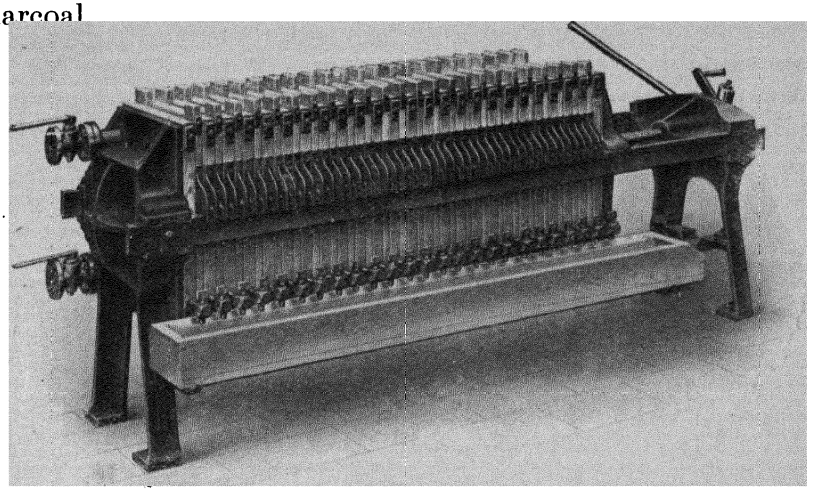


FIG. 7. FILTER PRESS SHOWING ORDINARY WOODEN CHAMBERS
This type still employed in this country, but is not so hygienic as the type illustrated below
(By courtesy of S. H. Johnson & Co., Ltd.)

Paper pulp is superior to kieselguhr or other adsorbents, and Bogue advises the use of the best cotton cellulose and a filter which allows for a loose packing of the pulp.

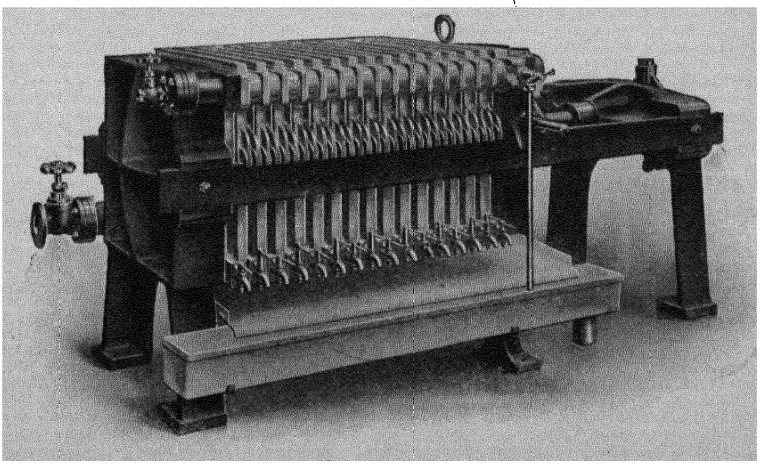


FIG. 8. MODERN FILTER PRESS SHOWING GUNMETAL CHAMBERS SUCH AS IS USED IN THE CLARIFICATION OF GLUE LIQUORS
(By courtesy of S. H. Johnson & Co., Ltd.)

The greatest care should be taken in the working of the presses. If they are not well washed after use, there is danger of moulds or green algæ forming, and these are particularly objectionable, resulting in a lowering of the quality of the gelatine. Rideal, in his monograph *Glue and Gelatine*, refers to the above—

A press, particularly a wooden one, should always be kept scrupulously clean ; if it is absolutely necessary for the wood to remain at rest for a time, it must be washed with dilute chlorine water, or very weak chloride of lime, then with clean good water and allowed to dry, but it is rare for a leak not to occur on resuming working.

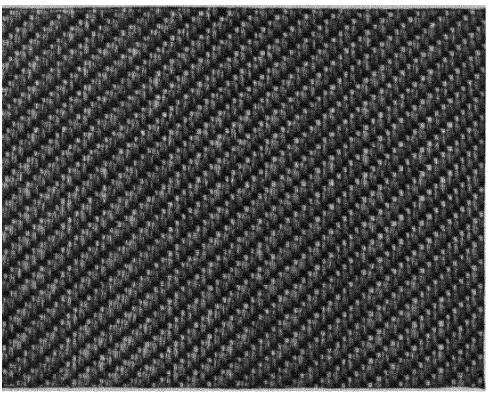


FIG. 9. MULTIPLEX FILTER CLOTH USED IN THE SCREENING OF GLUE LIQUORS
(*By courtesy of Wm. Riddell, Cousland & Co., Ltd.*)

Gunmetal presses are preferable to the wooden varieties, as they can be kept scrupulously clean and give a clearer and finer filtrate.

After filtration, the glue liquor will, in the majority of cases, still be found to be rather cloudy, so it has to undergo a process known as clarification before being ready for evaporation. Wire cloths are now in common use for screening glue liquors. One of the most popular makes is the "Multiplex" cloth, manufactured by Riddell, Cousland & Co.

Clarification. If the gelatine is of good quality, sometimes filtration is sufficient, but, generally, the solution needs clarifying in order to produce a bright and clear product.

Amongst the common clarifiers are alum, followed by a small quantity of milk of lime, calcium sulphate, albumin, blood, and oxalic acid. The best and oldest known material for coagulation is egg albumen dissolved in water ; this is used for really high-grade gelatines.

Egg albumen is made from the whites of eggs. The usual method of manufacture is to evaporate the albumen in shallow trays until the whole of the water has evaporated. The residue which remains is of a light, yellowish colour. It is worth noting

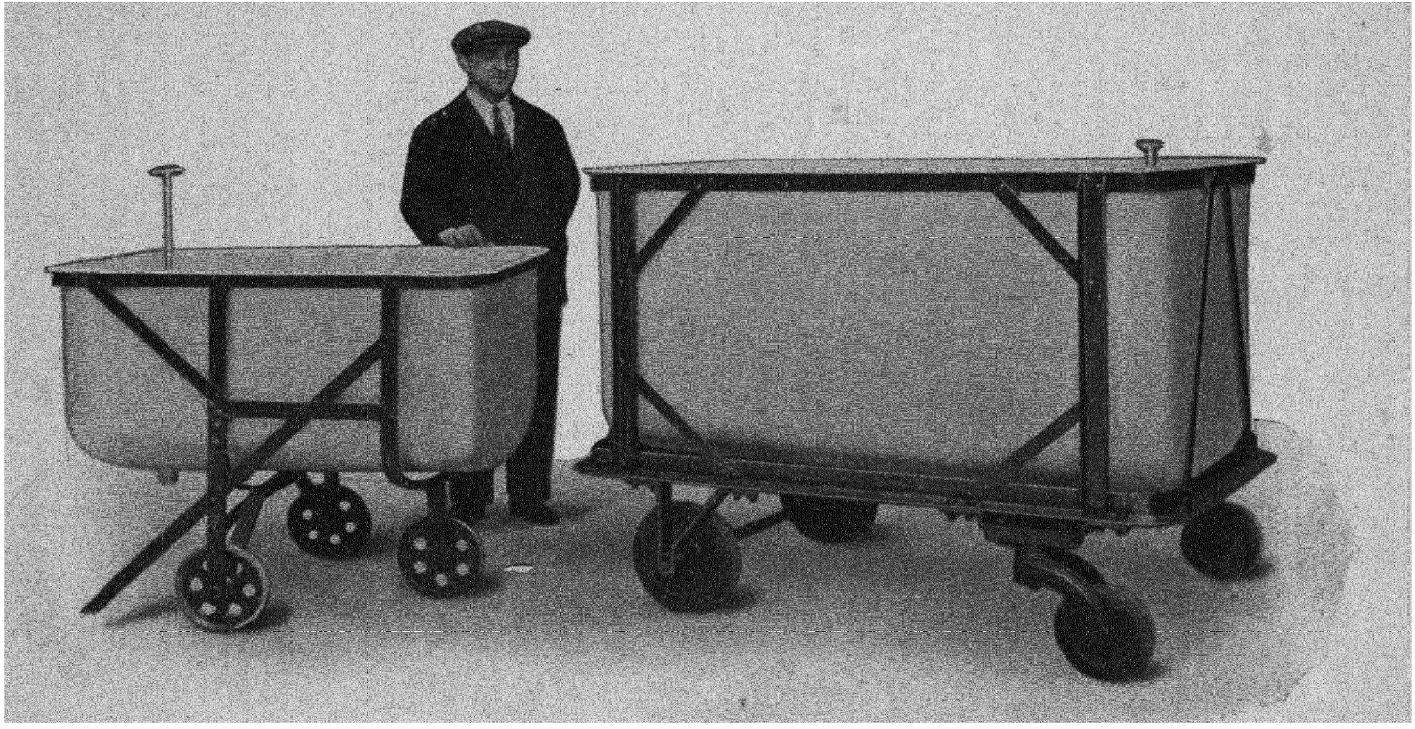


FIG. 10. ALUMINIUM TRUCKS FOR CONVEYING GLUE AND OTHER LIQUORS
Most Hygienic Method of Transportation

(By courtesy of the Aluminium Plant and Vessel Co., Ltd.)

that the temperature at which the evaporation is carried out is a matter of primary importance. As the albumen starts to coagulate over 120° F., this temperature should not be reached. About 120 eggs are necessary in order to make 1 lb. of egg albumen.

The mode of procedure for clarifying glue and gelatine liquor is as follows.

The glue liquor is run into vats provided with a steam column or coil, and some means of agitation. Crude sulphate of alumina is added and the mixture agitated, then heated to about 80 to 90° C. until coagulation is complete. The steam is then turned off, the liquor is allowed to cool, and the flocculent precipitate to settle, which takes about 5 or 6 hr.

When albumen is used, the temperature of the glue liquor should be about 50° C. before the former is added. The temperature may then be increased until 200° F. is reached—complete coagulation taking place. Generally, the period needed for absolute settlement is 30 hr.

Rideal points out that sulphited glues can be clarified with milk of lime, but the liquor must be left slightly acid or it will not clear.

Supposing that coagulation has taken place, the clear liquor is siphoned off and filtered.

For high-grade photographic gelatines, silver salts are sometimes used to remove the small quantities of objectionable proteins and salts present.

Bogue advises the use of " The Electrometric Apparatus " as a control. By means of this delicate instrument, it is possible to follow the coagulation process, plotting the various P_H figures of portions of liquid withdrawn at intervals during precipitation.

The reader will no doubt be well acquainted with the fact that titration with alkali affords no real guide to " the true acidity " of a solution, acidity being the concentration of hydrogen ions. " The Electrometric Apparatus " gives a true reading of the " acidity," and is in fact the only really accurate method available. The principle of the process, which is of great importance to the manufacturer, is well explained by Professor H. R. Procter in his treatise *The Principles of Leather Manufacture.*

If we imagine two galvanic cells, both alike, say, consisting of copper in saturated copper sulphate, or zinc in zinc sulphate solutions of equal

concentration, with their positive poles opposed to each other, and their negative also connected, there will be obviously no current produced, but if the zinc sulphate solutions are of unequal concentration, a current will be set up in such a sense that zinc will be dissolved in the weaker solution till its osmotic pressure and concentration become equal to the other, that is, a positive current will pass from the anode of the weaker to that of the stronger cell until equilibrium is restored. It is obvious that the energy which produces this current is the difference of ionic osmotic pressures, and as the relation between these two forms of energy is known, the electric pressure or " potential " can be calculated from the ionic concentration or vice versa.

The usual method is to measure the potential given by a single element, consisting of a calomel electrode and a hydrogenized platinum plate in the acid solution, the potential produced with a normal acid solution being already determined. Sörensen, an early pioneer in this field of physical chemistry, found that the potential of such an element with decinormal potassium chloride solution and calomel in the negative, and acid, normal with regard to the ionized hydrogen, in the positive cell (corresponding to $P_H^+ = 0$ on the old Sörensen scale), is 0·3377 volt, and as the potential rises with the dilution of the hydrion solution, the potential for any given dilution is

$$\text{Pot.} = 0{\cdot}3377 + 0{\cdot}0577 \times P_H^+$$

or conversely

$$P_H^+ = \frac{\text{Pot.} - 0{\cdot}3377}{0{\cdot}0577} \text{ at } 18^\circ \text{ C.}$$

Ordinary colour indicators, such as the well-known B.D.H. series, are inexpensive and invaluable for determining (approximately) the P_H^+ of a solution, using buffer solutions for comparison.

Bleaching is often practised by some manufacturers, using sulphur dioxide, sodium hydrosulphite, basic zinc salts or formaldehyde, and a large number of common reducing agents. If good quality stock has been used in the first place and the conditions of manufacture have been really hygienic, then bleaching is quite unnecessary, and it is most undesirable for edible and photographic gelatines.

Evaporation. The gelatine liquor is now ready for evaporation. This process is of very great importance, and cannot be dismissed in a few words. More attention has been paid by chemical engineers to the construction of evaporating vessels, than to any other plant used in the chemical industry.

The old forms of evaporators, such as the direct-heated metal vessel, steel jacketed pan, and open vessel provided with steam coil are now things of the past, as they have been proved both inefficient and uneconomical.

Vacuum pans and Multiple Effect Film Evaporators are now regarded as the best means of carrying out this difficult operation, although the former suffer from many grave disadvantages in practice. Multiple Effect Evaporators are now widely used in the glue and gelatine industry. A description of the principle of the plant will, no doubt, be appreciated at this stage.*

J. Arthur Reavell, in a paper on "Evaporation in the Chemical Industry with Particular Reference to the Kestner Evaporator," read at a meeting of the Society of Chemical Industry (Manchester Section), 11th April, 1918, gave the following description of the "Film" Evaporator—

Paul Kestner, in the course of a large experience in all types of evaporators, particularly studied the horizontal film evaporator, and found out its great limitations. He therefore set himself to discover, if possible, a means of producing a perfect film (account follows of the evaporator). The tubes are 23 ft. long. The liquor is fed into tubes from a tank about 3 ft. above the bottom tube plate, and assuming that this liquor is hot, on steam being applied to the outer surface of the tubes, ebullition at once commences inside, releasing a large volume of vapour which must find its way to a region of lower pressure by passing up the tubes. As a result, we have the phenomenon of the "climbing film." The liquor and vapour, on leaving the top of the tubes, meet a fixed centrifugal baffle, where the liquor is separated from the vapour, the liquor passing to the concentrated liquor tank, and the vapour to atmosphere or the condenser. The velocity of the liquor itself is thus used by means of centrifugal action to separate the vapours from the liquid.

In endeavouring to evaporate a liquid, one of the great objects is to transfer the maximum number of heat units per unit area from the heating medium to the liquor to be evaporated. Based on deductions from actual apparatus, and bearing in mind the results of theoretical and experimental research, the quantity of liquid evaporated in a tubular apparatus heated by steam would appear to vary with the following factors—

(1) Area of heating surface; (2) temperature drop or "temperature head"; (3) velocity of the liquid relative to the heating surface; (4) velocity of the heating steam; (5) specific volume of the heating steam; (6) viscosity of the liquid.

In practice, of course, the transfer is very far from being the heat conductivity obtained through the ideal cubic centimetre of pure metal.

* For most of the information dealing with Evaporation in Film Evaporators the author is indebted to Messrs. Kestners.

The conditions under which heat is supplied to the metal are very different, whilst the transfer takes place through a combined wall of water, oxide metal, and incrustation.

The table of relative heat conductivities of the various components of the evaporators, including incrustation, water and air is illustrative.

RELATIVE HEAT CONDUCTIVITY

Grm. calories per cm.² per cm. thick, per 1° C. drop per second		Comparative figures. Copper = 1000
Copper	0·9	1000·0
Iron	0·167	186·0
$CaCO_3$	0·005	5·56
Silica	0·0025	2·78
Water (not in motion)	0·0014	1·56
Air	0·000056	0·062
Kg. calories per m.², thickness 1 mm., per hour, 1° C. drop		
Copper	323,000	
Iron	60,000	
$CaCO_3$	1,870	
Silica	935	
Water	520	
Air	21	
Theor. kgs. steam condensed per m.², thickness 1 mm., per hour, 1° C.		**If the thickness is increased to 2 mm.**
Copper	605·0	302·5
Iron	112·0	56·0
$CaCO_3$	3·5	1·75
Silica	1·75	0·87
Water	0·98	0·49
Air	0·040	0·020

In referring to this table, Basil Heastie, in a paper on "Heat Transmission in Coolers, Heaters, and Condensers," read at a meeting of the Chemical Engineering Group, 9th March, 1923, gives the following interesting notes referring to the table—

From this it will be seen that a film of water 0·003 in. thick is equivalent in resisting heat flow to a copper wall 2¼ in., or assuming that the

average tube wall thickness is 0·08 in., the resistance of the metal is $2\frac{1}{7\frac{1}{8}}$ th that of the film. If steel be employed in place of copper, the resistance is increased by about $\frac{1}{4\frac{1}{7}}$ th ; whilst if a lead tube is used, the resistance is increased to $2\frac{1}{\frac{1}{8}}$th ; and since for mechanical reasons it would be necessary to increase the tube thickness where lead pipes are used, the resistance would be greater.

The next factor is heat drop. In an open coil pan the transmission of the heat depends (other things being equal) upon the heat drop, or temperature difference. That is to say, if the steam in the heating coils is at 10 lb. pressure, the temperature of the steam is at 115·5° C., and assuming there is water in the vessel, the boiling point of which is 100° C., then there will be a heat drop of 15·5° C.

When a vacuum is applied, the object is to increase this temperature drop. Taking the same figures as above, but with a closed instead of an open pan, the application of a 24 in. vacuum the temperature of the steam evolved from the liquor would be 60° C. instead of 100° C., so that the temperature drop is increased from 15·5° to 55·5° C.

Now as the rate of evaporation varies directly as the difference in temperature, a material advantage is gained by this increased temperature heat. However, while the rate of evaporation is proportional to the difference in temperature, there may be other factors which militate against this. That other factors do occur is evident, because, by increasing the steam pressure, the evaporation does not always increase proportionately.

In a " film " evaporator high temperatures can be used with advantage, because the surface is so disposed that the diameter is very small, even for great surface areas, whereas, in a bulk evaporator, such as a vacuum pan, a large surface area of tubes means a large diameter. Moreover, if high temperature, and consequently, high pressure is employed in this type of pan, many liquors which are sensitive to heat are destroyed, because they are too long in contact with the heating surface. In the " film " type evaporator which works continuously, the liquor is in contact with the heat for a few seconds only, and no " stewing action " takes place. Heat transfer also depends upon (*a*) the velocity of the liquor and vapour in relation to the heating surface, and (*b*) the velocity of the steam in relation to the heating surface. Speaking broadly, it may be said that the heat transmission varies directly as the square root of the velocity, so that if either velocity is quadrupled, the co-efficient of heat transmission is doubled. This is commonly spoken of as the effect of " circulation."

Considering now the principle of multiple effect evaporation, Reavell points out that—

All that happens in multiple evaporation is that, by alternate evaporation and condensation, the latent heat is exchanged successively, as a means of separating water from solids. Thus, neglecting losses and evaporation, etc., if 1 kilo of steam be condensed in the first calandria of a triple effect through which the liquor is passing, 1 kilo of condensed water would be produced from the liquor in each of the calandrias of Nos. 2 and 3, and 1 kilo of vapour would be produced in No. 3. If,

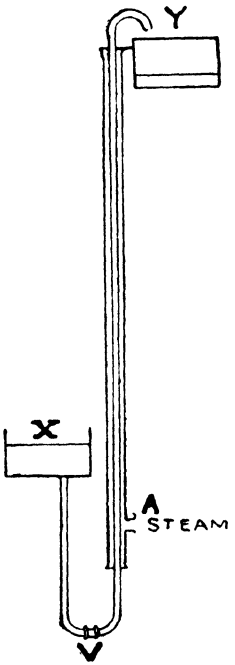


FIG. 11.
SKETCH ILLUSTRATING PRINCIPLE OF THE "CLIMBING FILM"

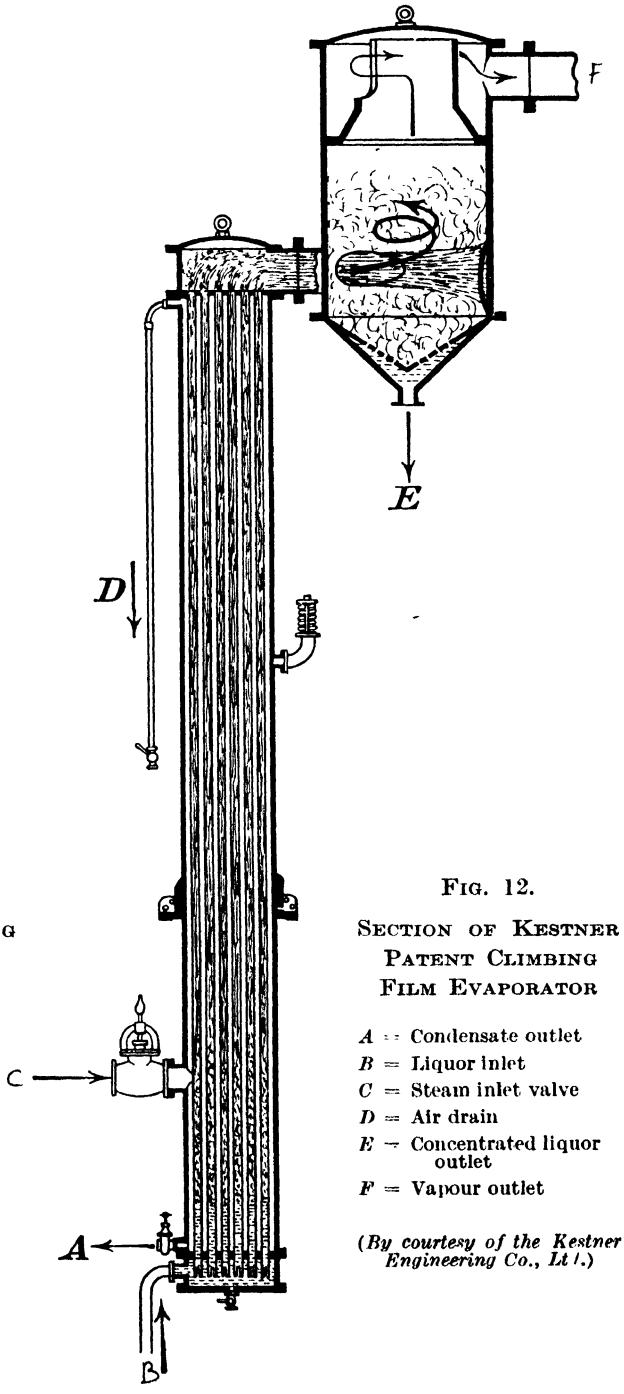


FIG. 12.
SECTION OF KESTNER PATENT CLIMBING FILM EVAPORATOR

A = Condensate outlet
B = Liquor inlet
C = Steam inlet valve
D = Air drain
E = Concentrated liquor outlet
F = Vapour outlet

(By courtesy of the Kestner Engineering Co., Ltd.)

