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DIRECT LIQUID EXTRACTION PROCESS FOR PURE LAC RESIN

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PREFACE.

In the first paper on " pure lac resin " an outline was given of several processes which might be used for the isolation of the " ether-insoluble " constituent of lac. It was frankly admitted that much work had to be done before any recommendation could be made of a process suitable for commercial development, even assuming that the interest in the special quality of lac produced justified attention being paid to the scheme at all. Since that time the reports received on the various samples of " pure lac resin," produced in the laboratory and issued to interested persons who have used the material for a variety of purposes, have been encouraging beyond all expectation. There is no doubt at all that " pure lac resin " gives air dried films which are in a class apart in respect of hardness and scratch resistance combined with flexibility and abnormally good adhesion to metal strip, particularly copper. Under stoving conditions these enhanced properties are still quite marked.

The demand for test samples of "pure lac resin" has been so great that a scheme for semi-technical scale manufacture of the material soon became essential. The details for the study which has been made prior to the acceptance of a suitable design for this plant are described in this paper. It is hoped that the information given herein will be found useful by those contemplating the production of " pure lac resin " on a commercial scale.

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SUMMARY.

(1) Of the methods available for obtaining " pure lac resin " from lac it is felt that the processes of partial distillation and the direct liquid extraction hold definite promise for industrial development.

(2) Direct liquid extraction processes are simple and in this respect are to be preferred to partial distillation. For this reason they have been investigated in detail.

(3) In the case of lac extraction by means of various solvents it has been shown that Partition Coefficient theory is untenable.

(4) A number of extraction equilibrium curves have been plotted. These furnish a great deal of information on lac extraction processes.

(5) In all cases where lac wax is absent the extraction equilibrium curves follow a simple power law (*i.e.*, they obey the equation $y = ax^n$, where y represents the concentration of " ether-soluble resin " in the extracting solvent and x the concentration of " ether soluble resin " in the product, a and n being constants characteristic of the process concerned).

(6) Curves representing extractions with trichlorethylene follow the same law even in cases where lac wax is present.

(7) Ether extraction curves follow an exponential law (*i.e.*, $y = be^{mx}$, where y and x have the same significance as above and b and m are characteristic constants for this process).

(8) The utility of these curves in relation to the design and development of efficient extraction processes has been demonstrated (see Appendix I and Fig. 12).

(9) Certain secondary factors render extraction calculations approximate. These have been considered and may be set out as :—

(*a*) the dispersion of " pure lac resin " in the solvent,

(*b*) the retention of solvent by the product,

(*c*) the loss of solvent by evaporation.

(10) The film forming qualities of " pure lac resin " improve with the progressive improvement in purity obtained by successive extractions up to about five.

(11) Apparatus is described for the quantitative extraction of lac by solvents lighter and heavier than the extracted material.

(12) A semi-large scale laboratory apparatus is described for making 1 lb. batches of " pure lac resin."

(13) Satisfactory product can be obtained with the plant of this type and solvent recovery is reasonably good in view of the fact that extracts are poured out hot in an open atmosphere.

(14) Encouraged by these results it is considered justifiable to build a larger scale pilot plant and such a plant is now in the course of construction.

DIRECT LIQUID EXTRACTION PROCESS FOR PURE LAC RESIN

INTRODUCTION.

In a previous publication(1), four different methods were described by which "pure lac resin" might be isolated from whole lac. Subsequently it was shown(2) that the "pure lac resin" so produced might be a desirable and valuable product for certain industrial applications. The next step obviously was to consider in detail which of the various possible processes suggested for the preparation of "pure lac resin" was most suitable for development as a commercial enterprise. The advantages and disadvantages of the four suggested processes as brought to light by the subsequent work may be summarised as follows :—

(1) Solution Extraction Process.

This process involves the extraction of a concentrated alcoholic solution of lac, by a relatively large quantity of extracting solvent. The chief difficulty found with this process arises from the fact that alcohol is partially miscible with the extracting solvents, so that part of the pure resin is lost in the extracting liquid and a part of the ether-soluble soft resin is left in the alcoholic solution. In short, the partition of the resin components is laborious and partial, a condition which is reflected in the performance value of the products. For these reasons, therefore, this method has not been further pursued. It should be mentioned that sometimes a small amount of solid matter, the nature of which is not known, is precipitated during these extractions.