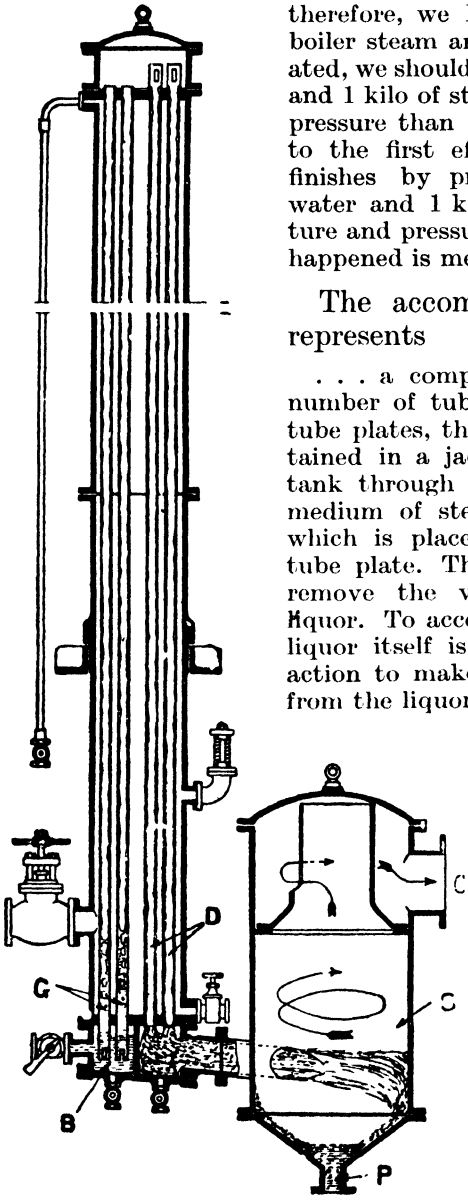


FIG. 13. SECTION OF KESTNER PATENT FALLING FILM EVAPORATOR

B = Liquor inlet box *D* = Falling film tubes
C = Vapour outlet *G* = Climbing film tubes
S = Separator *P* = Concentrated liquor outlet
(By courtesy of the Kestner Engineering Co., Ltd.)

therefore, we had commenced with 1 kilo of boiler steam and 3 kilos of water to be evaporated, we should have 3 kilos of condensed water and 1 kilo of steam at a lower temperature and pressure than that of the live steam supplied to the first effect. The cycle of operations finishes by producing 3 kilos of condensed water and 1 kilo of vapour at a low temperature and pressure—thus showing that what has happened is merely a transfer of heat.

The accompanying diagram, Fig. 12, represents

. . . a complete evaporator consisting of a number of tubes fitted into upper and lower tube plates, the whole of the tubes being contained in a jacket. The liquor passes from a tank through the tubes, being heated by the medium of steam, and rises to the separator which is placed immediately above the top tube plate. The object of the separator is to remove the vapour from the concentrated liquor. To accomplish this, the velocity of the liquor itself is used by means of centrifugal action to make the separation of the vapour from the liquor complete.

Fig. 13 shows a typical arrangement of a double effect "Falling Film" evaporator working under vacuum, complete with heater and condenser, used extensively for tan and glue liquors.

The triple effect illustrated (Fig. 14) is a most convenient form of apparatus for normal works conditions, as it gives a high economy in working, with a moderate capital cost, and, unless the quantities of water to be evaporated are relatively large, it is seldom advisable to go beyond this

Kestner & Co., Ltd., mention that—

A triple effect evaporator is usually operated with the last effect under vacuum, except in very special circumstances, the object being to get a high average temperature drop without excessive pressure in the first effect. In cases where the liquor to be evaporated is very viscous

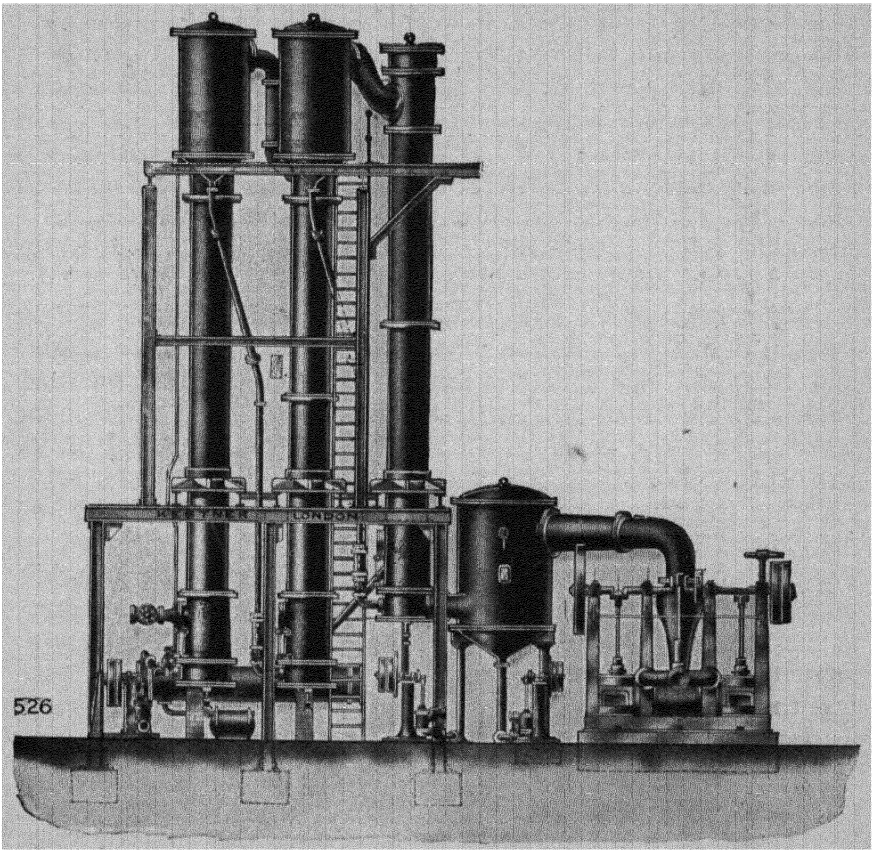


FIG. 14. KESTNER PATENT TRIPLE EFFECT EVAPORATOR
(By courtesy of the Kestner Engineering Co., Ltd.)

when cold we run counter-current, so that the weak liquid enters the third effect and leaves either from the first when full counter-current is adopted, or from the second when working semi-counter current. The steam passes from the first to the third effect as usual. The Kestner Evaporator is particularly well adapted for the counter-current working.

For bone glues, where the quantities dealt with are large, a double effect evaporator working under atmospheric pressure is usually employed, and this may be followed by a single effect

finisher evaporator when high concentrations are desired. Such a plant is shown in Fig. 15.

For gelatine and high-grade glues the plant usually consists of a double or triple effect evaporator working under vacuum. For both bone glue and gelatine, where the quantities are small, it is sometimes economical to install simple effect evaporators of the climbing and falling type.

It should be remembered that Multiple Effect Evaporators permit of rapid working at comparatively low cost. The circulation is very rapid, so that the rate of evaporation is unusually high, and the liquor passes through in the shortest time. This is of the greatest importance when dealing with unstable substances, such as gelatine, etc., where hydrolysis may possibly take place and the liquor deteriorate.

Bogue mentions " that if dry glue in thin sheets is to be produced evaporation may be omitted or carried to a glue concentration of only 5 per cent." In order to chill and work such a jelly it must necessarily be of the finest quality. For the lower grades the concentration may be pushed as high as 50 per cent.

When the glue liquor has been sufficiently concentrated and is allowed to cool, special care should be taken to prevent growth of micro-organisms. Air supply should be watched and the glue prevented from coming in contact with dirty surfaces. Some manufacturers add small amounts of antiseptics, such as formaldehyde, phenol, metallic soaps, etc., but these should not be employed unless absolutely necessary, as they cause a lowering in the quality of the glue, by affecting the jelly consistency test.

" Additives," such as sugar, glycerine, or tar oil may be added at this stage to endow the glue with special properties. There are a large number of chemicals employed to give greater flexibility, and generally manufacturers are very uncommunicative regarding the identity of their own favourites.

The use of copper vessels sometimes means that traces of copper creep into the products. C. G. King and G. Etzel (*Ind. Eng. Chem.*, 1927, 19, 1004–1005) found that down to 5–10 mg. of copper per day may produce toxic results. They also found that the presence of this metal accelerates the destruction of vitamin-C. Experiments were made on the extraction of the metal by milk boiled in copper vessels,

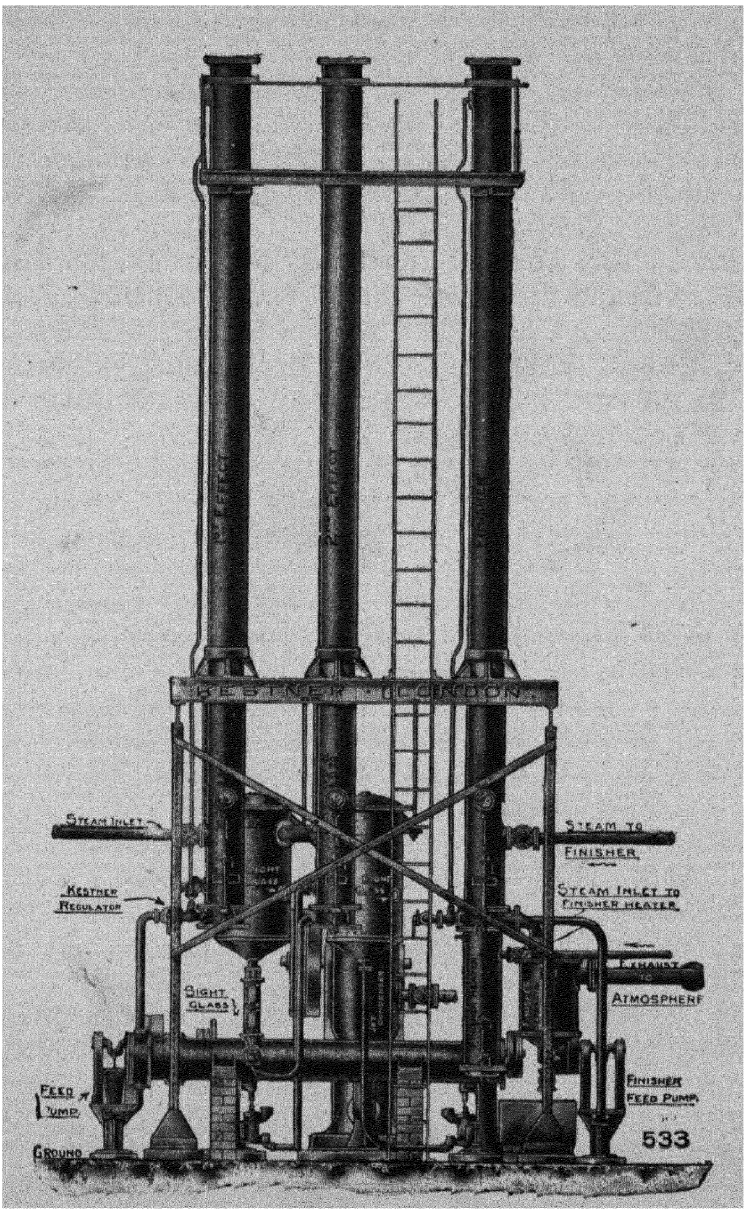


FIG. 15. KESTNER PATENT DOUBLE EFFECT COMPLETE WITH HEATER AND CONDENSER

(By courtesy of the Kestner Engineering Co., Ltd.)

with the result that the pasteurization in copper apparatus added 0·1 part per million.

The presence of excessive proportions of copper in food products depends very largely upon the acidity of the product. Gelatine containing excessive amounts of volatile or mineral acids would be very liable to dissolve appreciable quantities of copper.

Cooling. This is one of the most dangerous processes, i.e. from the manufacturer's point of view, in the whole process of gelatine production, as there is a great liability of the gelatine's being ruined by liquefying bacteria such as bacillus subtilis, which are present in the air and the spores of which are not destroyed, even at a temperature of 120° C.

The danger can be more or less overcome, providing that the room where the cooling takes place is well ventilated, the air properly circulated, and the temperature and humidity regulated.

From the evaporating pans the liquor is run into metal cooling pans made of stout sheet zinc or heavily galvanized iron or aluminium, preferably the latter. A temperature is maintained by means of one of the many refrigerating machines now on the market. The temperature should never be allowed to go below 33° or 34° F.. as if frozen, the jelly is hard and the cutting rendered extremely difficult.

Sulphites, if they have been used for bleaching, should be completely removed by means of hydrogen peroxide or some other suitable oxidizing agent.

When the jelly has cooled sufficiently, it is removed from the pans or vessels by cutting, immersing in hot water for a short time, or exposing to steam, the pan being returned for refilling. The cakes of jelly are then cut into thin sheets, either by machine or hand, and these laid out to dry on fibre or zinc netting.

Drying. In England, the drying of the sheets is generally done in well-ventilated lofts supplied with pans screened from dust, and suitable cooling apparatus. The sheets are generally spread out on fibre netting and allowed to dry at a temperature not exceeding 21° C.

In America the drying is conducted in long tunnels, so constructed as to receive trucks stocked with, perhaps, twenty frames covered with zinc wire netting supporting the glue sheets.

The alley is just sufficiently long to ensure that the sheets are perfectly dry when they leave it. As regards circulation of the air, this is cooled and drawn through the tunnels counter current to the progress of the trucks.

Considerable care must be taken in thundery weather to see that the gelatine liquor or jelly does not become liquid or foul. Rideal, in referring to the danger, writes—

> Glue liquor and jelly absorb ozone with avidity, and are decomposed by it into oxidized products with no gelatinizing or adhesive power; this may be the reason why an approaching thunderstorm is reputed to cause great damage in destroying the coagulating powers of the glue soups, or causing the glue to turn on the nets.

A wet or dry bulb thermometer is now always used by the up-to-date manufacturer, in order that the humidity and temperature of the drying rooms or tunnels may be accurately determined.

When perfectly dry the gelatine is taken off the nets or frames, when it may be regarded as ready for sale, powdering or flaking, according to its quality. Best quality edible gelatines are generally sold in the form of thin sheets.

Manufacture of Glue from Chrome Leather Waste. There are many methods of stripping chrome leather, but the author intends to deal only with the most important, and to consider in detail the " pros and cons " of each.

(The author is indebted to the Editor of *The Waste Trade World* for permission to reproduce the following, which he contributed to that journal in 1927.)

Trotman, in an early patent dealing with the detanning of chrome leather waste, treated the finely-divided leather with dilute acid or weak alkali such as lime-water, then subjected it to an oxidizing agent capable of liberating hydrogen peroxide, such as sodium peroxide.

The chromic oxide is converted into the alkali chromate, which can of course be recovered, while the hide substance is in a fit condition for conversion into glue.

Lamb (Eng. Pat. 132,864/1920) utilized for detanning saturated dibasic acids such as tartaric, malonic, and oxalic, and also acids of the lactic acid series. The leather waste which should, of course, be in a finely divided state, is soaked in this acid solution until complete detannization occurs. The chrome is recovered and the glue stock utilized in the usual way.

Stripal (Eng. Pat. 3437/1910) detans chrome leather by treating the shredded material with 1–5 per cent solution of either hydrochloric or sulphuric acid at a temperature of 50–100° C. ; the patentee claims that the leather is completely detanned.

A fairly modern method is due to A. A. Bergin (Eng. Pat. 226,722/15-4-24). The leather scrap is boiled with water containing 1–2 per cent of " caustic burnt magnesite " calculated on the weight of the leather. 0·035 per cent of lime or other alkali can be added if desired. The leather is boiled repeatedly in the alkali solution, and after each boiling the glue liquor is run off ; this is continued until all the leather has been extracted.

J. Mayer Sohn (Eng. Pat. 235,548/26-5-25, Conv. 16-6-24) is responsible for an excellent method of detannizing chrome leather. He subjects the finely-divided leather to the action of barium peroxide under pressure in an autoclave. The barium sulphates and chromate are separated from the glue liquor, which is then processed in the usual way. The barium chromate is treated with sodium sulphate and hydrochloric acid, and the barium recovered as sodium chromate.

By far the most efficient method of extracting the chrome from leather is by treating the leather with a solution of Rochelle or seignette salt, the method being due to Wilson and Procter. The process relies upon the well-known fact that the salts of hydroxy-acids, such as tartaric, form complex ions with chromium, and thus render its removal from chrome leather comparatively easy. Berestovoj and L. Masner (*Jour. Soc. Leath. Trades Chem.*, 1925, 9, 449–453), in discussing the efficiency of chrome extracted by means of Rochelle salt, give some conditions which have to be fulfilled before satisfactory results can be obtained. The most important factors to take into consideration are temperature, surface of the leather, the amount of salt, and concentration of solution. They found that 1·5 grm. of sodium potassium tartrate per 1 grm. of leather gives the best results. The optimum temperature for the reaction was found to be from 60–80° C., and the extraction of the chrome to be independent of movement of the leather, but proportional to the time of extraction, temperature, presence of neutral salt, and the concentration of the solution.

The chromium compounds were found to be very difficult to

recover from the solution, but the tartrate could easily be recovered with sulphuric acid (this is contrary to Procter and Wilson ; see *Jour. Soc. Leath. Trades Chem.*, 1916, 156).

Wolff, in a German patent, obtains chrome alum from the recovered chromium from waste chrome leather. The shredded material is treated with sulphuric acid at 80–90° C. until it has all dissolved, when excess of lime is added to precipitate the chrome together with all the sulphates present. The precipitate is dissolved in a definite quantity of sulphuric acid and potassium sulphate, and from this solution, after suitable classification and concentration, the chrome alum is crystallized out and used in the making up of one bath chrome liquors. It is necessary to add that the glue liquor is freed from any traces of lime by passing through it a current of carbon dioxide.

J. Landau and E. Trepka (Ger. Pat. 365,448/19-10-21) treat the shredded leather with a fat-splitting agent, such as Twitchell reagent, contact oil, or Pfeibring preparation in the presence of an alkali.

A very interesting method of detannization, in which enzymes are utilized, is due to Röhms's German patent No. 303,184. The leather is subjected to the action of dilute caustic soda, and the residue treated with the enzymes of the pancreatic juices. Ammonium salts, amino acids, etc., are added with the enzymes, and are said to act as an " inhibiting " agent.

In reviewing the many methods of detanning chrome leather, the author considers that one or two are of outstanding merit, and warrant some practical trial by tanners. Wilson and Procter's method, embracing the use of Rochelle salt, is, without doubt, the best method, as this salt can be recovered from the solution, which, of course, considerably cheapens the process ; also a very good quality glue stock is obtained, and this cannot be said about many of the other processes. The method due to Lamb, when oxalic acid is used, is a very cheap one, the only drawback being that the glue liquor contains a small percentage of the free acid which, to some extent, lessens the tenacity of the glue.

Although other hydroxy acids are mentioned, such as tartaric, malonic, etc., these cannot be used on any practical scale on account of their excessive price. The method due to J. Mayer Sohn, using barium peroxide under pressure in an autoclave, is one which recommends itself on account of the

speed of the reaction and efficiency, that is, when a large quantity of leather is to be treated.

The other processes are interesting, but one is forced to the conclusion that considerable improvements are necessary before they can become really "practical methods." Although the use of enzymes strikes a new note in this recovery process, the author does not consider their application to be of any real practical importance. In these days enzymes are utilized for all manner of purposes, from the manufacture of artificial bates to tooth paste. They remind one very much of "King Charles' Head" in *David Copperfield*, as they continually crop up in the most unlikely places. In practically every sphere of life we meet these wonderful "enzymic preparations," and in every case they are guaranteed to accomplish the most difficult tasks in a short space of time and under very involved and intricate conditions. No doubt Houdini was acquainted with the use of these marvellous enzymes, and. probably, the "vanishing elephant trick" was due to their wholehearted application.

There is no doubt that at the present time the leather and similar trades are suffering from "enzymitis," an infectious disease, whose only cure is experience. When these much-advertised preparations have been extensively tried, then, and only then, will the scales fall from the tanner's eyes.

The manufacture of glue from chrome leather waste is a sound commercial proposition, but the same cannot be said about the detannization of vegetable-tanned waste. After a

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(F. Hudson, *Jour. Soc. Leath. Trade Chem*, May, 1927.)

FOUR SAMPLES OF GLAZED KID

	American	American	Spanish	Unknown
Moisture	15·42	13·6	15·45	17·2
Fat and sulphur	9·04	3·18	7·03	5·11
Sulphur	0·31	—	—	—
Chromium sol. in pet. ether	0·052	Nil	0·0178	Nil
Water solubles	1·50	1·29	1·10	2·42
Hide substance	61·32	65·21	57·0	62·86
Cr_2O_3	3·49	3·66	3·38	4·18
Basicity	70·3	53·4	1·809	60·4

large number of experiments, based on the many patents referring to this subject, the author is led to believe that the extraction of glue from vegetable-tanned leather is not a practical process, as it necessitates some considerable expenditure and little or no return, for the glue obtained is of very poor quality. In view of this, the tanner is recommended to utilize the vegetable-tanned leather waste in other ways.

Dealing with this question of manufacturing glue from chrome leather waste, the analysis (given on p. 94) of chrome leathers may prove informative.

CHAPTER VII

ANALYSIS OF GLUE AND GELATINE

Notes on the different varieties of gelatine

Testing of Glue. INSPECTION. A considerable amount of knowledge can be obtained by a close inspection of the glue. To the initiated the colour, odour, brittleness, presence of cracks, and air bubbles in any sample will be sure indications as to its quality.

A good glue will be of a firm, solid nature, free from cracks and of a clear translucent appearance, unless, of course, it has been rendered opaque by some added colouring matter. Furthermore, a good glue, when fractured, should not appear splintery, as this is a sure sign that it has not been well boiled.

The colour of glue varies from light amber to dark brown, but it should never be black. Glue of a good quality will not possess a disagreeable odour when dry, and will not develop such an odour after 48 hr. in solution.

Light amber-coloured glue is most likely to be of bone origin, while the light and dark brown glues are generally derived from hide and skin stock. Bone glues nearly always present a milky appearance, due to a little calcium phosphate.

The smell of a hot solution of glue will often indicate the source ; hide glue, pig's foot, bone, and fish all having definite, well-defined odours. If the glue is badly cracked it is a weak sample, if muddy or of a dark colour and opaque it signifies that the sample contains the end products of hydrolysis, i.e. amino acids or proteoses.

Although simple inspection is a good criterion of the quality of the glue, this is not the only test which the manufacturer employs ; there are others, both chemical and physical, the most important of which will now be mentioned.

Before discussing the usual chemical tests, it is perhaps advisable to mention a simple chemical method of differentiating hide and bone glue. This method is due to E. Sauer (*Farben-Ztg.* 31, 721-2, 773-4, 1925).

The ash of bone glue consists chiefly of phosphates, and the bulk is much greater than that obtained from hide glue. The

ash from the latter is composed chiefly of calcium oxide and chloride. Hide glues are mostly neutral in reaction, bone glues more or less acid. Tannin solutions, such as sumach or gall nuts, may be used as a precipitating agent instead of sulphite waste liquors as prescribed by Stein (*C. A.* 17, 2521) to differentiate the two varieties of glues. A concentrated solution of tannin, and a small quantity of $MgCl_2$ and AcOH are added to 1 per cent of glue at 50° C. Hide glue produces only a slight turbidity; bone glue, a brown, sticky precipitate. This test really indicates the glutin content of the glues.

The action of alum on glue solution (C.A. 16, 3230) serves as a differentiation test when 10 c.c. of a glue solution at 30° c. is thoroughly shaken with 2 c.c. of 5 per cent alum solution; with hide glue, gelatinization occurs in 1 to 2 min.; with bone glue, no change occurs. With glue mixtures the time required for complete gelatinization is an indication of the relative amount of hide glue present.

Iron alum has a stronger gelatinizing action than aluminium alum, and the yellow gel produced with hide glue is streaked with red and white, which serves as a further differentiation from bone glue.

Hide glue, after sufficiently long heating, shows similar physical properties, and the same reactions with alum as bone glue. The difference between these two glues consists in variations, not only of glutin content, but also of other attendant components.

Physical Tests. VISCOSITY. This may be determined by using the Engler viscosimeter. This consists of a reservoir in which the liquid to be tested is placed, enclosed in a water or oil bath for maintaining a definite, stable temperature.

From the centre of the reservoir a short capillary tube, about 2 cm. in length, permits the outflow of the liquid.

The temperature at which the viscosity is determined is of the utmost importance, as it has a great influence on its magnitude. The viscosity at a temperature of 32 to 35° C. has been found by numerous investigators to correspond with the true melting point, and to be accurately indicative of the gelatine content and the joint strength of the product. Bogue says that this temperature is one above which evidence of plastic flow could not be observed, while C. R. Smith found that the gel form could not exist above it.

An 18 per cent solution is the strength usually employed for viscosity determinations.

The viscosity may be worked out by means of the following equation (Herschel)—

$$\frac{\mu}{\gamma} = At - \frac{B}{t}$$

in which μ is the viscosity in poises; γ the density in grams per cubic centimetre; t the time of discharge in seconds, and A and B are instrumental constants which are for the Engler viscosimeter.

$$0{\cdot}000147 = A \text{ and } 3{\cdot}7400 = B.$$

NOTES ON VISCOSITY. The most accurate method for measuring the viscosity of gelatine solutions is due to Clarke E. Davis and Henry M. Salisbury (*Ind. Eng. Chem.*, Vol. XX, No. 8).

Ordinary distilled water was added to sufficient gelatine to give a solution of 1 per cent (day basis) when made up to 200 c.c., together with the amount of acid (0·1 M/HCl) or base (0·1 M/NaOH) that gave a solution of the desired P_H^+ value. The P_H^+ measurements were made by use of indicators, the hydrogen electrode, and the quinhydrone electrode. The age of the solution was reckoned from the time the gelatine was placed in contact with the water.

As soon as the mixture was made, the flask was placed on an asbestos-covered hot plate and brought to 75° C. in 15 to 18 min. with stirring. The solution was then rapidly filtered and placed in the thermostat at 40° ± 0·02° C.; when cooled to this temperature, 5 c.c. were pipetted into a well-cleaned and dried Oswald Viscosimeter previously immersed in the thermostat.

After 1 hr. and 25 min. the solution was drawn up through the capillary tube into the bulb and above the top mark. The run was then made, timing from mark to mark with a stop watch.

The viscosimeters were previously calibrated, using boiled distilled water at the desired temperature. The viscosity of the gelatine was calculated in absolute units (centipoises) by the usual formula.

Specific gravity measurements of the gelatine solutions were made by means of a pycnometer.

$$\eta \text{ Gelatine} = \eta \text{ for water} \frac{\text{seconds gelatine soln.} \times \text{sp. gr. gelatine soln.}}{\text{seconds water} \times \text{sp. gr. water.}}$$

η for water at 40° C. = 0·6560
η for water at 25° C. = 0·8937
Specific gravity of water at 40° C. = 0·99225
Specific gravity of water at 25° C. = 0·99707

To simplify the calculations, a constant (K) was calculated for each viscosimeter.

$$K = \frac{\eta \text{ for water} \times \text{sp. gr. gelatine soln.}}{\text{seconds water} \times \text{sp. gr. water.}}$$

Then η (gelatine) = K (seconds gelatine soln.).

Consistency and Bearing Weight of the Jelly. The following method is due to Lipowitz, 1861, and is taken from Rideal's *Glue and Glue Testing*—

A 10 per cent hot solution is allowed to stand 12 hr. at 18° C. in a cylinder of uniform width to gelatinize. A metal rod is soldered to the centre of the interior of a small tin cup, and is supported vertically by passing loosely through holes in two horizontal plates, one of which forms the cover of the cylinder, the other being fixed a little higher. The upper end of the rod carries a funnel, which can be loaded with fine shot. The cup is allowed to rest on the jelly, and the funnel is loaded until it sinks a certain distance into the jelly ; the weight of shot then gives the Lipowitz number. The cylinder should be surrounded by a water jacket to maintain a definite temperature. The result is also affected by the diameter of the cylinder and of the cup.

Lipowitz gives the following figures—

Variety of Glue	Weight Required to Force the Saucer Down
	lb.
Breslau	3·74
Russian	3·18
Cologne	2·67
Muhlhausen I . . .	1·60
Närdlingen . . .	1·59
Muhlhausen II . . .	0·85

A rough and ready method of testing the jelly consistency is by means of the finger test, which would seem to be the usual control test in America. A full account is given in Bogue's *Technology and Chemistry of Glue and Gelatine.*

Foam Test. The following method is the one used by Trotman and Hackford (*Jour. Soc. Chem. Ind.*, 25 (1906), 104).

A graduated cylinder 70 cm. in length and provided with a glass stopper is taken and half filled with a 10 per cent solution of glue ; it is then placed in a water bath and the temperature maintained at 60° C. The stopper is then replaced and the cylinder shaken for 1 min. ; the foam is then read off, the reading in cubic centimetres being known as the foam figure.

Grease Test. The glue to be examined should be ground to a very fine powder and 10 grm. taken for the determination. This is placed in a large Soxhlet extraction thimble, a layer of fat free cotton being placed above and below the sample. Some chemists mix the glue with sand, and they say that if the two

substances are mixed well together the extraction is quicker and the yield of fat greater. The glue is then extracted for 8 hr. with petroleum ether, which distils between 50° to 80° C. The receiver, which should previously have been weighed, is then removed, and the solvent evaporated off on the electric heater or steam bath. The flask is then placed in an oven at 100° C. for 1 hr., cooled in a desiccator, and weighed. The increase in weight represents the amount of fat or grease in the 10 grm. of glue.

$$\frac{\text{Weight of fat} \times 100}{10} = \text{per cent fat.}$$

Tensile Strength. Full details concerning estimation may be found in Chapter VIII. The following simple method may, however, be considered at this stage.

Make up a 10 per cent solution of glue, and take strips of filter paper 1 in. by 18 in. and dip in the glue solution, which should be at a temperature of 50° C., and then hang up to dry. When dry dip again, and dry the other way up. After air drying, place the strips in a water oven for 1 hr., and then cut out two or three lengths from the centre of the strips and fix in a balance and find the weight required to break them. A blank determination should be performed to find the tensile strength of the paper, which should, of course, be deducted from the total.

A good glue should require 9 to 10 lb. to break the strip.

Melting Point. There are many methods for determining the melting point of glue.

Küttner and Ulrich describe the use of Cambon's fusiometer, which consists of a metallic bowl of given dimensions and weight. A glue is allowed to gel therein, a rod being held in a vertical position in the solution.

The whole is then placed in a beaker of warm water, suspended by the rod, and the temperature at which the bowl drops from the rod taken as the melting point.

The simplest method is that of Herold, who allowed a thermometer to become fixed in a test tube of glue, and noted the temperature at which the tube fell away from the thermometer when suspended in warm water. The thermometer should be graduated to tenths of a degree, the tube small, and the space between the bulb of the thermometer and the wall of the tube not more than 1 mm. On no account should the temperature

of the water bath be 1·5 to 2·0° C. higher than the suspected melting point of the jelly.

The determination of the melting point of every sample of glue, no matter whose method is adopted, should be carried out with the greatest possible accuracy, as the smallest error will often mislead the investigator as to the purity of the specimen under examination.

Chemical Tests. MINERAL ASH. The general method of estimating the ash is as follows—

A convenient amount of the sample is weighed out and incinerated in a platinum crucible. Sometimes it is necessary

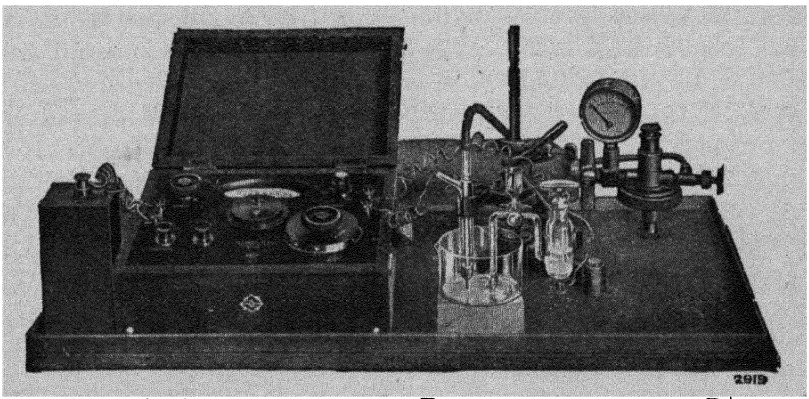

FIG. 16. APPARATUS FOR THE DETERMINATION OF THE PH OF A SOLUTION

(By courtesy of the Cambridge Scientific Instrument Co.)

to make a complete quantitative analysis of the ash, but for general practical purposes it is sufficient to simply test the ash for phosphates by the usual ammonium molybdate test. The presence of phosphates indicates that the sample is of bone origin.

ACIDITY. Acidity in glue may be due to the presence of $H_2S\,O_3$, this being formed by the SO_2 used in bleaching, or to traces of hydrochloric acid used for deliming.

By far the most accurate method of determining the total acidity, is by means of the electrometric apparatus for the determination of the hydrogen ion concentration, or, in other words, the P_H^+ value of the solution. The Cambridge & Paul Instrument Co., Ltd., have on the market a portable electrometric apparatus suitable for determining the hydrogen ion

concentration in industrial processes (see Fig. 16) which the author can recommend.

This apparatus consists of a self-contained portable potentiometer together with suitable electrodes. The potentiometer consists of a pointer galvanometer of the unipivot type, an adjustable resistance to standardize the battery circuit with the galvanometer, a five-range switch to give steps of 200 millivolts, and a fine adjustable resistance. The electrodes are connected to the right-hand terminals of the instrument, a dry cell being connected to the left-hand terminals. With the standardizing key depressed, the rheostat is adjusted until the pointer of the galvanometer is directly over the red mark on the scale. The " X " key is then lightly depressed and the range switch set to give the minimum deflection while the circular graduated disc is at zero. To obtain the final reading the latter is rotated until the pointer comes to zero. The reading of the circular disc is then added directly to the number of millivolts indicated by the range switch, this total giving the E.M.F. of the electrodes. Readings are obtained directly to 1 millivolt.

Volatile acids are estimated by passing steam through a solution of glue, 15 grm. preferably, dissolved in distilled water free from carbon dioxide. The distillate is collected in a flask containing $N/_{10}$ Na OH and three drops of phenolphthalein. About 250 c.c. are distilled over, and then the distillate treated to neutrality with $N/_{10}$ HCl.

The difference between the amount of alkali and the acid used, indicates the amount of alkali required to neutralize the volatile acids in the 15 grm.

$$\frac{\text{c.c. alkali} - \text{c.c. acid} \times 100}{15}$$

= Acidity due to volatile acids in terms of $N/_{10}$HCl per 100 grm.

In works practice it will generally be found sufficient to perform simply the direct titration and just determine the total acids in the jelly.

MOISTURE. This is a most important estimation. About 10 grm. of finely-ground glue is placed in a nickel or platinum dish which is put in an air oven at 110° to 115° C., or a vacuum oven at 80° C. and allowed to remain until the weight is constant. The loss in weight sustained by the sample is moisture. It is advisable to mix the ground glue with dry silver sand, as

this tends to shorten the time taken for drying and admits of more accurate results.

The moisture may vary within large limits, in the low grades from about 9–12 per cent to about 14–18 per cent in the highest grades. The moisture should not, however, be too low, as this is a sure indication that the drying of the glue has been carried too far.

Testing of Gelatine. The purest forms of gelatine occurring commercially are colourless and transparent, of horny toughness,

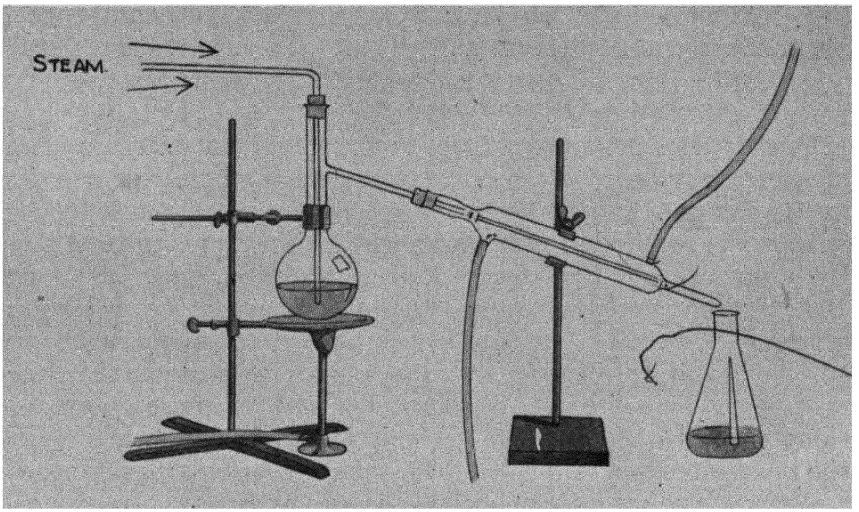

FIG. 17. APPARATUS FOR THE ESTIMATION OF SULPHUR DIOXIDE IN GELATINE

and having a specific gravity of about 1·3, the average moisture content being approximately 10·8 per cent.

Gelatine possesses no definite melting point, but begins to soften with decomposition at about 140° C. It is insoluble in cold water, alcohol, ether, chloroform, carbon disulphide, benzene, absolute alcohol, etc., but in the first-named it swells to a transparent jelly. Tannic acid precipitates gelatine from solution in form of tannin gelatine, and picric acid as gelatine picrate when excess of the former is used.

Of the common reactions for proteins the Xanthoproteic, Millon, sulphur, and Adamkiewiez's reactions are very faint. Gelatine is not precipitated by concentrated mineral acids, and

mercuric chloride has no action in neutral solution, but precipitates gelatine in the presence of hydrochloric acid. Phosphomolybdic and phosphotungstic acids cause voluminous precipitates, the complete separation, however, requiring several hours. An acid solution of chromic acid precipitates gelatine, but not peptones. Platinic chloride and basic lead acetate also throw down gelatine, but the amount of precipitate varies with the hydrogen ion concentration of the solution and the concentration of the jelly. Potassium dichromate and formaldehyde react chemically with gelatine, forming well-defined compounds, which are of considerable importance in photography and pharmacy. All the tests mentioned, whilst referring to glue, are generally applied to gelatine also, together with one or two more.

One of the most important of the chemical determinations made with gelatine is the estimation of the amount of peptones in the sample.

The best method of performing the estimation is the one given by Trotman and Hackford (*Jour, Soc. Chem. Ind.*, 23 (1904), 1072). They first determine the total nitrogen by Kjeldahl's method, then the " albumoses " by precipitating with zinc sulphate and subjecting the precipitate to a Kjeldahl determination. The nitrogen obtained by both of these determinations is multiplied by the factor 5·33. The difference between the total nitrogen × 5·33 and the proteoses is taken as peptones.

A good-glass gelatine should not give more than 1·8 per cent peptones.

Sulphur dioxide is generally determined in gelatine, the usual method being to distil about 10 grm. of the gelatine dissolved in 500 c.c. of water to which has been added 5 c.c. of a 20 per cent solution of glacial phosphoric acid. The distillation is

	Nelson's		Coignet Extra	Swiss Gold Label
	A	B		
Water	18·96	17·10	19·4	17·84
Ash	4·19	3·80	1·50	1·47
Gelatine (total N × 5·56) .	76·73	78·26	78·34	79·67
Non-nitrogenous organic matter	0·12	0·84	0·75	1·02

carried out in an atmosphere of CO_2, and the SO_2 distilled into a known excess of $N/_{20}$ iodine. After 200 c.c. have distilled over, the distillate is titrated with an $N/_{20}$ thiosulphate solution.

1 c.c. of $N/_{20}$ iodine solution = .0032 grm. SO_2.

Rideal gives the analysis (given on p. 104) of four high-grade samples of gelatine.

Manufacturers of high-class gelatines have very curious methods of evaluation. They sometimes employ numbers of symbols, which convey little if anything to the buyer. An explanation of existing nomenclature would require many pages, and even then be unsatisfactory. For the present purpose, however, it is sufficient to state that a "Grade I" and "A" quality, or "Gold Label Gelatine," may be considered eminently suitable for medical and general food purposes. Only the most reputable firms should be dealt with, that is, to any appreciable extent.

Best French gelatine enjoys a great popularity among professional buyers in this country, and there is no doubt that this variety is looked upon with favour by ordinary householders.

Edible gelatine should contain only the merest traces of metallic impurities and sulphites. R. M. Mehurn (*Ind. Eng. Chem.*, 1923, 15, 942, 3) found that the purest commercial gelatine containing only 10 per cent water, yielded on the average approximately 1·5 per cent ash. Of the heavy metals, iron occurs in the ash to the extent of 1·25 per cent, copper varies up to a minimum of 0·17 per cent. An average ash may be said to contain CaO 53·46 per cent, MgO trace, FeO_3 1·22 per cent, P_2O_5 5·4 per cent, SO_3 36·36 per cent, SiO_2 3·36 per cent.

The above figures may be taken as representative of good qualities of gelatine (edible).

Besides the metallic impurities mentioned, gelatine is "liable" to contain very small, almost infinitesimal, amounts of arsenic. The proportions of arsenic, copper, and zinc should not exceed the following amounts—

30 parts per million (copper)
100 ,, ,, ,, (zinc)
1·4 ,, ,, ,, (arsenic)

Sulphites are most objectionable in edible and photographic gelatines. They may be accounted for by the fact that sulphurous acid is sometimes used by manufacturers to delime the raw material. The sulphurous acid is generally made on the

spot, by passing sulphur dioxide gas through the water containing the raw material to be treated. After this the pieces of skin, ossein, etc., are thoroughly washed, in order to free from the presence of sulphites and sulphurous acid. If, however, this washing is not carried far enough, then, of course, these sulphur-containing impurities remain in the skin. E. Gudeman (*Jour. Ind. Eng. Chem.* 1 (1909), 81) gives the following results of three analyses of gelatines by his own method (direct titration)—

Home-made gelatine	0·0000 per cent sulphur dioxide
French gelatine	0·0260 ,, ,, ,,
American gelatine	0·0120 ,, ,, ,,

Very small quantities of sulphites or sulphur dioxide, less than ·02 per cent, have no deleterious action on foodstuffs, etc.

To sum up, it may be stated that a " good edible gelatine " should have a low ash content varying from ·5 per cent to 2·5 per cent (gelatine containing 10 per cent moisture), and contain less than ·03–·02 per cent sulphites. Other factors of lesser importance are moisture content, which should be from 15–20 per cent, and peptones or hydrolytic products due to bacterial contamination. Bogue gives the following amounts of bacteria in five representative samples—

I.	113,000,000	bacteria	per grm.	(inferior quality)
II.	14,000,000	,,	,,	,,
III.	35	,,	,,	(good quality)
IV.	4,200	,,	,,	(fair quality)
V.	85,000	,,	,,	,,

It will be at once realized that III is a " good edible gelatine," others being unsuitable for inclusion in foodstuffs.

According to Zsigmondy, the following gold numbers are attributed to the proteins. It should be noted that a small number indicates a good-quality gelatine endowed with marked protective properties—

Gelatine	0·005–0·1
Isinglass	0·01–0·02
Fresh egg white	0·08–0·15
Dextrin	10–20
Potato starch	25

CHAPTER VIII

THE APPLICATIONS OF GLUE

In veneering, bookbinding—General uses of glue

A LARGE amount of glue is used in the manufacture of furniture, wooden and cardboard containers, and also for aeronautical purposes, but it is a fatal mistake to think that there are only two requirements of a glue for the above work, namely, that it should stick and be cheap.

In the July, 1928, No. of *The Packing Gazette*, the editor explodes the above view in the following words, referring to use of glue in manufacture of containers—

> A cheap adhesive may stick under the conditions in which it is applied in the packing room, but the work of any adhesive has only commenced when it has dried. There follows a long and trying period, during which goods are in transit or store awaiting purchase under conditions which cannot always be foreseen and can never be controlled by the packer. Such hazards are increased for manufacturers of pre-packed goods sold in overseas markets. Normal conditions of climate alone form an exacting test for all pre-packed goods in certain overseas markets, but such conditions are often intensified by local facilities for storage and sale. In a word, only an adhesive of first-rate quality can be expected to perform its work satisfactorily in such cases. That the goods are beyond the maker's inspection and control makes it doubly necessary to ensure, so far as possible, that the adhesive is equal to the strain imposed upon it.

Of course, for ordinary packing work slightly inferior glues can be used. Cold fish glues are now in fairly common use, as they economize heat and labour in making up.

Whilst on this subject of glue for packing work, it should be pointed out that a lot of bad work is caused because the operators do not realize the putrescible nature of the material they use. Thus, glue boxes are seldom cleaned out, and in consequence bacterial action takes place with resultant hydrolysis and lowering of tensile strength of the gel. Again, the glue should never be thinned down with cold water, as the inevitable result will be lack of uniformity in results—the same strength of glue must be used throughout the whole operation.

Veneering demands a high-grade glue with a rising tensile

strength and high viscosity. The glue should be free from colour and grease. Presence of hardening materials is not desirable, as the veneer will not adhere so well to the "base wood." It is very important that the glue should not form a foam, as this might decrease the setting power and, possibly, injure the delicate light-wood veneers.

Glue used for aeronautical and similar work must be of exceptional quality—the highest tensile strength and viscosity are absolutely essential.

Tensile Strength. This test is of vital importance, and will be considered at some length. The Government Research Committee working on "Adhesives," published in 1922, an account of their work on glue and gelatine. Discussing the question of tensile strength, they described an interesting and simple method evolved by workers at the Aeronautical Inspection Department.

The description of the process is as follows—

1. The test pieces in the earlier work consisted of carefully selected pieces of hard, dry, American, straight-grained walnut, 2 in. wide, 9 in. long, and $\frac{3}{8}$ in. thick. The flat sides are planed true, and are toothed with a fine toothing plane (25 teeth per inch).

2. The glue is soaked in the requisite amount of water at room temperature for 24 hr., after which it is heated between 60 and 80° C. for a short period and allowed to cool to 60° before application.

3. Before making test joints the wood is allowed to remain for several hours in a constant temperature oven at 35° C.

4. Two pieces of warm wood are then removed from the oven and the glue is quickly applied with the fingers to one surface of each test piece; the pieces are then placed together in such a manner that a simple 1 in. overlap is obtained, giving a joint with 2 square inches of glued area. During the application of the glue, care must be taken to avoid the formation of air bubbles.

5. The joint is then secured in a wooden frame with the aid of an iron clamp. By means of tested box-springs a standard pressure of 400 lb. is applied for 12 to 18 hr.

6. The joint is unclamped at the end of this time and allowed to stand 3 days. Its breaking stress is then determined in a form of Avery or Buckton Cement-testing Machine adapted to the testing of wood joints, the usual precautions being taken. In a more recent type of Avery Machine, shorter pieces of wood (only $4\frac{1}{2}$ in. in length) are employed.

The Committee recommends that four test joints should be made from each sample of glue and the mean breaking stress of the four joints determined. They point out, however, that the

test, valuable as it undoubtedly is, cannot be regarded as "an absolute criterion of the value of a glue." It seems that there are a number of discordant factors to be taken into consideration in estimating the tensile strength of a sample; these are summarized as follows—

(*a*) Variations in porosity of the wood.
(*b*) Variations in the heating of the glue and in the temperature of the wood.
(*c*) Variations in the thickness of the glue films due to differences in the viscosities of the glues.
(*d*) Changes in the humidity of the temperature of the atmosphere.
(*e*) Irregular applications during testing.

The British Engineering Standards Association adopt the following standards—

Class	Breaking Stress	Use
Propeller glues	1,100 lb. per sq. in.	Airscrew manufacture
Class I	1,000 ,, ,, ,,	Important stress-bearing work
Class II	900 ,, ,, ,,	No stress-bearing work

Figures given by the Committee illustrate the great difference between the tensile strength of hide and bone glues—

	Tensile Strength
Hide glues I	1,390 lb. per sq. in. (1 pt. glue to 2 pt. water)
,, ,, II	1,390 ,, ,, ,, ,, ,, ,, ,,
,, ,, III	1,355 ,, ,, ,, ,, ,, ,, ,,
Bone glues I	851 ,, ,, ,, ,, ,, ,, ,,
,, ,, II	829 ,, ,, ,, ,, ,, ,, ,,
,, ,, III	437 ,, ,, ,, ,, ,, ,, ,,

In a previous chapter it has been pointed out that it is the common custom of manufacturers to add chemicals to the glue in order to increase tensile strength—the ordinary sugars being the usual additives. The figures (given on p. 110) worked out by "The Research Committee," give an indication of this increase.

TENSILE STRENGTH

10 grm. gelatine in 30 c.c. of

Sugar	$M/_1$ Soln.	$M/_2$ Soln.	$M/_4$ Soln.	$M/_5$ Soln.	$M/_{10}$ Soln.
Glucose	940	900	—	810	910
Maltose	990	780	—	1,190	1,090
Laevulose	950	980	—	870	800
Cane sugar	—	1,200	850	870	830
Control (in water)	870	—	—	—	—

The sugar was purified and used in molar solutions and fractions of same.

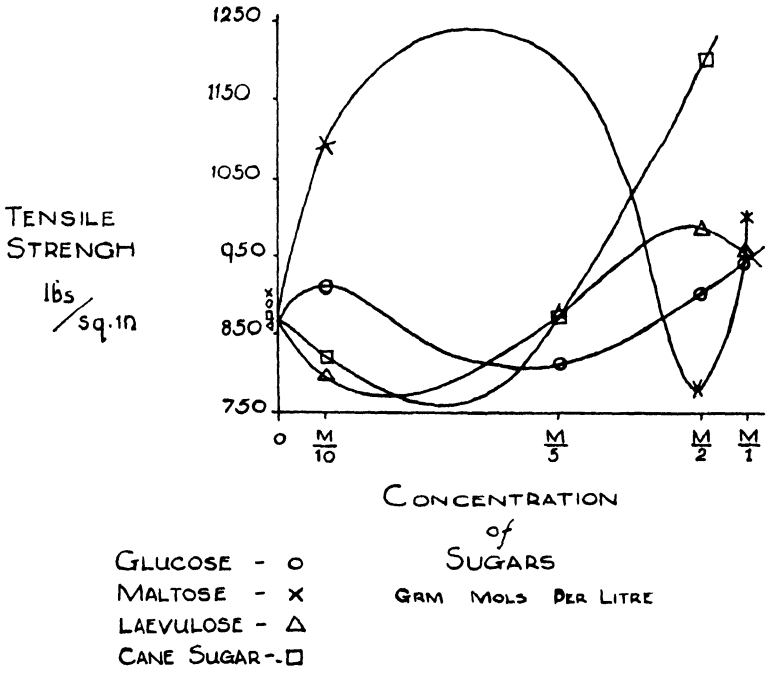

FIG. 18. GRAPHICAL ILLUSTRATION OF THE EFFECT OF SUGARS ON THE TENSILE STRENGTH. 10 GRM. GELATINE IN 30 C.C. SOLUTION

From the above figures maltose would appear to have the greatest effects, although cane sugar in $M/_2$ solution gives 1,200.

Veneering. The home of woodwork and of every other art, fine and applied, was Ancient Egypt. Renan described this hub of industry in the following well-known couplet—

> The Queen of Nations and the Boast of Time
> Mother of Sciences and the Home of God.

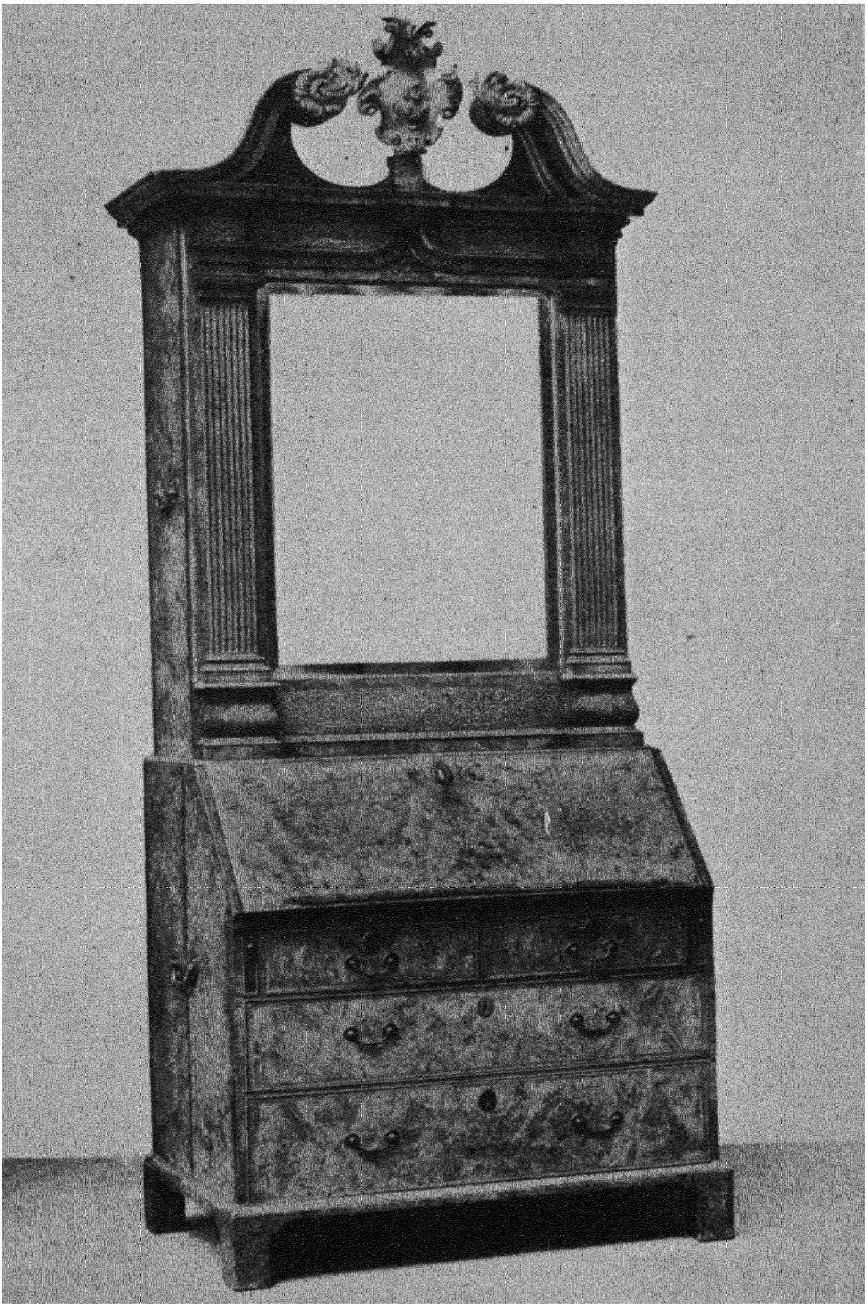

FIG. 19. BUREAU BOOKCASE BY S. BENNETT. AN EXCELLENT EXAMPLE OF WALNUT VENEER

(Reproduced by the kind permission of the Victoria and Albert Museum)

There is no doubt that the palaces of Egypt and Nineveh were furnished very luxuriously. The ancient Egyptians were not satisfied with the mere rudiments of comfort as enjoyed by their more primitive neighbours ; they desired to be surrounded by an atmosphere of riches.

Articles of furniture were regarded in many cases as vehicles for precious stones, rare metals, and enamels ; it was the age of magnificence as opposed to comfort. The chief woods used by the Egyptian craftsman were ebony, cedar, acacia, and sycamore, whilst ivory was much used for purposes of ornamentation. It is known that veneering was practised, and there are in existence many examples of this work.

To pass on to a somewhat later civilization, namely, the Roman, we find a queer mixture of austerity and richness bordering on the ornate. Up to the time of the Punic Wars the wealthy Roman citizen was content with simple, almost severe, furniture, and his mode of living might aptly be described as Spartan. It was after the siege of Carthage that the Romans began to introduce new ideas into their lives and homes. They ransacked the world for its most priceless treasures, nothing was too good or too costly for their marble villas on the Tiber. The excavations at Pompeii prove how sumptuous was the home of the wealthy Roman.

It is interesting to note that Cicero paid the equivalent in Roman money of £9,000 for a table of citrus. Veneered articles of furniture were very popular, and different names were given to veneers of woods showing peculiar markings ; thus, when spotted like a swarm of bees the wood was called " apiatus," and " tigrinus " when it resembled the stripes of the tiger.

To trace the evolution, or some might think involution, of this difficult art of veneering, would take too much time and space for the present purpose. In England, up to the seventeenth century, veneering was practically unknown. The furniture, even in the palaces of kings and princes, was extremely crude and heavy. Oak was the principal wood employed, and this was fashioned in the true Gothic style until the end of the reign of Henry VIII. Then came the Elizabethan period, when furniture design was closely studied. An examination of furniture of this period will show that a common fault was over-elaboration. Thus, every possible inch was carved

FIG. 20. HAREWOOD AND SATINWOOD COMMODE

(Reproduced by the kind permission of the Victoria and Albert Museum)

with the most intricate designs, which often gave the article a " cheap " appearance.

Inlays were in fairly common use, and generally took the form of conventional leaf and floral work, or of simple, conventional design. The Jacobean was a far more artistic period, though the carving generally was not of such a high order as that of the Elizabethan. After the heavy Cromwellian we come to the Stuarts. In the reign of Charles II a certain lightness and ornateness was creeping into the designs. It is strange to relate that even at that advanced age chairs, except for ceremonial occasions, were not in common use. In confirmation of this statement one has but to turn to the immortal diarist, Pepys. Under the date 4th March, 1669, the following is recorded—

And so walked to Deptford, and there to the Treasurer's house, where the Duke of York is, and his Duchess, and there we find them at dinner in the great room, unhung ; and there was with them my Lady Duchess of Monmouth, the Countess of Falmouth, Castlemagne, Henrietta Hide, and my Lady Peterborough. And after dinner Sir Jer. Smith and I were invited down to dinner with some of the maids of honor. Having dined, and very merry, etc., and so we up ; and there I did find the Duke of York and Duchess, with all the great ladies, sitting upon a carpet, on the ground, there being no chairs, playing at " I love my love with an A, because he is so and so, and I hate him with an A, because of this and that " ; and some of them, but particularly the Duchess herself and my Lady Castlemagne, were very witty.

Towards the second half of the seventeenth century great changes were taking place in the design of furniture. The old square and heavy articles were giving way to finer shaped and more artistic work. Walnut was coming into vogue and veneers introduced. These latter enabled the usual carved and moulded work to be superseded by a flat decorative treatment obtained by the employment of finely-figured woods and marquetry.

To pass on to the restrained and rather heavy Dutch period, we find a retrogression. It was during the eighteenth century that really beautiful and artistic furniture of a light nature was made by the master craftsmen, namely, Hepplewhite, Robert and James Adams, and Chippendale.

Sheraton, the last of the eighteenth century designers, worked with satin- and the rose-woods, and his veneered work can be seen to-day at Christie's and other large auction rooms commanding enormous prices, which shows that even in these days

of " utilitarianism carried to excess," real artistic works can still fetch big prices.

On the Continent, veneering was freely practised, and the Italians were masters of this craft, using tortoiseshell, ivory, and ebony, and inlaying with pearls and precious stones. To appreciate the magnificence of Italian art a visit must be paid to Florence, the City of Flowers, and there in the museums and palaces, especially the Bargello, some beautiful examples of early Italian furniture are to be found illustrating the high standard of the " veneers."

Veneering is the only way to use the rose-woods, such as the " curls " in satin-wood and mahogany, " burrs " in walnut or amboyna, and cross-grained and " freaky " wood, which would be practically impossible to use in the ordinary way.

The old moulding and carving are now superseded by this method of flat decoration, which is really more effective and artistic, as the natural grain and colouring of woods is used to decorate the article.

It is essential that the veneer be laid upon a hard-wood, such as plain Honduras mahogany, as this warps and shrinks far less than any other wood. Soft and porous woods are quite useless, as the glue is absorbed and the veneer will curl. Workers recommend that in the case of light-coloured woods, such as maple, holly, etc., the glue should be whitened in order not to stain the fine clear wood.

Wells & Hooper (*Modern Cabinet Work, Furniture, and Fitments*) gives the following account of veneering, or rather the most important part of it, " Laying "—

LAYING. Two methods are used ; one with a " hammer " for knife-cut veneers, and the other with " cauls " under pressure for the thicker or " saw-cut " sheets. The hammer is usually home-made, of beech or ash, with a blade of $\frac{1}{16}$ in. steel let into the head, and pinned through. The edge of the blade should be rounded to prevent cutting. Other tools for hammer veneering are a hot iron and a " swab " or sponge. When everything is quite ready—glue, clean, hot and fairly thin—cover the ground quickly with a large brush, and see that it is free from any specks of grit ; then carefully lay the veneer on, flattening it with the hand, damp it with hot water, and press the flat-iron over rapidly without much pressure. Hold the hammer in the right hand, with the left pressing on the head, and starting in the centre, work it backwards and forwards with a zigzag motion towards the outside edges, going over the whole surface quickly, and repeating the strokes from the centre until the air and surplus glue are forced out. To test the laying, tap the

veneer with the fingers or hammer handle ; a hollow sound will soon show any blisters or air spaces, and if these occur, damp again and use the hot iron sparingly ; as lumps may appear where the glue has clogged, which the hot iron and hammer should disperse. Wipe off, and stand on one side to dry, where the air can get round both sides, and hand-screw or clamp across to keep flat whilst drying. Blisters are sometimes found when the veneer is dry, and to get them down properly it will be necessary to prick or slit them to let the air out, then warm them with the iron and flatten with hammer.

Glue in Bookbinding. Bookbinding is real art and not just a method of preserving the pages from the effects of wear and tear.

Some of the finest bookbindings in existence are Persian, executed in the late eighteenth or early nineteenth century. It may be said that illumination in Persia reached its epoch during the Timurid dynasty. It was during the subsequent dynasties that lacquer-painting on leather and papier mâché came into vogue. F. R. Martin, in his masterly work on Persian miniatures, describes one of the results of the decadence referred to above—

. . . it was during this period of decadence that lacquer-painting received a new impetus . . . very charming works being made of this material, particularly at the commencement of the Safanid rule—book-bindings and qalamdan (boxes for pens and inks and ink pots), small cupboards decorated with hunting scenes, etc.

At the present time there is a tendency for Western art to follow along the lines of Oriental art, and there is no doubt that the Far East has much to teach us. The Chinese, during the thirteenth and fourteenth century, were, indeed, masters of the technique of this beautiful craft.

Glue for bookbinding should be of very good quality, especially when expensive leathers are to be used. Good clear colour, high tensile strength, and freedom from odour are eminently desirable characteristics.

Rideal mentions that—

" Some inferior glues which have been chemically bleached turn almost black in the pot, owing to the bleaching agent not having been properly removed or neutralized."

Sometimes antiseptics are added to the glue in order to keep away the moths and other parasites which cause such fearful damage. The best of the many chemicals available is mercuric chloride and iodide mixed together in the proportion of 3 per cent of the chloride to 1 of the iodide.

Sometimes glue is mixed with paste, as in the case of roan, Morocco, and Russia leather, etc. Cloth is always covered with glue, and the same applies to suede, although the turning-in is usually done with the best quality paste.

Zaehnsdorf (*Art of Bookbinding*, page 93) recommends that "paste should always be used for Morocco, calf, Russia, and vellum, all leathers with an artificial grain should be glued." Generally an inferior glue, cold glue, is used for fastening the leaves together.

Rideal gives the following recipes for bookbinder's size (*Glue and Glue Testing*, page 73)—

No. 1. Water, 1 qt.; powdered alum, ½ oz.; Russian isinglass, 1 oz.; curd soap, 20 grains. Simmer 1 hr., strain through linen or a fine sieve, and use while warm.

No. 2. Water, 1 gal.; best glue, ½ lb.; alum, 2 oz. Prepare and use as above.

No. 3. Water, 1 qt.; isinglass, 2½ oz.; alum, 120 grains.

General Uses of Glue. Large quantities of glue are used in the manufacture of printing rollers and hectograph plates.

Rideal gives the following recipes for printing rollers—

	I	II	III	IV	V	VI	VII	VIII
Glue	8	10	4	2	32	2	1	3
Treacle	12	—	8	1	12	6	2	8
Paris white	1	—	—	—	—	—	—	1
Sugar	—	10	—	—	—	—	—	—
Glycerine	—	12	—	—	56	—	—	—
Isinglass	—	1½ oz.	—	—	—	—	—	—
India-rubber in naphtha	—	—	—	—	10	—	—	—

Formaldehyde is frequently added to prolong the life of the roller, as it renders the gelatine insoluble in water.

F. Steinitzer (*Kunststoffe*, 4 (1914), 161) gives the following details concerning the composition of hectograph plates—

Glue or gelatine	15	10·0	25	10
Glycerine, 30° Bé	60	50·0	90	50
Kaolin, kieselguhr, etc.	—	2·5	10	10
Sugar	—	—	10	—

Bogue mentions that a small amount of some hardening agent, such as bichromate, alum, or formaldehyde is usually added.

Other uses for glue are in the manufacture of wallpaper, the sizing of textiles, and in the preparation of various artificial products, such as imitation leather, ivory and mother-of-pearl.

In the first instance the glue is used as a binder for the clay and other materials with which the papers are grounded. Glues to be incorporated with paper should be free from grease, of a good clear colour, and form no foam. Viscosity is very important, as it determines the covering property of the glue. Bogue writes—

> In the selection of glues that will be satisfactory for use upon wall-papers, the greatest diversity of possibilities which may make a given glue excellent or worthless for the purpose present themselves. In fact, for no other service for which glue is employed is the exact nature of the materials, both of the colour bases and the glue itself, so necessary to take into careful consideration.

The usual method of making sized paper entails a final coating of glue, instead of adding it to the beater, together with the pulp and pigments, etc.

Good-quality hide glues are used in the finishing of certain textiles. Thus, cotton goods are generally treated with a dilute solution of glue or gelatine in order to stiffen them. While carpets, curtains, etc., are heavily loaded with glue. In all these cases the glue used is derived from hide offal, and of a lower grade than that employed in sizing paper. The glue must be neutral, as the presence of acids or alkalis will affect the colours, and the inorganic ash should be low, as large amounts of neutral salts will affect the dyes.

CHAPTER IX

THE USES OF GELATINE IN THE MANUFACTURE OF FOODS

In cookery, pharmacy, bacteriology, chemical analysis; and the use of isinglass in brewing, and gelatine in the leather industry

It is surprising how many applications gelatine has in the foodstuff industries, and in pharmacy and medicine.

The most important uses of gelatine are in dietetics, when it is utilized to replace meat proteins; to add to the density of jams, jellies, and preserves; to assist in the setting and solidification of ice-cream, and to act as a protective colloid and emulsifying agent in milk, confectionery flavours, mayonnaise dressings, etc.

Meat extracts contain from 0·25 to 5·50 per cent gelatine. Rideal found in three well-known "Invalid Jellies" the following amounts of gelatine: 5·15 per cent; 5·48 per cent; 4·11 per cent.

Most prepared or desiccated soups contain appreciable quantities of gelatine, while the well-known "Jus-vis Tablets" are composed of meat, gelatine, and a mixture of vegetables.

Really good meat extracts are used to a very large extent in hospitals and other institutions. The chief value of these preparations lies in the fact that the nourishment obtained by their assimilation is greatly above the proportion of exertion required from the digestive organs. They are not infrequently given before operations, especially abdominal, the *raison d'être* being easy absorption and maintenance of the vital processes while leaving little waste.

It should be remembered that although gelatine can be used to replace certain "fixed" proportions of meat proteins in commercial meat extracts, it cannot be regarded as a true food, i.e. complete protein food.

J. Murlin (*Amer. Jour. Physiol.*, 20, 1907, 234) found that protein nitrogen might be replaced by gelatine up to half of the starvation requirement, while as much as two-thirds might be replaced, provided carbohydrates are present in sufficient amounts as to provide three-fifths of the calorific requirements. The reason why gelatine cannot be regarded as equivalent to

meat proteins, is because it is deficient in three amino acids : tyrosine, cystine, and tryptophane. Although gelatine cannot be regarded as a true food, it should not be supposed that its inclusion in food products is to be condemned. It is a useful *nitrogenous* food, and is easily digested.

Gelatine finds a ready use as a thickener in jellies, jams, fruit preserves, etc. The following analysis shows the relative amounts of gelatine in two samples of cherry jelly—

	Total Solids	Ash	Acids	Protein	Reducing Sugar
Cherry jelly (*a*)	61·60	60·0	—	1·100	59·80
„ „ (*b*)	79·00	70·0	—	1·200	77·20

(Atwater and Bryant, Bulletin 28, U.S. Department of Agriculture.)

" Protein may be said to be representative of gelatine present."

The presence of a small quantity of dextrin, tragacanth, gelatine, or the pectin bodies of the fruit juices, is necessary in order to give the jam or preserve a certain body. In many instances, however, gelatine is added to conceal the inferior qualities of the fruit used during the manufacture. Chocolate and cocoa are sometimes treated with gelatine, in order to give these substances the required density. It is interesting to note that the presence of any thickening substance in cream, such as sucrate of lime, gelatine, and starch paste is forbidden under the Public Health (Preservatives in Food) Regulations.

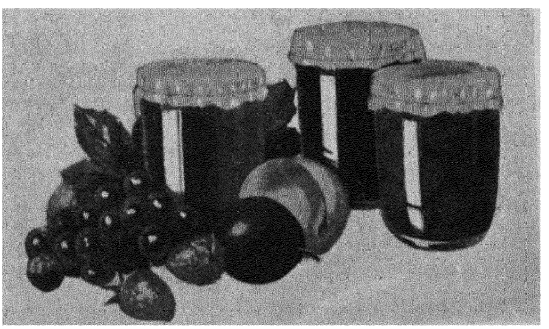

Fig. 21. Most Jams Contain Small Quantities of Gelatine or Isinglass to give them Body

A small quantity of gelatine is sometimes used in the preparation of children's patent foods.* Hutchison, in his *Composition of Patent Foods*, gives the constitution of a large number of

* The author is indebted to the Editor of *Food Manufacture* for permission to reproduce the above notes on gelatine in foodstuffs.

products, in which the protein matter (mostly vegetable) varies considerably—fluctuating in some cases from 4 to 14 per cent.

In the manufacture of sweets, such as gums, Turkish delight, etc., gelatine is employed to give the requisite body or stiffness.

The Uses of Gelatine in Cookery. The best French and English leaf gelatine is used to a comparatively large extent in the preparation of jellies, jams, and special fancy dishes.

Gelatine sold for this purpose must be free from all traces of sulphites, and conform to the high standards regarding mineral ash as specified in the British Pharmacopoeia and Pharmaceutical Codex. The presence of fibre, bubbles of air, and cracks is not so important, and may be more or less disregarded, but the sheets should be water-white and uniform in size and thickness.

By the kind permission of Mrs. D. D. Cottington Taylor, Director of Good Housekeeping Institute, the author is priviledged to quote some useful recipes published in *Good Housekeeping*, August Number, 1928, under the heading of " Gelatine in Summer Dishes."

STRAWBERRY JELLY

1½ tablespoonfuls strawberry jam
1 tablespoonful cold water
½ pt. milk
½ pt. boiling water
1 oz. gelatine
3 tablespoonfuls lemon juice

Directions are as follows—

Soak the gelatine in the cold water. Add the boiling water to the jam, strain, and add the milk and gelatine. Allow to cool until it begins to thicken, then add the lemon juice. Whip to a fresh consistency, and mould.

Another recipe for " Simplified Charlotte Russe " necessitates the use of gelatine—

1 packet raspberry jelly
Boiling water
1 teaspoonful gelatine
3 tablespoonfuls milk
½ pt. cream
4 cherries
5 Savoy fingers

Directions are as follows—

Half fill glasses with jelly. Dissolve gelatine in the milk by standing in hot water. Whip up the cream, and fold in the dissolved gelatine.

Place the whipped cream in spoonfuls on the jelly. Cut the Savoy fingers in half, place around cream. Decorate with cherries.

A recipe for jellied vegetables is quite original—

½ oz. gelatine
4 tablespoonfuls cold water
½ pt. boiling water
½ oz. sugar
3 tablespoonfuls vinegar
1 tablespoonful lemon juice
1 tablespoonful salt
1 gill carrots (cut into dice)
1 gill peas
1 gill cucumber (cut into dice)
1 spring onion (cut in very thin slices)

Soak the gelatine in the cold water, dissolve the sugar and salt in the boiling water. Cool, and add vinegar and lemon juice. When it begins to stiffen, add vegetables and place in mould. When cold, turn out and serve on lettuce leaves.

Gelatine is used in the preparation of soups and meat teas. In the preparation of pork pies, brawn, and similar foods a considerable proportion of good leaf gelatine is employed in order to help the meats to set in a firm jelly.

FIG. 22. AMERICAN ICE-CREAM SUNDAE

The majority of ice-cream dishes contain small percentages of gelatine to give the cream a solid consistency

Gelatine is extensively used, both in this country and America, in the manufacture of ice-cream. Bogue states that upwards of 250,000,000 gal. of ice-cream are consumed annually in U.S.A., and that 1 lb. of gelatine is used with every 500 gal. ice-cream, so that 5,000,000 lb. find their way into this delicacy every year.

There are many advantages and disadvantages attached to the use of gelatine in ice-cream. Dealing with the former, it may be said that gelatine can produce a jelly at very low temperatures, and also prevent the sugars from crystallizing out. Another important advantage in using gelatine in ice-cream is that it acts, like all emulsoids, as an emulsifying agent in preventing the milk fat emulsion from separating into its

constituents. When 0·25 per cent gelatine is used in the cream, appearance and keeping qualities are enhanced materially. Thus, it has a firmness and evenness of texture which render it of great use in sundaes and other preparations.

This ice-cream can keep in excellent condition at a higher temperature than the ordinary variety, the maximum being 26° F. for the gelatine-containing cream, and about 22° F. for cream without gelatine. If a larger quantity than 0·25 per cent is used, then the flavour is destroyed owing to the absorbing property of the gelatine. Ice-cream blocks contain gelatine in appreciable quantities.

One of the chief objections to the use of gelatine in ice-cream is that it masks the age and inferior quality. Thus, a cream could be sold as fresh, which had perhaps been made a week.

Emulsion flavours, salad dressings, etc., all contain gelatine as an essential ingredient. The action of the gelatine in these instances is to act as an emulsifying agent. An emulsion may be said to consist of one liquid dispersed in another. Of course, violent shaking will often produce an emulsion, for example, oil and water, but on standing, the two separate out. In order to stabilize this emulsion a third substance is added, generally gum or gelatine. The theory of emulsions occupies a most important niche in physical chemistry, and our present knowledge is due in a degree to the researches of Pickering, Bancroft, Fischer and Hatschek, to mention just a few prominent workers.

Very briefly, the mechanism of emulsification may be explained. According to Pickering and Bancroft, the essential factor in emulsification is the formation of a solid film around individual droplets, which prevents them from coalescing and the emulsion from breaking down. Particles of the emulsifier differ appreciably in size, but it may be taken that the smaller the size of these particles the more stable the emulsion.

Fischer's apposition theory affirms that in the case of a gelatine and oil emulsion the gelatine is a hydrophilic colloid, which with water forms a colloid hydrate. It is in this medium that the oil is dispersed, and not in water.

Although the two theories enunciated above appear to have little in common, they are stated to be reconcilable, and it appears extremely probable that the true explanation of emulsion formation will embrace both the interfacial film

theory of Bancroft and Pickering and the hydration theory of Fischer.

Owing to the fact that gelatine is an ideal protective colloid, it is made use of in medicine for preventing the coagulation of milk during digestion. When used in conjunction with lact-albumin, it greatly assists the digestive organs of infants and invalids. A. Jacobi advocated the addition of gelatine to cow's milk for infant feeding as early as 1889. C. Herter, in *Infantilism from Chronic Intestinal Infection*, observes that gelatine is of great assistance in severe cases of malnutrition. In these cases the gelatine prevents the milk fat from coalescing, and thus helps digestion.

Miss K. Pearson has found that in the majority of cases of malnutrition in children, fat cannot be assimilated, and in these instances the curds are separated from the milk by means of rennet and then sieved through into water—the curd and water mixture being used in place of milk.

A gelatine containing extract, made entirely from bones, is sometimes used in treating certain cases of rickets in children. A similar preparation composed of extracted ossein from bones, together with small amounts of inorganic substances, is used in the treatment of dogs suffering from rickets.

General medical uses of gelatine are as follows: injected hypodermically, 1 to 2 per cent in normal saline solution (sterilized), it is sometimes used to facilitate the formation of clot in aneurisms, also to assist haemorrhage from the lungs and kidneys. Five per cent solutions of gelatine (in sterilized saline) have been used by rectal injection for purpura and haemoptysis. It should be noted that the gelatine used in medicine must be absolutely pure, containing no traces of pathogenic bacteria. Cases have been known where the patient, after a rectal injection, has contracted tetanus—on examination, the gelatine has generally been found contaminated with the bacilli. In view of this, it is always advisable to sterilize the gelatine by heating to 90° C., or thereabouts, for a few minutes, repeating this procedure two or three times. "Vigorous boiling" is apt to hydrolyse the jelly and thus cause deterioration.

The Uses of Gelatine in Pharmacy. Generally speaking, the ordinary commercial edible gelatine on the market is of no use for pharmaceutical purposes, a "super-product" being essential for this work.

The large firms specializing in the manufacture of capsules, pastilles, suppositories, etc., generally buy gelatine on the results of detailed analysis as carried out by their chemists. First of all the buyers, sent out by the pharmaceutical manufacturers, examine the market for good stock, and then send samples of high-class gelatine to their employers for examination and approval.

Gelatine for suppositories must contain no string fibres. Where it is the practice to dry the gelatine on fibre netting instead of zinc, there is a great liability of stray wisps of string adhering to the surface of the gel.

A gelatine containing a trace of sulphites, but devoid of fibre, would perhaps be quite suitable for suppositories, whereas the presence of a little fibre would not matter, if the gelatine were to be used in the manufacture of pastilles ; sulphites, however, would be distinctly objectionable. Air bubbles in gelatine are regarded with great disfavour. It is found that they affect the tensile strength to a very great degree, and in the moulding of capsules, etc., the gelatine, or rather glyco-gelatine, is apt to tear if air bubbles are present. Samples containing air bubbles are disregarded on inspection. For household use, leaf gelatine containing air bubbles would be quite suitable, providing, of course, that sulphites were absent and heavy metals below the approved standard.

As already indicated, tensile strength is always tested by the pharmacist. It is of vital importance that the glyco-gelatine should be able to withstand the tearing action of moulding. Each manufacturer has his own particular tensile strength-testing apparatus, and works according to the best conditions of his plant. Thus, after considerable experience, a workable figure is found, and this is rigidly adhered to ; gelatine, with a strength below this standard is rejected.

The mineral ash for gelatine used in pharmacy is 2 per cent maximum. Constituents of the ash which are particularly objectionable are the heavy metals, the most important being copper and arsenic. About two parts per million of these metals is the standard generally accepted. Sulphites are, of course, supposed to be absent from edible gelatine, according to recent Health legislation, and although a trace is allowed in some cases, the presence of these chemicals denotes an inferior product.

The following tests are employed by the manufacturer before purchasing gelatine—

1. General inspection. Particular importance paid to colour, air bubbles, cracks. Tensile strength.
2. Determination of mineral ash. (*a*) Estimation of copper and arsenic.
3. Sulphur dioxide estimation.
4. Acidity or alkalinity.
5. General qualitative tests sometimes applied first.

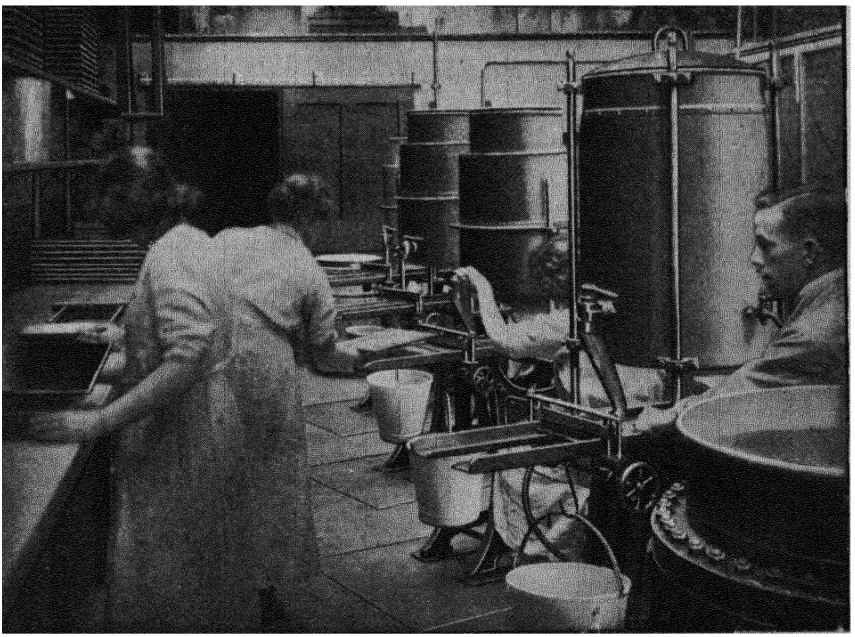

FIG. 23. PHOTOGRAPH SHOWING A STAGE IN THE PREPARATION OF GELATINE CAPSULES (*b*)

The following is inserted by courtesy of Boots Pure Drug Co., Ltd.—

Photographs showing stages in the preparation of gelatine capsules—

(*b*) Tin-lined copper water-jacketed containers for the gelatine emulsions. Specially prepared steel plates are placed in the grooves illustrated, and the gelatine flows on to them through an adjustable gauge. The plates pass under in regular rotation, and the surplus gelatine is kept back. The coated plates are dried in the drying oven seen at the end of the photograph.

(*c*) The moulds are in two parts, and may cost as much as £100. A

film of clear gelatine is laid upon one half, the correct amount of medicament (e.g. castor oil) passed in, and another gelatine film put on top. The other half of the mould is put in place, and the whole compressed in the hydraulic press for a few seconds.

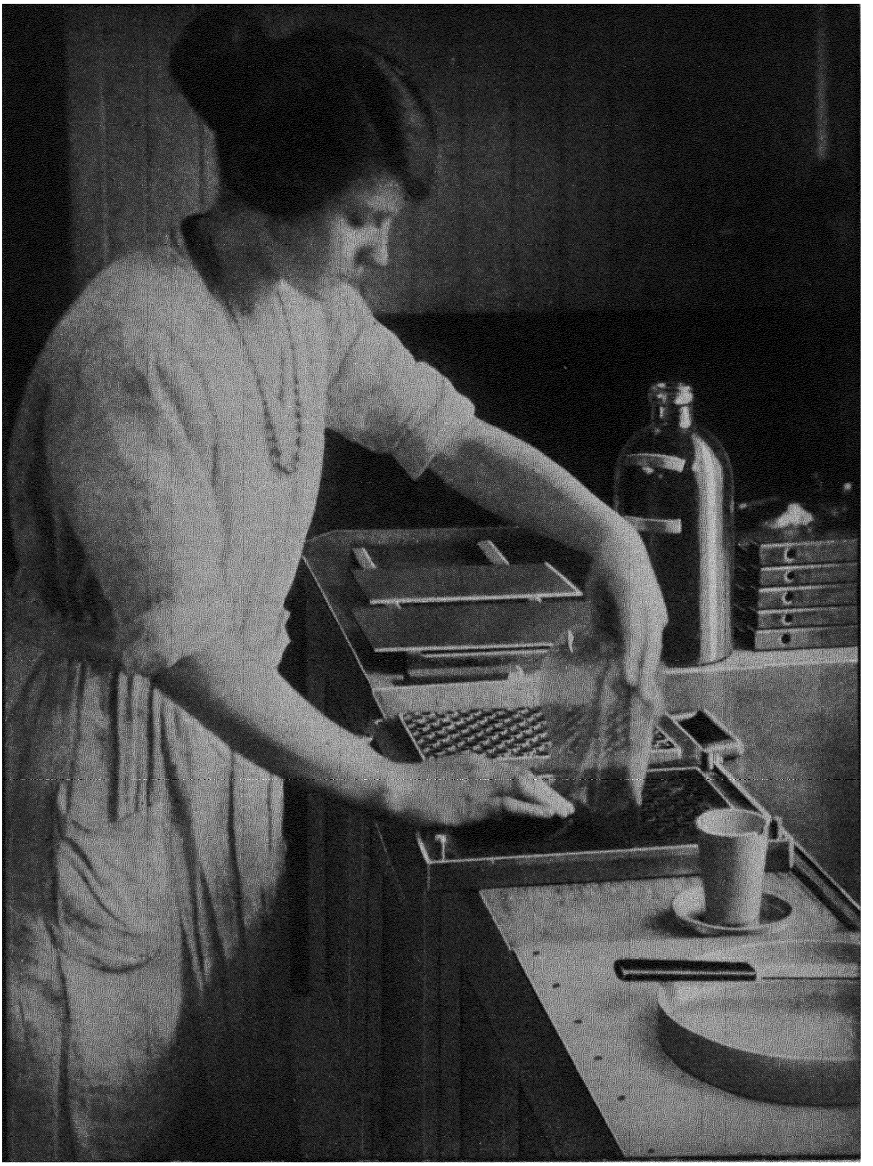

FIG. 24. PHOTOGRAPH SHOWING A STAGE IN THE PREPARATION OF GELATINE CAPSULES (*c*)

(*d*) Hydraulic compressor, 3,360 lb. per sq. in.

(*e*) The mould is then opened, and this photograph shows the perforated gelatine sheet with the capsules removed.

Note. It is remarkable that during the operation no oil is lost and perfect sealing obtained. The gelatine envelope is, of course, very hygroscopic, and on this account is easily broken down by the gastric juices, and as the medicament is liquid it is quickly assimilated.

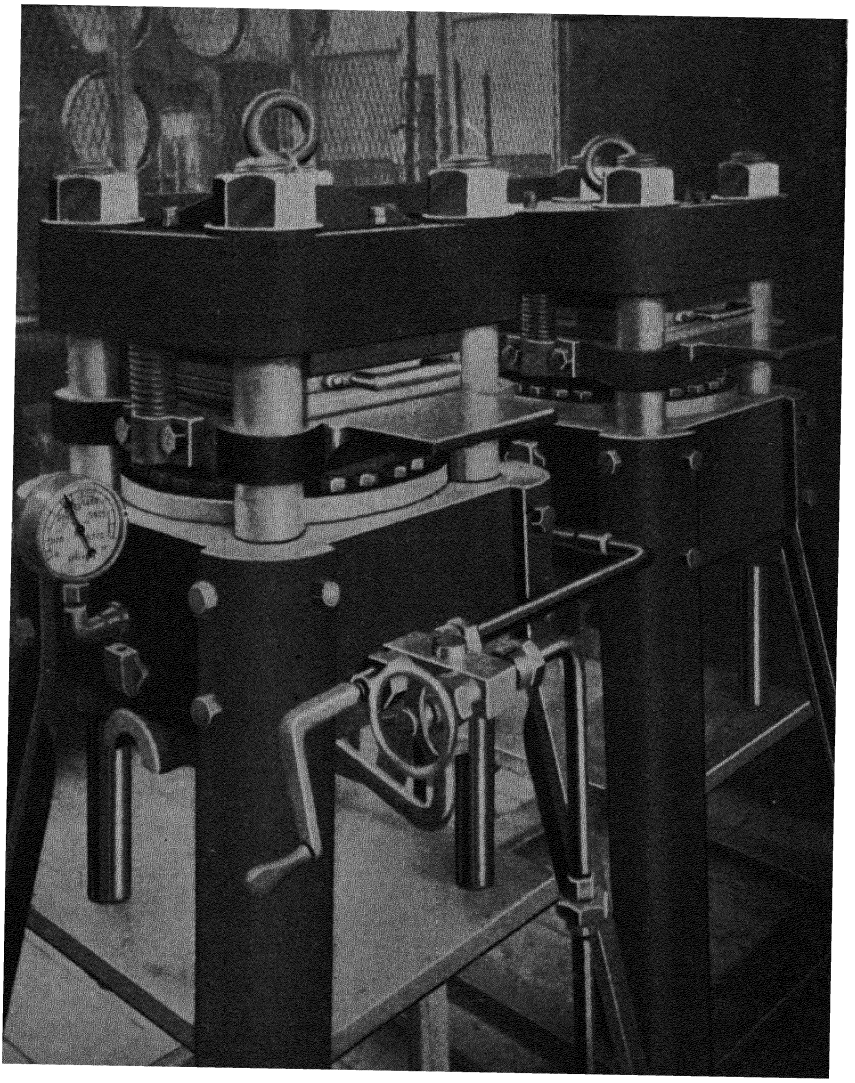

FIG. 25. PHOTOGRAPH SHOWING A STAGE IN THE PREPARATION OF GELATINE CAPSULES (*d*)

FIG. 26. PHOTOGRAPH SHOWING A STAGE IN THE PREPARATION OF GELATINE CAPSULES (*c*)

Regarding acidity or alkalinity, the P_H of the gelatine is usually determined. Acid gelatines are objectionable for lamellae, where small quantities of foreign impurities may pass into the medicament, which in the case of such substances as adrenalin and other alkaloids used in apthalmina, must be of unquestionable purity.

Dealing with the detailed application of gelatine in pharmacy, the first product, containing quite appreciable quantities, to be mentioned, is the ordinary glycerine throat pastille.

The British Pharmaceutical Codex gives the following formula for Glycogelatinum—

GLYCOGELATINUM

Gelatine	12·00
Glycerine	40·00
Distilled water	20·00
Orange-flower water	20·00
Sugar	5·00
Citric acid	2·00
Oil of lemon	0·10
Solution of Carmine	1·00

Soak the gelatine in the distilled water until quite soft, add the glycerine, heat gently on a water bath until the gelatine is dissolved, and add the orange-flower water, in which the sugar and citric acid have previously been dissolved; then add the oil of lemon and solution of carmine, mix thoroughly, strain through muslin, and allow to solidify. The product should weigh about 100.

Glycogelatinum is used as a basis for throat pastilles, the medicament being dissolved or suspended in the melted glycogelatine, the mixture poured into trays to solidify, and cut up into the required number of pastilles; or the melted mass may be poured into suitable pastille moulds.

Pessaries and urethral bougies also contain proportions of gelatine.

GLYCERINE JELLY

I		II		III	
		Soft		Hard	
Gelatine	35 grm.	Gelatine	15 grm.	Gelatine	25 grm.
Glycerine	450 ,,	Water	30 ,,	Water	25 ,,
Water	500 ,,	Glycerine	55 ,,	Glycerine	50 ,,
Salicylic acid	3 ,,				

Soak the gelatine ½ hr. in water, add glycerine, and heat until dissolved.

W. A. Poucher (*Perfumes, Cosmetics, and Soaps*, 1926, Vol. II, page 350)—

Gelatine must be water-white and odourless. 2 per cent in warm water gives a jelly when cold, so that the consistency of any product can be based on the percentage used in comparison with this figure.

Gelatine	30 grm.
Glycerine	170 c.c.
Orange-flower water-triple	800 ,,

Place the gelatine in 500 c.c. water and stand overnight. Then warm till dissolved. Add glycerine and rest of water.

As gelatine, even the purest Gold Leaf, contains quantities of objectionable soluble salts, it is sometimes the practice to purify it if an extra pure product is desired, a water-white product being obtained. The best method is to soak the sheets in successive changes of distilled water for several days. The gelatine is then dissolved in hot water and filtered into absolute alcohol. The white mass is then re-dissolved in hot water, re-precipitated, and finally dried—the subsequent gelatine will contain as low as ·4 per cent to ·7 per cent ash.

F. Winter (*Handbuch der Gesamten Parfumerie und Kosmetik*, 1927, page 326) gives the following recipe—

ZINC JELLY

Gelatine	15 grm.
Water	45 ,,
Glycerine	25 ,,

Add to this a mixture of

ZnO	10 grm.
Glycerine	15 ,,

and make up to 100 grm. with distilled water.

Pastes of gelatine with glycerine are made up containing zinc oxide, resorcin, and other medicaments for application to the skin in the case of skin diseases. A well-known paste of this kind is Ichthamol Paste.

ICHTHAMOL PASTE

Ammonium ichthosulphonate	10·00
Gelatine	10·00
Glycerine by weight	60·00
Distilled water	25·00

Gelatine dissolved in water, glycerine added, then the ammonium ichthosulphonate.

Other gelatine ointments are given by Winter, thus—

Zinc jelly . . .	30 grm.
Rub in—	
Lanolin	48 grm.
Zinc Oxide . . .	20 ,,
Glycerine . . .	20 ,,
Water	50 ,,

Incorporate medicaments by adding them first to the lanolin. Apply by melting and painting with a brush on to the skin, and then sprinkle lycopodium on to it. This gives a lasting, non-sticky film on the place of application.

Gelatine is used for pill coating, thus the following recipe is typical (*Pharmaceutical Formulas*, 1899, page 587)—

Gelatine	2½ oz.
Gum acacia mucilage	1½ ,,
Boric acid	2 drm.
Water	7½ oz.

Other important applications of gelatine in pharmacy are in the preparation of formo-gelatine, an antiseptic product employed as a surgical dressing, also the manufacture of court plasters.

"Lamellae" are discs of gelatine with some glycerine, weighing $\frac{1}{50}$ to $\frac{1}{30}$ gr., and containing a minute dose of some powerful alkaloid. They are dissolved in water for ophthalmic and hypodermic use; four kinds are specified in *The British Pharmacopoeia*.

The gelatine basis from which the pharmaceutical discs are made is prepared as follows—

Gelatine	10·50
Glycerine	1·25
Distilled water . . .	82·25

The Pharmaceutical Codex gives the following formulae for important varieties of lamellae—

ATROPINE DISCS

(¼ grain)

Atropine sulphate, 13 mg.
Sufficient quantity of distilled water
Gelatine basis, 75 dg. (grains 115)

The above preparations are used in ophthalmia to dilate the pupil.

COCAINE DISCS

Cocaine hydrochloride, 13 dg. (20 grains)
Distilled water, a sufficient quantity
Gelatine basis, 5 grm. (77 grains)

Gelatine is sometimes used in cosmetic preparations. It forms a transparent, jelly-like mass which melts on the skin, and is used for chaps and sunburn. Glycerine, the principal constituent of these mixtures, is the healing agent. Manufacturers are finding that gum is more suitable than gelatine, as it tends to ooze moisture, i.e. in a collapsible tube, a drop of liquid often appears at the nozzle when the tube is squeezed.

The following two recipes may be of general interest to pharmacists—

GELATINE CAPPING

Gelatine, 33 lb.
Soak for 1 hr., then dissolve by heat in 5 gal. of water.
Add glycerine, 5 lb.

Stir in a sufficient quantity of colouring matter, such as burnt sienna or vegetable black, until the mass nearly sets. In use, warm till melted and dip bottle previously corked, into the mixture.

WATERPROOF PAPER

Gelatine . . .	10 grm.
Water	40 ,,
Glycerine . . .	10 ,,

Paint on both sides of paper (hot), cool, and then cover with

Formalin . . .	750 grm.
Water	5000 ,,

The Use of Isinglass in Brewing. Isinglass is now used fairly extensively in the brewing industry in the form of what is technically known as " finings."

Finings may briefly be said to consist of solutions of isinglass in tartaric or sulphurous acid, and are used to clarify beers. Their action is quite mechanical, and depends upon the well-known coagulating property of isinglass—precipitating the suspended particles and brightening the product to a very appreciable degree. The use of finings is sometimes deplored by writers, but providing the minimum amount is employed they cannot be regarded as objectionable adulterants. Generally speaking, a quart, irrespective of strength or gelatine content, is the amount used per barrel. The volume of beer displaced by the " finings " may be looked upon as a definite saving.

Only the very best quality gelatine is used in the preparation of " finings," preferably " Penang." Other well-known varieties are " Leaf Glass " and " Pipe Glass." The former is a

thin transparent variety, whilst the latter is about three times as thick.

Tartaric, sulphurous, acetic and lactic acids are all used to dissolve the isinglass. J. Ross Mackenzie, in his manual *Brewing and Malting*, writes—

The first-mentioned acids—tartaric and sulphurous—have each of them their defects as " cutting agents." The former, though yielding an effective finings, encourages the development of mildew ; the latter, though protective against mildew, produces a much less effective finings. Isinglass " cut " with tartaric, to which a proportion of sulphurous acid is afterwards added, yields finings, the power of which is not much lessened, while its resistance to mildew is sufficient for all practical purposes.

Messrs. Matthew & Lot, in a most interesting paper read before The Institute of Brewing, state that the best kind of acid is sulphurous ; they also mention that lactic is superior to acetic. They found, as the result of some considerable research, that beyond a certain concentration (·7 to 1·0 per cent H_2SO_3) the effective cutting increases in inverse ratio to the strength of the acid. Thus, undiluted commercial acid (7·4 per cent H_2SO_3) cut very slowly, and gave a very thin solution. Messrs. Matthew and Lot state that at the commencement of the reaction (cutting) 1 per cent acidity (1 gal. of commercial acid per barrel), and at the close ·2 per cent, is a good and workable strength. Recipe given—

One gallon of commercial sulphurous acid (7·4% H_2SO_3) diluted with 6 gal. of water at first, and made up eventually to 36 gal. The amount of isinglass utilized by the brewer varies according to the quality, but the writers of the paper recommended 2¾ of best Russian or 3½ of inferior kind.

J. Ross Mackenzie gives the following recipe for a finings solution—

To 7 lb. of good isinglass, covered with water, add 1 lb. of tartaric acid, dissolved in warm water, and 1 gal. to 1½ gal. of H_2SO_3, the latter added in small portions at intervals. Add fresh water as the isinglass swells. Rub through coarse and fine sieves, with intervals between each rubbing. Make up to 72 gal.

The cutting of isinglass is a very difficult and lengthy operation, and takes anything from a month to six weeks or more. Usually, a series of large tubs, hogsheads, is employed. The isinglass, swollen, of course, to a very appreciable degree, is sieved through the coarsest sieve first, and the finer ones in

succession. Generally a mechanical action afforded by revolving brushes in the sieve, facilitates the passage through the interstices, and reduces the isinglass to a very fine state of suspension in the water.

Finings are usually added to the beer before dispatch to the publican, etc.—the "brightening" takes only a relatively short time for completion.

F. Prollius (*Dingler's Polyt. J.*, CCXLIX, page 425) gives the following table of foreign samples of isinglass. (For the viscosity, one part of the specimen was dissolved in twenty parts of water)—

	Water	Ash	Insoluble Matter	Time Required for Solution to Run Out
	Per Cent	Per Cent	Per Cent	Seconds
Astrakhan, from Schmidt and Dihlmann, Stuttgart	16·0	0·20	2·8	507
Astrakhan from a collection	18·0	0·37	0·7	485
Astrakhan, fine irridescent, Russian quality, Tubingen collection	17·0	1·20	1·0	500
Astrakhan, Russian, from Gehe of Dresden	19·0	0·80	3·0	491
Astrakhan, in laminal from Gehe	19·0	0·50	0·4	480
Astrakhan, in threads, known as Hamburg threads	17·0	0·40	1·3	477
Hamburg isinglass	19·0	1·30	2·3	470
Another quality	19·0	0·13	5·2	—
Rolled Northern, fish bladder	1·5	3 20	10 8	467
Icelandish bladder	17·0	0·60	21·6	463
Indian isinglass	18·0	0·78	8·6	437
Yellow, quality unknown	17·0	2·30	15·6	360

Rideal, in his *Glue and Gelatine Testing*, mentions some substitutes for isinglass. thus—

> Isinglassine made from calves' feet and other sources, and reduced by machinery to a pliable homogeneous mass, rolled out into sheets, dried, pressed, and shredded; each round is cut into about 125,000 shreds or staples.

Other substitutes are Irish Moss and Chinese Moss, both of which are of vegetable origin, and do not concern us at the moment.

The hydrogen-ion concentration of the beer affects the "fining" to an appreciable degree. It is suggested that a P_H somewhere near the isoelectric point of isinglass is the best figure—beer of too great an acidity refuses to take finings.

The Uses of Gelatine in Bacteriology. The finest leaf gelatine is used in bacteriology for the preparation of nutrient gelatine media.

In this case, the gelatine must be perfectly free from all micro-organisms; this is most essential. The presence of foreign bacteria in the gelatine will complicate the whole process of growth of the particular organisms under observation. Unreliable data may be obtained in this manner.

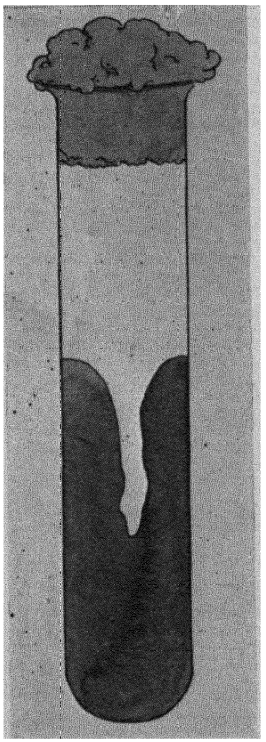

FIG. 27.
A STAB CULTURE
The liquefying property of certain micro-organisms is well illustrated by the above

Air bubbles and the presence of string fibre can be more or less overlooked, whilst sulphites and phenolic additives, etc., are extremely detrimental to free growth of organisms.

Where gelatine is used for plating out, then the presence of antiseptic bodies has a tendency to cause the colonies to become huddled together, instead of spreading out over the entire surface.

Colour is also important. The formation of colour pigments is one of the chief indications that a certain type of organism is present. If the colour is masked by the prevalent dark hue of the gelatine, then the test cannot be carried out with any degree of accuracy.

Some manufacturers add sugar and glycerine to their gelatine products, in order to increase tensile strength, etc. The presence of these substances in gelatine to be used for bacteriological research, may quite possibly result in fermentation's taking place during growth, and as a consequence—incorrect diagnosis.

From the above notes it should be evident that the gelatine used in bacteriology must necessarily be of the finest possible quality.

Gelatine favours the growth of a comparatively large number of organisms, but there are some types which have a decided liquefying effect, and so cannot be cultivated in this media. In order to ascertain the gelatine liquefying properties of an organism, it is usual to make what is commonly known as a "stab culture."

A test tube is half filled with sterile gelatine solution, and the

latter allowed to cool to form a firm jelly. The surface of the gelatine is then pierced by means of a platinum wire contaminated with the bacteria to be tested. Some organisms liquefy the gelatine in a few hours, while others take days or weeks.

To form a nutrient gelatine medium, Stitt (*Practical Bacteriology, Blood Work and Parasitology*) gives the following directions—

Place in a mortar 3 grm. Liebig's Extract, 10 grm. peptones, and 5 grm. NaCl. Dissolve the whites of one or two eggs in 1,000 c.c. of water. Then add this egg-white water, little by little, to the meat extract, peptone and salt in the mortar, until a brownish solution is obtained. Pour this into the inner compartment of the rice cooker and bring the temperature to 45° C. (This preliminary elevation of temperature is better carried out in some heated water in a pan, as the heating by means of the salt solution in the outer compartment of the rice cooker is difficult to control, so that a temperature approximating 70° C. might be obtained and the albumin of the white of egg coagulated. The temperature in the outer compartment might be approaching boiling before the contents of the inner would show 45° C.) Now take about 120 grm. of " Gold Label " or any other good-quality gelatine (12 per cent), and crush it down in the meat extract, egg and water solution in the inner compartment of the rice cooker.

The gelatine quickly goes into solution at 45° C. Gelatine, being quite acid, it will be found upon titration that the reaction is about + 4 per cent. $N/_1$ NaOH solution is added to bring the reaction to about + 1 per cent or 3 c.c. of $N/_1$ NaOH for each 100 c.c., provided the reaction was exactly at + 4 per cent. The procedure is the same as for bouillon. The colour reaction is not quite as distinct with gelatine as with bouillon.

Having neutralized and allowed to boil for 15 min., we filter through filter-paper in a hot funnel. As it is very important that gelatine should be perfectly clear, it is better to filter through filter-paper than through cotton. The filter-paper should be very thoroughly wetted with very hot water before filtering gelatine or agar. Tube the medium and sterilize, either in the Arnold on three successive days, or in the autoclave at 8–10 lb. pressure for about 10 min. The tubes should be cooled as quickly as possible in cold water after taking out of the sterilizer.

In the preparation of media for bacteriological work the following rules should govern choice of ingredients (Rep. Com. of Amer. Bact. to Com. of Amer. Pub. Health Assn. Meeting, Philadelphia, Sept., 1897)—

1. Distilled water in all cases.
2. Meat used should be fresh, lean beef.
3. The peptones should be Witte's Peptone, dry, made from meat.
4. Only C. P. NaCl should be used.
5. For rendering alkaline C. P. sodium hydrate should be used in $N/_1$ solution.
6. For acidification, C.P. HCl in $N/_1$ solution.

7. Glycerine, redistilled variety.
8. Agar-agar, finest grade of commercial thread agar.
9. Gelatine, the best commercial sheet gelatine washed as free as possible of acid and impurities.
10. Chemicals and carbohydrates should be as pure as possible.

North gives the following recipe for an "Agar Gelatine Medium"—

Lean chopped beef or veal . . .	500 grm.
Agar	10 ,,
Gelatine, Gold Label	20 ,,
Peptone, Witte's	20 ,,
Sodium chloride	5 ,,
Distilled water	1000 c.c.

The beef is extracted with about half a litre of water for 8 hr., and the solution then strained through muslin and combined with ingredients in the usual manner. The media is adjusted to $P_H 7$, or thereabouts, using the comporator or electrometric apparatus if available, otherwise phenolphthalein should be employed.

North states that the medium is excellent for streptococci, pneumococci, and diphtheria bacilli because it is soft and moist, and can be used at 37° C.

The Uses of Gelatine in Chemical Analysis. Gelatine finds some use in chemical analysis. An important application in applied research is in the examination of enzyme bates and similar preparations used in the leather industries.

As it is well known, enzyme bates depend for their main action on the common proteolytic enzymes.

Pickard (*Jour. Soc. Leath. Trades Chem.*, Sept., 1924) mentions the following methods for the measurement of proteolysis—

1. The casein substrate method. Based on the solubility of pure casein in alkali, and its precipitation method. After complete proteolysis, the casein is not precipitated.
2. The gelatine substrate method. Based upon the relative setting power of gelatine solutions before and after proteolysis.
3. The fibrin substrate method. Generally arranged colorimetrically by the liberation of a suitable dye from fibrin.
4. The Formol method (Sörensen). A titration method after proteolysis of a suitable protein. Amino acids are formed, which, after the addition of pure formaldehyde, are converted into methylene derivatives.

$$\begin{array}{l} R.CH:NH_2 \\ \quad\quad\quad + HCHO \\ COOH \end{array} \longrightarrow \begin{array}{l} R.CH.N:CH_2 \\ \quad\quad\quad\quad\quad + H_2O \\ COOH \end{array}$$

The late Mr. J. T. Wood, undoubtedly the greatest authority on the mechanism of enzyme bates, was in favour of the gelatine method of proteolysis, following the rules laid down by Fermi (Wood and Law, *Jour. Soc. Chem. Ind.*, 1912, page 1108).

In referring to the effect of enzymes on the substrate, Pickard writes—

The use of different substrates may lead to widely different results unless the relationship between enzyme and substrate is logically considered. Bill salts, for example, show no activation of trypsin when the latter is tested in a gelatine substrate, but if a fatty casein be used as a substrate, the trypsin is better able to hydrolyse the casein owing to the fat-removing action of the bill salts, and the consequent exposure of the real substrate (casein) to enzymic activity.

Northrop (*Jour. Gen. Physiol. Chem.*, 1919, page 216) finds " the rate of hydrolysis of gelatine and casein to be constant when the concentration of the latter reaches 3 per cent."

Bogue points out that Grete (*A. Grete, Ber.*, 21 (1888), 2762; 32 (1909), 3106) has used gelatine in the volumetric estimation of phosphorus as phosphate. In his own words he finds—

" An addition of gelatine, or similar substance as peptone, results in a precipitate of phosphomolybdate that is whitish and voluminous, such that a very small amount of phosphoric anhydride, e.g. 0·000125 grm., will reveal itself as a distinct cloud in the clear liquid. By a short warming, the gelatine separates from the phosphomolybdate and the precipitate assumes the usual yellow compact form and settles readily and quickly. Upon a further addition of a little molybdic acid solution, so long as any phosphoric acid remains, a voluminous gelatine—containing precipitate—will again come down. It is possible by this means, through continued additions of molybdic acid and subsequent heating and settling of the precipitate, to titrate to a sharp end point."

The Uses of Gelatine in the Leather Industry. Gelatine is much used in leather manufacture as a finish, although it is not so well suited for this purpose as others of the mucilages.

Flemming (*Practical Tanning*) gives the following recipe for a " Bright Blacking Varnish for Shoe Leathers "—

For use, dissolve 2 oz. of gelatine (isinglass) by boiling in 1 qt. of water. To this solution add 1 oz. of indigo blue and 2 qt. of cold water. Let the solution cool, and place it so as to be able to see that the mixture is not too thick, as the heat of the shop or summer weather has much to do with the amount of water the gelatine will absorb. The mixture should be like thin jelly. It is prepared by heating the gelatine a little and straining through cheese-cloth; then mix equal parts of alcohol, gum, and gelatine, and stir until the mixture gets thick. While stirring, add to each gallon of the mixture 1½ oz. of glycerine. When well set, the mixture is ready to be applied to the leather.

Two thin coats should be evenly spread on the grain with a sponge and well rubbed in with a fine sponge or with a soft hairbrush in a warm room.

Let the first coat get dried in before applying the second. After the last coat is absorbed, glaze the leather slightly by hand so as to produce the soft feel the stock had before the varnish was applied. If these instructions are carried out, the leather will have a pleasing finish.

High-grade gelatine is used in the finishing of hat leathers. It is important that the gelatine used for this purpose should be free from iron and other mineral impurities likely to discolour the band.

Lamb suggests that the following facts should be taken into account when considering the preparation of a gelatine mucilage—

The best form in which to apply either glue or gelatine is as a thin, soup-like mucilage. It is impossible to give quantities, as these depend entirely upon the solidifying power of the particular glue or gelatine that is being used. Very often a 1 per cent solution of gelatine of fair quality makes a much stronger mucilage than a 4 or 5 per cent solution of a common quality glue. That is to say, that 1 lb. of gelatine is in many cases equal to 4 or 5 lb. of glue, so that it therefore often pays to buy a good quality gelatine rather than a common quality glue.

A very common use for gelatine is as a bottom before staining, especially for common leathers, where the grain is poor and needs adequate covering. Again, the gelatine prevents the dye from sinking right into the centre of the leather and causing uneven results.

Lamb (*Leather Dressing*) mentions that gelatine or glue rendered insoluble by the action of formaldehyde makes an excellent waterproof finish for hat leathers, upholstery and bookbindings—

To 100 parts of a 2 per cent solution of a gelatine of good quality, 5 parts of a 40 per cent solution of formaldehyde is added, and a light coat of this season is given to the leather ; the leather being then dried and in a fairly warm stove, in order to drive off the excess of formaldehyde. Only sufficient of the finish for the requirements at the time of making it should be prepared, for the reason that during a long standing the formaldehyde is steadily acting upon the glue and making it insoluble, so that when the mixture has become set, it is impossible to remelt it again. If desired, the gelatine solution may be applied first to the leather, afterwards making the application of formaldehyde. The leather should be finally dried and at a moderately high temperature.

In conclusion, it should be pointed out that whenever possible the same make of gelatine should be used, and thus the

same quantity can always be employed, this making for uniform results. The glue pot must on no account be allowed to become foul, otherwise intensive hydrolysis will take place and the glue lose much of its adhesiveness. Every possible care has to be taken to ensure absolute cleanliness, as the gelatine liquor forms an ideal media for the cultivation and rapid growth of gelatine-liquefying micro-organisms.

CHAPTER X

GELATINE IN PHOTOGRAPHY AND PHOTO-LITHOGRAPHY

GELATINE is employed to a very large extent as a protective colloid in the preparation of photographic emulsions. It is really astounding the enormous number of applications which gelatine has in this comparatively recent industry. It is used alike in the manufacture of the simple roll film of the holiday snapshotter; the delicate and expensive plates of the aerial surveyor, or the ultra-sensitive emulsions used in radiography and x-ray photography. There is no doubt that photography plays a very important part in twentieth-century life. It is not merely a luxury, but an actual necessity, as it forms such an integral part of contemporary existence.

Research workers are now concentrating on the many problems confronting the industry, and as the manufacture of photographic materials goes hand in hand with science, the standard of the various preparations is remarkably high. Literature, scientific and technical, devoted to photography is massive, and the author cannot attempt anything like a résumé of the new physics and chemistry of photography, but must confine his attentions to a general description of the uses of gelatine in the industry.

Gelatine to be used in photography must necessarily be of the very finest quality. First of all the sheets must be uniform in thickness. It has been suggested that the thickened edges of a sheet of gelatine possess perceptibly different physical properties from the remainder of the sheet. The explanation given, is that this phenomenon is due to the different rate of drying.

Gelatine should be free from air bubbles, fibre, and cracks. A good, clean colour and absence of any odour when boiled in water are important indications of quality. Any fog or cloudiness in the sheet might possibly lead to a diminution of the brightness of the latent image on developing the emulsion.

Metallic impurities are highly objectionable on account of their action on the sensitive silver halides. Organic hydrolytic products, such as peptones and similar bodies, are objectionable

on account of their "weakening" action on the protective envelopes. Other important factors in judging a gelatine for photography are—

1. Percentage of water.
2. Percentage of grease.
3. Percentage of acidity.
4. Tensile strength.
5. Formation of foam.
6. Rate of drying.

The hydrion concentration of the gelatine forms a most important factor in the manufacture of emulsions. Loeb pointed out that, at the isoelectric point P_H^+ 4·7, gelatine is relatively inactive, i.e. cannot combine with either cation or anion. But at a $P_H^+ > 4{\cdot}7$, gelatine can combine only with cations, and at a $P_H^+ < 4{\cdot}7$ only with anions. Commercial gelatine has a P_H somewhere round about 7, so that combination of the protein with the metal, forming a metal gelatinate, is apparently inevitable.

If the gelatine has a P_H^+ on the acid side of the isoelectric point, then combination with the anion takes place—a gelatine chloride or sulphate being produced.

It would be interesting to know what is the optimum P_H^+ required for a photographic gelatine, and whether a certain percentage of the metal gelatinate is really essential for the proper working of the photographic emulsion.

In order to clear up certain points concerning the quality of a photographic gelatine, the author got into communication with Ilford, Ltd., the well-known manufacturers of photographic plates, films, and paper, etc. Through the generosity and courtesy of the above firm the following questions were answered, which shed some considerable light upon the subject:

Question 1. What are the chief requirements of a photographic gelatine?

Answer. The chief requirements of a photographic gelatine are cleanliness (that is, freedom from suspended matter from dirt in the nature of grease); freedom from a serious proportion of degradation products which may be formed in the actual manufacture of the gelatine; freedom from colour; freedom from excessive acidity or alkalinity; freedom from insoluble particles (gelatine itself may easily be rendered insoluble by overheating in the drying process); and freedom from adulterants, such as antiseptic agents, or hardening agents, such as chrome alum.

Question 2. What are the principal tests employed by the photographic manufacture ?

Answer. Several of the tests made by the photographic manufacturer are indicated in the answer to Question 1, other tests employed being those to determine the actual strength of the gelatine, chiefly viscosity, setting point, and jelly strength of the solution. The details of the methods adopted for this work are not yet standardized ; descriptions of some of them can be found in standard works on glue and gelatine testing. Apart from these laboratory tests, photographic manufacturers almost invariably employ an emulsion test if the gelatine is to be used for the manufacture of an emulsion.

Question 3. Do the gelatines to be used for different purposes, e.g. ordinary and panchromatic plates and films, vary appreciably in quality ?

Answer. The answer to this question is partly indicated in the answer to Question 2. Gelatines required for different processes do vary, but the precise nature of the variation is not yet known. A gelatine suitable for one emulsion is not necessarily suitable for another emulsion, and the differences lie between the emulsions rather than between the purposes for which the emulsions are required, that is to say, whether for plates, papers, or films.

Question 4. Is gelatine purified before use ?

Answer. Gelatine is not normally subjected to any process of purification before use.

Question 5. What is the normal P_H^+ of a photographic gelatine ?

Answer. The normal P_H^+ of a photographic gelatine is about 5 to 6.

Question 6. Is a similar type of gelatine used in the manufacture of filter screens as for emulsions ?

Answer. A similar type of gelatine is used for the manufacture of filters as for that of emulsions.

Note. As you are probably aware, gelatine can be obtained from quite a number of different sources, skin, bone, horn pith, fish skins, and the gelatines obtained from these sources vary quite appreciably in their qualities. There appear, in fact, to be several different gelatines, varying appreciably in chemical constitution, and the various sources of gelatine do not produce the same modifications, or produce them in different proportions. For this reason, the question of purity, which you emphasize in your second question, is probably somewhat misleading, as it is not so much a question of actual purity of the gelatine as of the nature of the gelatine. Most of the photographic gelatine used for emulsion purposes is prepared from animal skins. Gelatine prepared from bones and from other sources is not so generally suitable for photographic work.

The Development of Photography. Probably no other industry has such a fascinating history as the one engaged in the preparation of photographic materials.

Briefly, it may be said that the experiments of Wedgwood and Davy, in 1802, concerning the action of light on sensitive paper, formed the basis for future investigators to work upon.

The utilization of glass and celluloid supports for the light sensitive material were later and obvious improvements. It was left to Maddox, in 1878, to give the greatest impetus to this new industry. He found that gelatine made a far better material for the sensitive silver halides than any other substance, and he advocated its general utilization as a " protector." Bennet, in 1878, extended the experiments of Maddox and discovered the well-known " ripening process," which in some unknown manner stabilizes the emulsion.

The word emulsion is entirely a misnomer, as it is really an exceedingly fine suspension of minute crystalline particles of silver halide in gelatine. Colloid chemistry was only just " in the air," so that the early workers were unacquainted with the real meaning of the word " emulsion."

The constitution or make-up of this emulsion has attracted the attention of chemists for many years, and although some interesting theories had been evolved, it was not until the introduction of X-ray analysis that reliable data was obtained. X-ray analysis cast a new and somewhat unexpected light upon the subject. It was found that whilst silver chloride and bromide crystallize in the cubic system, the iodide crystallizes in both cubic and hexagonal. These two factors, though apparently insignificant, are of vital importance in constructing a theory of " grain structure." Evidence was forthcoming to show that the relative sizes of these grains differed appreciably, thus, although some were ultra-microscopic, others attained a dimension of 10 ft. across. In all cases, large or small, an identical lattice-work structure was presented. Authorities state that in an ordinary emulsion, the number of grains per square centimetre is of the order of 10^9.

It must not be supposed that the action of light on the emulsion relies entirely upon the number of grains of silver halide per square centimetre. Svedberg, in Sweden and Tóy in England, in 1922 found that there are present in the grains what they called " reduction centres." Supposing the development of exposed grains to cease suddenly and the latter to be then examined, it will be found that the grains have started to develop at just a few points scattered haphazard over their surface.

It was thought that a possible explanation might be found by embracing Einstein's modification of Planck's light quantum

theory, and Silberstein, working on these lines, evolved the celebrated "light-darts" hypothesis. He suggested that the reason why certain points on the surface of the grains are more sensitive than the other parts, is because they have been affected by "light-darts."

Toy dismissed Silberstein's theory as untenable, and sought to show that reduction centres were due to the presence of minute quantities of chemicals which acted as "photo-catalysts."

A recent advance in photography is the manufacture of panchromatic plates. It is well known that the ordinary emulsion is sensitive only to light of short wave-length, blue, violet and ultra-violet, that is why it is possible to develop in a dark room illuminated by means of a red lamp. By treating the plates or films with certain dyes, such as eosin, fluorescein, etc., it was found that the silver halides were rendered sensitive to light of a longer wave-length, e.g. yellow and green light. By extending the number of dyes, Pope and Mills were able to prepare emulsions sensitive to light merging into the red end of the spectrum It is now possible to obtain emulsions sensitive to wave-lengths between 1850 Å.U. and over 7000 A.U.

Although the incorporating of dyes in the gelatine plate renders the latter more sensitive to colour, real panchromatism is not yet possible without the aid of filter-screens, which cut down the blue and ultra-violet lights according to the results desired. In some special cases, light of short wave-length is allowed to pass through, and the yellow and green lights screened.

Considering the formation of photographic emulsions, D. F. Bloch, in his Streatfeild Memorial Lecture, 1927, "The Chemist in the Photographic Industry," gives the following excellent description—

Roughly speaking, the emulsion is prepared by adding silver nitrate to a warm solution of gelatine in water containing an excess of soluble bromide, a little iodide being usually present, and more or less ammonia. The silver halide, which is sub-microscopic at the time of formation, grows during the digestion which is subsequently given, the operation being termed ripening. In the absence of a silver solvent the grains of halide do not grow. How do they grow ? By aggregation crystallization, i.e. the adhesion of clumps to form a crystalline aggregate ? By a process of solution of either the smaller or more soluble grains, or by the possible formation of colloidal silver in the grains, which might afford crystallization nuclei ? Or, if the solution velocity of colloidal silver bromide is greater than that of crystalline silver bromide, there would

FIG. 28. TWO EARLY ITALIAN VASES FIG. 29.

Fig. 28 was taken with the ordinary **Ilford Plate**. Fig. 29 was taken with **Ilford Panchromatic Plate**, using a special colour filter.

(By courtesy of Messrs. Ilford, Ltd.)

be a tendency to form the latter. Even at this early stage, we are in some doubt as to the rationale of the process. Ripening is carried on for some length of time necessary to endow the emulsion with such potentialities as may be desired within the limits of its capacity, and during this time the halide grains increase in size. The emulsion is set, shredded, and washed, and may subsequently be further digested, during which process its latent capacities can be exploited to a greater or less extent. If, at any stage, the processes are pushed too far, the emulsion tends to give fog upon development, i.e. the difference between the unexposed and light exposed halides grows less. Plain silver bromide precipitated in the dark is at once reduced by developers of normal strength, but it is possible to develop a latent image from it after exposure by the use of a very dilute or an acidified reducing agent. In the emulsion the colloid acts as the protecting medium, making it possible to develop the latent image, but if the emulsion be left in the developer for a considerable length of time reduction gradually takes place. Thus, in the case of a fast emulsion, we are working upon the border-line of fog ; and it is not a little remarkable that a product of such a character should retain its properties unimpaired over a long period of years. The emulsion, once made, is coated upon a suitable base, and the pretreatment of this base, the spreading and drying of the emulsion, often present difficult problems to the chemist and engineer.

The principal action of gelatine is, of course, protective ; quite possibly it may act as an absorbent for the halogens, but this is by no means proven. Recent workers, notably Renwick, suggest that in the complex silver bromide grain, which is, in fact, a microcosmic laboratory, highly unstable silver occurs in solid solution. On exposure to light in the usual manner, this undergoes a swift metamorphosis, being changed into an " electrically neutral form of colloidal silver," which, owing to its fine dispersion, is capable of acting as a catalyst for development, accelerating the coagulation of the silver. The idea of " light sensitive silver nuclei " is a comparatively recent theory, and much work is now being done along these lines.

Sheppard and his co-workers have done much work upon the isolation of the actual " sensitizer " in the gelatine. They examined large quantities of deliming liquor from the gelatine factory, and found that there was present a small amount of a chemical which conferred high sensitivity to the emulsions made from purified gelatine. This chemical, allyl isothiocyanate (C_3H_5. NC : S), exists in normal gelatine at a concentration of from 1 : 300,000 to 1 : 1,000,000. Allyl isothiocyanate, commonly known as allyl mustard oil, is one of the best examples of the isothiocyanates. On hydrolysis they yield primary amines

$$S : C : NX + H_2O \rightarrow XNH_2 + COS$$

and also on reduction—

$$S:C:NX + 4H = NH_2X + CH_2S.$$

It should be remembered that the thiomethylene formed in the last reaction polymerizes to $(CH_2S)_3$ almost immediately.

In discussing the action of this agent, Bloch gives a brief summary of the supposed mechanism of its action as a sensitizer.

It is believed that the isothiocyanate is converted into this—carbamide. This is known to combine with the silver halides to form complex compounds which, in alkaline medium, break down, yielding silver sulphide ; these, it is suggested, form the sensitivity nuclei, and if they attain more than a certain dimension yield fog upon development.

A soluble sulphide cannot form these nuclei, since it acts at once and directly upon the silver bromide grain, giving silver sulphide without nucleus formation by means of an intermediate complex.

The sulphide is supposed to act as a nucleus in the reduction on development, and it is suggested that it deforms the lattice structure of the silver bromide—but this is speculative. The existence of definite nuclei at which development starts seems to be fairly well established, but the evidence for the existence of sensitivity nuclei is not convincing. It is not known, for instance, whether the silver sulphide specks themselves behave as light sensitive centres, or whether they act indirectly by promoting local instability, though the latter seems the more probable explanation.

Gelatine Light Filters in Panchromatism. If you look at a landscape, or in fact at any coloured scene, through a piece of blue glass or gelatine film, you will notice that the light filter has removed all variety of colour from the scene, and what is more, the brightnesses of the different colours will be found quite " wrong." Thus, the bright yellows, reds and yellowish greens of ripened corn, cottages, trees, and fields will have become dark, while the dark blues and violets will have become light.

The filtering action of the blue glass or gelatine is typical of the result obtained when an ordinary photographic plate or film is used. Unfortunately, emulsions cannot yet be made which are not more sensitive to blue than to other colours, so that in " panchromatism " a piece of yellow glass or gelatine must be placed in front of the lens to stop the blue and violet light before it reaches the plate.

Yellow filters are not the only ones employed for the purpose, the shades differ according to the use to which they are to be put, and the amount of blue or violet light to be stopped down. The use of light filters is recommended by experts—yellow-coloured emulsions used without filters do screen off some of the

ultra-violet light, but this entails longer exposure ; the results are not nearly so satisfactory as when filters are employed.

Ultra-violet light is the " bug-bear " of every photographer. This section of the spectrum consists of exceedingly short light waves, too short to affect the eye, but which have a swift action on the ultra-sensitive silver salts used in the preparation of panchromatic plates, and it is essential that for true or relative colour effects they should be stopped down as much as possible.

Generally speaking, a bright filter which screens the ultra-violet and blue light is far better for reproducing dark objects with sharp effects than a much darker filter which allows the ultra-violet light to pass through.

As mentioned above, the light filters can be purchased as gelatine films or coloured glasses. The former are, of course, cut to fit the lens, the front combination of which is unscrewed and the film put inside. Great care should be taken not to mark the surface of the filter with the hands. The lens combination is then replaced.

One of the chief disadvantages attached to the use of gelatine filters is that the surface can be badly marked with the fingers. The film is also affected by moist atmospheres.

Gelatine Colour Screens in Photo-micrography. Gelatine light screens are much used in photo-micrography. Magnifications used in this branch of applied photography are from a few diameters to one or two thousand, and the object may vary from the proboscis of a fly at five diameters to a blood parasite at two thousand.

The reason for the use of colour filters in photo-micrography is primarily to achieve good definition and resolution. Thus, green filters are most frequently employed, as it is found that green light has a higher luminosity than either blue or violet. Again, the spherical corrections of the objectives are more accurate for this light than any other monochromatic light. By using a monochromatic light, increase of contrast is obtained. If no colour screen is employed in photo-micrography, then it is found that no sharp contrast is obtained between the object and background ; this is particularly noticeable when the slide is stained with methylene blue.

Hind & Randles (*Handbook of Photo-micrography*) give the following rules governing the use of colour screens.

RULES FOR THE USE OF COLOUR SCREENS

1. *To Improve Resolution and Definition—*

(*a*) Use a monochromatic screen with a transmission in the yellow-green corresponding to best corrections of the objective.

(*b*) In certain cases, when light of very short wave-length is desired, use a monochromatic blue screen ; this is generally not so satisfactory as (*a*) with achromatic objectives.

2. *To Increase Contrast—*

Use a screen complementary in colour to the object, or to that part of the object that it is desired to make darkest in the photomicrograph.

3. *To Decrease Contrast or Increase Detail—*

Photograph by light corresponding in colour to the transmission of the object, or the part in which detail is required. This is most useful for yellow or red preparations.

4. *To Get Correct Colour-rendering—*

Use a screen properly adjusted to the light and plate, to absorb just the correct amount of the more actinic rays, in order that all the colours of the spectrum may act on the plate in the proportion of their visual luminosities.

The real value of light filters depends upon—

1. The respective rays of light they transmit or absorb.
2. Sharpness of the transmission band or bands.
3. Degree of luminosity of light transmitted.

For really accurate work it is advisable to examine the transmitted light in the usual manner by means of the direct-vision spectroscope.

Gelatine is particularly useful for light filters for this special branch of photography, on account of the fact that coloured glass is liable to refract the light that passes through it more or less unevenly, which is fatal to really accurate work. Again, a variety of delicate colours can be used when gelatine is employed, as this material dyes very readily, whereas glass is difficult to colour the correct tint ; it is generally a little lighter or darker. Gelatine films are best mounted between optical flats, and not on old plates or lantern slides.

Hind & Randles recommend the following method for making gelatine screens—

The solution of gelatine is made by soaking 1 part of best gelatine in 10 to 13 parts of water until well softened ; complete solution is obtained by placing the containing vessels on a water bath, or in a shallow saucepan of boiling water. The solution is filtered whilst hot through glass

wool and a little poured on the clean glass. By carefully tilting first to one corner and then to the others an even coating is obtained, and any superfluous gelatine is put back into the bottle. When the film has set, it is dyed by immersion in the dilute dye solution, 1 part dye in 1,000 parts water, until it is judged to be dark enough, then rinsed in water and left to dry.

Amongst the dyes used may be mentioned picric acid, methylene green, and Victoria green and chrysoidine.

Photo-lithography. The process of photo-lithography depends upon the action of light on chromed gelatine. Thus gelatine is treated with a strong solution of bichromate of potash in the dark and exposed through a photographic negative to a strong light. Formerly, the jelly was formed on a glass plate, but at the present time zinc is used for this purpose.

The action of light is interesting. Where the negative is "thin" and the light can penetrate to the jelly, then the gelatine will be rendered insoluble, whilst the dense parts of the negative protect the gelatine and light has little effect upon it. Gelatine affected by the light will not swell, and vice versa. A mirror copy of the negative is thus produced on the film of gelatine. The plate is usually covered with graphite and a plate of copper deposited upon it in an electrolytic solution.

The two- and three-colour process involves complications into which the author cannot enter at this stage. The secret of photo-lithography lies in the formation of the photo-sensitive chromo-gelatine.

Bogue gives the following equation as typifying the reaction—

Bichromate, first reduced by the action of light on gelatine, forming the chromium sesquioxide.

$$K_2Cr_2O_7 \rightarrow Cr_2O_3 + K_2O + 3O.$$

Oxygen absorbed by gelatine, participating in its insolubilization. The potassium oxide is, of course, changed to the hydroxide, and reacts with more of the bichromate with the formation of chromate,

$$K_2Cr_2O_7 + 2KOH \rightarrow 2K_2CrO_4 + H_2O.$$

The neutral chromate acts on the gelatine in the presence of light in a manner quite similar to that of the bichromate, but with extreme slowness,

$$2K_2CrO_4 \rightarrow Cr_2O_3 + 2K_2O + 3O.$$

Finally, the sesquioxide reacts with the excess of bichromate to form chromium chromate,

$$K_2Cr_2O_7 + Cr_2O_3 \rightarrow CrO_3, Cr_2O_3 + K_2CrO_4.$$

In the opinion of Bogue, the above equations, due to Lumière

and Seyewetz, need some revision. Thus he suggests that the last equation might better be written

$$K_2Cr_2O_7 \rightarrow K_2CrO_4 + CrO_3,$$
$$3CrO_3 + Cr_2O_3 \rightarrow Cr_2(CrO_4)_3.$$
$$2Cr_2(CrO_4)_3 \rightarrow 5Cr_2O_3 + 9O.$$

Gelatine is used in the modern collotype process to an appreciable degree. The faults ascribed to it, however, are irregularity and slowness of printing.

There is no doubt that the irregularity arises from a perfectly natural cause, namely, that an equilibrium of swelling has to be maintained in a substance quite unstable of which the capacity for absorption is influenced, to an appreciable degree, by external factors.

Success depends upon the choice of the gelatine, the strength of the sodium or potassium bichromate, and the exposure. In collotype printing it suffices for the moistening of the plate after each print to use an ordinary damping roller as in lithography.

INDEX

Acetic acid, 21, 134
Acidity of glues and gelatines, 101
Action of lime on hide proteins, 47
Active mass, 62
Adamkiewiez reaction, 103
Adams, James, 114
——, Robert, 114
Additives in glue, 88
Adhesives Committee's Report, 108, 109
—— Research Committee, 65, 69
Adsorption, 18
Ægean Sea, 4
Aerobic bacteria, 29
Aeronautical Inspection Dept., 108
Agar, 44, 138
Age of raw materials, 8
Agitation during extraction, 64
Air, 44
—— bladder, 37
—— bubbles in gelatine, 125, 136, 142
—— drying, 138
—— supply, 88
Albumins, 21, 23, 25, 53, 78
Alcohol, 32, 133
Allyl isothiocyanate, 148, 149
—— mustard oil, 148
Alumina, 45, 50
Aluminium, 63, 90
Alum leather waste, 19
Amines, 60
Amino acids, 21, 23, 27, 58, 59
—— groups, 17
—— (α)—β-indol-propionic acid, 22
—— (α) propionic acid, 21
—— (β) propionic acid, 21
Ammonia, 16
—— in limes, 47, 60
Ammonium carbonate, 38
Analysis of a mellow lime, 59
—— of bone fat, 72
—— of glue and gelatine, 96–106
—— of pure air, 43
—— of water, 40
Anatomical structure of the hide, 31
Ancient Egypt, 3, 5
—— Rome, 4
Animal oils and fats, 1
Antiseptic action of salt, 50
Antiseptics, 54, 57
—— in glue, 116
Ape men, 1
Applications of glue, 107
Aqua regia, 71
Arsenic depilatories, 13
—— in gelatine, 105, 125
Ash in gelatine, 131
—— of bone glue, 96
Asseomucoid, 16
Astrakhan isinglass, 135
Atkin, W. R., 60
Atropine discs, 132
Australian mud-fish, 37
Autoclaves, 65
Available lime, 46
Azilians, 3

Bacillus, butyricus, 44
——, liquefaciens, 30
——, putidus gracilis, 30, 47
——, putrificus, 30, 47
——, subtilis, 90
Bacteria, 27, 57
—— in gelatine, 106
—— in water, 40
Bacterial action, 107
Bacteriology of liming, 47, 48
——, uses of gelatine, 135–138
Bad lime, 45
Baer, Prof. Van, 36
Bancroft, 123
Bargello, 115
Barks, 3
Baryta water, 27
Bayliss, 28
B.D.H. (British Drug House), 33, 61, 67, 81
Bennet, 145
Benzene, 23, 71
Benzol, 66
Berestovoj, 92
Bergin, A. A., 92
Berthensen, 25
Berzelius, J. J., 20
Beta-napthol, 54
Bible, 6
Biebrich Scarlet, 33

Bio-chemistry, 21
Bladder, 38
Blank, I. H., 48
Bleaching glue and gelatine, 101
Bloch, 146, 149
Blood, 78
Bogue, 5, 15, 55, 56, 61, 66, 70, 76, 80, 88, 97, 99, 122, 139, 152
Bohr's scale, 50
Bone fat, 15, 16, 70, 71, 72
—— glues, 68
—— oil, 16
Bones, 6, 15, 16, 34, 64, 65, 66, 67
Bookbinding, 116
Boots Pure Drug Co., Ltd., 126
Borax, 54
Boric acid, 9, 54
Bottle skin, 4
Box-calf, 10
—— -making, 107
Boyle's law, 73
Brassworkers, 4
Brewing, 133, 134
Brill, 14
British Engineering Standards Assn., 109
—— Pharmaceutical Codex, 121, 130
—— Pharmacopoeia, 121, 132
Brittleness of glues, 96
Buckton cement-testing machine, 108
Bureau bookcase, 111
By-products, 8

Calcium bicarbonate, 39
—— butyrate, 71
—— carbonate, 83
—— hydrate, 47
—— hydroxide, 45, 46
—— lactate, 71
—— oxide, 45, 46
—— phosphates, 17, 96
Calfskins, 9, 10, 34
Calories, 83
Canada Balsam, 33
Candle making, 72
Capillaries, 31
Caproic acid, 47
Carbon disulphide, 66
—— monoxide, 45
Carboxyl group, 23
Carter, Howard, 3
Carthage, 4, 112
Cartilage, 35
Carvings, 3
Casein, 21
—— subtrate method, 138
Cat fish, 36
Caustic alkalis, 27, 56
Cell action, 13
Chalk, 45
Chandrigen, 9, 10
Charles Law, 73
Chemical analysis of enzymes, 28
—— mechanism of putrefaction, 30
Cheshire, 49
China, 5, 6
Chinese moss, 135
Chippendale, 114
Chlorides, 55
Chromed gelatine, 152
Chrome leather scrap, 18
—— shavings, 19
Cicero, 112
Clinical Pathology and the Use of Stains, 33
Clothing, 2
Cocaine discs, 132
Cod, 14, 36, 37
Coignet's gelatine, 104
Cold fish glues, 107
—— storage, 35
Collagen, 10, 15, 25, 26, 27, 62
Colloid, 18, 35
Colloidal particles, 76
—— silver, 148
Colour of gelatines, 63, 136, 142
—— of glues, 96
Colt in sheepskins, 11
Comparator, 60
Composition of rock salt, 49
Condensation, 17
Cone mill, 55
Connective tissues, 32
Constitution of leather, 17
Consuls, 4
Cooper Hewitt lamps, 40
Copper, 83
—— in gelatine, 90, 125
—— vessels, 88, 90
Cordwainers, 4
Corium, 61
Cottington Taylor, Mrs., 121
Cracks in gelatine, 96, 142
Cresylic acid, 9
Cromwellian furniture, 114
Curriers, 4
Cutting agents for isinglass, 134

Davis, C. E., 98
Decalcifying bones, 67
Degreasing bones, 65
Deir el Bahari, 5

Deliming, 60, 61, 62
Dendy, Arthur, 1, 14, 37
Derbyshire, 45
Dermis, 31
Desiccation of hide and skin offal, 53
Determination of chlorides in water, 42
—— —— —— in the P_H^+ of a gelatine, 101
—— —— —— in volatile acids in gelatine, 102
—— —— of magnesia in water, 41
—— —— of permanent hardness in water, 41
—— —— of temporary hardness in water, 38, 40
Dietetics, 119
Dilute acids, 61
Diphtheria bacilli, 138
Distillation, fractional, 20
Distinguishing bone from hide glues, 97
Droitwich, 49
Drying glue and gelatine sheets, 90
—— skins, 1
Dutch glue manufacturers, 6
Dyers, 4

EBONY, 5
Edible gelatine, 104, 105
Egg-white, 21
Egypt, 110, 112
Einstein's quantum theory, 145
Elastin, 21
Electrometric apparatus, 80, 101, 102
Elizabethan period of furniture, 112, 114
Embalming, 3
Emulsions, 123, 145
Engler viscosimeter, 98
Enterokinase, 28
Enzymatic action, 13
Enzyme bates, 138
Enzymes, 27, 28, 93, 94
Eosin, 33
Epidermis, 15, 31, 48
Equilibrium of swelling, 153
Equipment, leather, 4
Erepsin, 28
Estimation of available lime, 46
—— of dissolved hide substance, 59
—— of iron in water, 42
Etzel, G., 88
Europe, 6
Evaluation of gelatine, 104
Evaporation of glues, 83–90
Exodus, 5
Extraction of bones, 66, 68
—— of fish waste, 69,70
—— of hide and skin offal, 64

FACTORS in judging a photographic gelatine, 143
Fahrion, 17
Fat bone, 16
Fat skin, 11
Fatty acids, 70
Ferric oxide, 49
Fertilizer, 11, 15, 17, 19, 70
Fibre in gelatine, 142
—— netting, 90
Fibres of hide, 48
Fibrin, 28
Filter presses, 77, 78
Filter screens, 146
Filtration, 74–78
Finings solution, 133, 134, 135
Fischer, Emil, 23, 123
Fish fat, 14
—— skin, structure, 15
—— waste, 6, 13, 34, 35
Flemming, 139
Fleshings, 10, 11
Florence, 115
Flower, G. W., 45
Flow of liquids, 72, 73
Flute players, 4
Foam of glue, 63
Formaldehyde, 9, 81, 117, 140
Formo-gelatine, 132
Formol method, 138
Freundlich, 18
Fuller's Earth, 76
Furrier's waste, 19

GELATINE, 9, 10, 15, 17, 21, 24, 26, 35, 36, 38, 39, 40, 43, 51, 54, 70
—— capping, 133
—— capsules, 126–129
—— colour screens, 150
—— emulsions, 144
—— in chemical analysis, 138, 140
—— in cookery, 121
—— in cosmetics, 133
—— in foods, 119, 120, 121, 122
—— in ice-cream, 122, 123
—— in medicine, 124
—— in pharmacy, 124–133
—— in photography, 143–151
—— light filters, 144, 149–151
—— liquefying organisms, 54
General uses of glue, 117
Gesso, 5

Girdle of leather, 5
Glacé kid, 13
Glacial periods, 2
Glazed kid analysis, 94
Globulin, 28
Glue, 11, 15, 24, 38, 51, 54, 56
—— and gelatine testing, 99
—— boxes, 107
——, early method of manufacture, 5, 6
—— from chrome leather waste, 91–94
—— manufacturers, 9
Glycerine, 32, 133
Glycocoll, 21
Glyco-gelatine, 125
Goatskins, 4, 13
Gold, 4
—— leaf gelatine, 131
—— number of gelatines, 105
Good Housekeeping Institute, 121
Gothic style of furniture, 112
Grease, 74
—— in gelatine, 143
—— test, 99, 100
Greek, 4
Green bones, 65
Grinding bones, 65
Gudeman, E., 106
Guilds, 4

HACKFORD, 99
Haddock, 14
Haenlein, 50
Hair tankage, 19
Hake, 14, 36
Halibut, 14
Halides, 51
Hamburg isinglass, 135
Harewood and Satinwood commode, 113
Harness, 3
Hat leathers, 140
Hatschek, 74, 75, 123
Hat-shep-sut, 5
Heastie, Basil, 83
Heat of formation of calcium hydrate, 46
—— transmission, 83
Hectograph plates, 117
Henry VIII, 112
Hepplewhite, 114
Herdman, W., 14
Herold, 100
Herring, 14
—— oil, 14
Herschel, 98
Herter, C., 124
Hide and bone glues, 97, 109
—— and skin glues, 96
—— —— pieces, 8, 51
—— offal, 6, 8, 10, 34, 53, 64
—— proteins, 8, 9, 20, 29, 34
Hind and Randles, 151
Histological action of lime, 48
Histologists, 15
Hofmeister, 23, 26
Hollander, 55
Homer, 4
Honduras mahogany, 115
Horn piths, 17, 35
Hudson, F., 94
Humidity, 43
Hyaline layer, 61
Hydrating lime, 46
Hydraulic press, 11
Hydriodic acid, 27
Hydrion concentration of photographic gelatine, 143
Hydrochloric acid, 27, 60, 61
Hydrogen peroxide, 90
—— sulphide, 39
Hydrolysis, 9, 11, 20, 26, 27, 28, 51, 56, 62–64, 88
Hydrolytic action, 55

ICELANDISH isinglass, 135
Ichthylepidia, 15
Iletz Zaschtchiti, 49
Ilford, Ltd., 143
Iliad, 4
Indian isinglass, 135
Indole, 23
Indol group, 22
Industrial chemistry, 75
Inspection of glue and gelatine, 96
Interfibrillar substance, 32
Iron, 83
—— compounds in salt, 49
—— estimation, 42
—— haemotoxylin, 32
—— in water, 38–40
Isinglassine, 135
Isoelectric point of gelatine, 143
Isomers, 25
Ivory veneer, 5

JACOBI, A., 124
Jellied vegetables, 122
Johnstone, James, 14
Jones, Alfred Seymour, 11, 52
Junk bones, 65
Jus-vis tablets, 119

KERATIN, 31
Kernot, J. C., 65, 67, 69
Kestner, Paul, 82
—— evaporators, 84–89
Kieselguhr, 75, 77
Kilns, 45
King, C. G., 88
Kings, i (8), 5
Kjeldahl, 59, 104
Küttner, 100

LACTIC acid, 134
Lamb, M. C., 91, 93, 140
Lamellae, 132
Landau, J., 93
Law, D. J., 139
Laying veneers, 115, 116
Leaf isinglass, 133
Leather, 3, 4, 35
—— scrap, 17, 18
Leucin, 30
Lewkowitsch, 71, 72
Lieber-Kuhn's jelly, 27
Liebig's Extract, 137
Lime, 10, 32, 44–46, 56
—— soaps, 70, 71, 74
Lime water, 27, 46, 51
Limestone, 39
Liming, 13, 53–58
—— and lime, 69, 78
Ling, 15
Lipase, 13
Lipowitz, 99
Liquefying bacteria, 90
Loeb, 143
Louis, Paul, 4
Lucretius, 6
Lumière, 152

MACKENZIE, J. Ross, 134
Maddox, 145
Magnesium chloride, 49
—— salts, 50
Marlowe, 6
Marrow, 16
Martin, G., 50, 73
——, F. R., 116
Master craftsmen, 7
Matthew, iii (4), 5
—— and Lot, 134
Matthews, 16
McLaughlin, G. D., 48
Meat extracts, 119
Mellow lime, 47, 59
Melting point of glue, 100
Mercuric chloride, 9
Metallic impurities in gelatine, 104, 142
Metallic salts, 35
Meta-proteins, 27, 28, 56
Methylene-glycol, 30
Methyl orange, 41
Methyl-pyridines, 16
Meunier, 17
Micro-cocci, 51
Micro examination of sections of hide, [32
Micro-organisms, 88
Microtome, 32
Millon's reaction, 24, 103
Mineral ash in gelatine, 101, 125
Moisture in glue and gelatine, 102, 103
Moore & Partridge, 40
Morner, 15
Mould, 128
Mucins, 25, 74
Multiple effect evaporators, 82, 84, 88
Multiplex cloth, 78
Murlin, J., 119

NANTWICH, 49
Napthols, 9
Natural fats of the skin, 48
Neanderthalers, 1
Nelson's gelatine, 104
Nencki, 30
Neolithic, 3
Nerves, 31
New Stone Age, 3
Nineveh, 112
Nitric acid, 42
Nitrogen in the air, 43
North, 138
Northrop, 139
Northwich, 49
Notes on the extraction of bones, 65
Nucleus, 31, 32
Numa, 4

OCCURRENCE of salt, 49
Octadecapeptide, 23
Oil immersion, 44
Oils, 5
Oleic acid, 72
Open process of extraction, 63, 64
Ophthalmia, use of gelatine in, 132
Optimum of a photographic gelatine, 143
Ossalbuminoid, 16
Ossein, 16, 17, 35, 67
Oswald's viscosimeter, 98
Ox, 34

Oxides of nitrogen, 39
Ozone, 91

P_H^+, 28, 61, 67, 80, 81, 138
Paddles, 55, 65
Palmer, W. E., 60
Panchromatic plates, 146
Panchromatism, 149
Paper pulp, 77
Papillary layer, 31
Paraffin method of preparing sections, 32
Pasteurization, 90
Pathogenic bacteria, 124
Patroclus, 4
Pearson, Miss K., 124
Pepsin, 28
Peptones, 27, 28
Pepys, 114
Permanent hardness of water, 38
Persia, 116
Pessaries, 130
Pharaoh, 5
Pharmaceutical codex, 121, 132
—— formulas, 132
Phenol, 54
Phenolphthalein, 47, 58, 62
Phosphorus, 26
Photographic emulsions, 148
—— gelatines, 80, 104
Photo-lithography, 152, 153
Photo-micrography, 150, 151
Pickard, 138
——, J. A., 75, 76
Pickering, 123
Pigments, 5
Pill coating, 132
Pipe glass isinglass, 133
Plaice, 14
Planck's Quantum theory, 145
Plimmer, 21
Pliny, 6
Pneumococci, 138
Polypeptides, 23–25, 27
Pompeii, 112
Pope and Mills, 146
Porosity of bones, 68
Potassium thiocyanate, 42
Potters, 4
Preservation of glue stock, 51, 57
Primary amines, 148
Printing rollers, 117
Procter, H.R., 27, 45, 48, 53, 61, 80, 93
Prollius, F., 135
Propeller glues, 109
Propionic acid, 21
Protective action of gelatine, 148
Protein nitrogen, 119
Proteins, 15, 23, 25, 28, 55, 56
Proteolytic bacteria, 30
—— enzymes, 28, 148
Proteoses, 27
Psalmist, 4
Psychrometric experiments, 43
Punic Wars, 112
Putrefaction, 28, 29, 54
Pyrrole, 23

Raw material for glue, 44
Reavell, J. A., 82, 84
Recipes, 7
Refrigerating machine, 90
Relative heat conductivities, 83
Renaissance, 112
Renan, 110
Renwick, 148
Rideal, 80, 91, 99, 116–119, 135
Ripening process, 145
Rochelle salt, 92
Rockwell, G. E., 48
Röhms, 93
Rolled northern isinglass, 135
Roman civilization, 4
Romans, 112
Roundings, hide and skin, 10, 11
Rules for the use of colour screens, 151
Russia, 36, 37

Salicylic acid, 9, 54
Salisbury, Henry M., 98
Salt, 19, 53
Salted stock, 10
Salting, 51
Saponifying action of lime, 48
Schroeder, Von, 25
Schryver, S. B., 23
Scleroproteins, 25
Screening bones, 65
Sebaceous glands, 15
Senate, 4
Shakespeare, 6
Shark skins, 15
Shaw, G. B., v
Sheepskin offal, 10, 11
Shukoff, 72
Silica, 47, 83
Silver nitrate, 55
Sizing textiles, 118
Skin diseases, 131

Skin offal, 8
—— waste, 67
Skins, 2
Smith, C. R., 97
——, Z., 16
Sodium chloride, 38, 49, 50
—— hydroxide, 60
Sohn, J. Mayer, 92, 93
Sole, 14
Solid solution theory, 17
Solvents, 67
Sörensen, 81
Soxhlet principle of degreasing bones, 66
Speer, Miss N. E., 65, 67, 69
Spores of mould, 44
Sprat, 14
Staining leather, 140
Staphylococci, 44
Steapsin, 13
Steinitzer, F., 117
Stiasny, 58
Stratum corneum, 31
—— granulosum, 31
Streptococci, 44
String fibre in gelatine, 125
Stripal, 92
Stuart period of furniture, 114
Sturgeon, 36
Sub-cutaneous tissue, 10
Sugars in glue, 110
Sulphate of alumina, 80
Sulphites, 90
—— in gelatine, 125
Sulphur, 26
—— dioxide, 39, 103, 104
Sulphuric acid, 19, 27, 72
Sulphurous acid, 60, 61, 67, 134
Sulphydrate of calcium, 60
—— of sodium, 60
Suppositories, 125
Suy Dynasty, 5
Swelling action of lime on the fibres, 48
—— of gelatine, 26, 61
Swimming bladders, 36
Swiss Gold Label gelatine, 104

TAGGART, 16
Tang Dynasty, 5
Tankage, 70
Tanner, 9
Tanning, 3
Tanyard, 8
Tartaric acid, 134
Temperature of extraction, 64
Temporary hardness, 38
Tensile strength of gelatine, 125
—— strength of glue, 100, 108–110
Testing of gelatine, 99, 103, 104, 105
Tests employed for pharmaceutical gelatines, 126
Theories of tanning, 17
Thomas, A. W., 51
Thothmes, 5
Thymolphthalein, 60
Timurid Dynasty, 116
Total alkalinity of lime liquors, 57
Toy, 145
Trepka, E., 93
Trotman & Hackford, 91, 104
Turbot, 14
Tut-ankh-Amen, 3, 5
Two and three colour processes, 152
Tyrosin, 47

ULRICH, 100
Ultra-microscope, 145
—— -violet light, 150
Urethral Bougies, 130
Uses of gelatine in chemical analysis, 138
—— of isinglass in brewing, 133

VACUUM pans, 82
Valley of the Kings, 3
Value of light filters, 151
Veneering, 107–116
Viscosity, 63, 135
—— of glue, 97, 98
Vitamin C., 88

WALLPAPER, 118
Washing and deliming, 60
—— bones, 65
—— glue stock, 53, 54
Water, 83
—— supply, 38
—— vapour, 43
Waterproof paper, 133
Wedgwood, 144
Wells & Hooper, 115
Whiting, 14
Wielicza, 49
William III, 6
Wilson and Procter, 92, 93
Winter, F., 131, 132
Witts, 17
Wolff, 93
Wood, J. T., 50, 139

XANTHOPROTEIC reaction, 24, 26, 103
X-ray analysis, 145
Xylol, 32

YEAST, 44
Yellow isinglass, 135

ZAEHNSDORF, 117
Zenker's reagent, 32
Zinc in water, 38, 40
—— jelly, 131
—— oxide, 131
—— salts, 81

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