(2) Partial Precipitation Process.

In this process, advantage is taken of the unlimited miscibility of water with alcohol and the immiscibility of water with the

(1) London Shellac Research Bureau, Technical Paper No. 1, 1934.
(2) London Shellac Research Bureau, First Bulletin, 1935.

extracting liquids. To a solution of lac in a mixture of alcohol and an extracting liquid, water is added, whereby the solvent power of alcohol for lac is reduced whilst the solvent power of the extracting liquid for the ether-soluble resin is maintained. As a result, the " pure lac resin " precipitates out. This is a neat process for laboratory scale work, but gradually it became evident that it was not a simple matter to handle the soft and sticky precipitate on a large scale, especially when it was necessary to redissolve and re-extract three or four times successively.

After close examination, the conclusion has been reached, though with some reluctance, that this method is not likely to lend itself to large scale development.

(3) Partial Distillation Process.

This is a variation of the above process, in which the alcohol is fractionally distilled off instead of being displaced by water.

Obviously the extracting liquid used must have a higher boiling point than alcohol. The process is comparatively simple, but it involves the use of two liquids and the necessity of fractionating one and subsequently distilling the other. On the other hand this process has certain distinct advantages such as the facility with which the extracting liquid is brought into intimate contact with the lac.

(4) Direct Liquid Extraction Process.

In this method, lac is treated directly in the molten state with the extracting liquid at or slightly below the boiling point of the liquid. A small amount of alcohol may be added in order to maintain the lac in a fluid form, but this addition proportionately impairs the yield of the "pure lac resin" obtained, by promoting its solubility in the extracting liquid. On the other hand, the addition of alcohol will improve the quality of the product, since the extraction will be more complete.

Of the four processes the last described, namely, the Direct Liquid Extraction, was thought to be the most suitable for large scale development, and it has been investigated with that object in view. The present paper, therefore, is concerned with the detailed study of the various aspects of this Direct Liquid Extraction process.

Choice of Solvent for the Extraction.

Having decided on the type ot process operation the choice of solvent or solvents is the most important question. Some consideration has been given to this problem of choice of solvent in Technical Paper No. 1. In the following table is a list of the

commoner solvents which by reason of boiling range and other considerations are likely to be useful, with the value of the initial partition coefficients in relation to lac, the meaning of which will be explained later.

The chlorinated solvents are particularly attractive because of their non-inflammability and in the preliminary experiments trichlorethylene gave promise of being useful, except for the fact that lac in contact with it became seriously polymerised, presumably due to the slight acid decomposition to which the solvent is liable under the influence of heat and light.

TABLE I.

Possible Extracting Solvents.

Solvent	Boiling Range °C.	Initial Partition Coefficient, k_w
1. Benzol	78-82	0.19-0.25
2. Toluol	110-112	0.34-0.42
3. Xylol	135-145	0.32-1.01
4. Solvent Naphtha	120-170	0.18-0.20
5. Trichlorethylene..	86-88	—
6. Perchlorethylene	119-121	0.05-0.08

It is possible, however, to stabilise trichlorethylene by a small quantity of various materials, about which there is extensive literature(3) ; we have found it convenient to use 0.1 per cent. of triethylamine for this purpose. As triethylamine boils at 89°C., it distils and is mostly recovered with the trichlorethylene so that it is only necessary to make good the loss. With this addition trichlorethylene has been used in a series of repeated extractions without affecting the lac adversely. When reference is made to trichlorethylene it will be understood that the material contains 0.1 per cent. of triethylamine.

(3) See U.S. Patent Nos. 1,816,895 (1931), 1,904,073 (1933), 1,910,962 (1933), 1,917,073 (1933), 1,925,602 (1933), Fr. Patent No. 726,362 (1931), Ger. Patent No. 562,820 (1932), British Patent No. 397,915 (1933), Can. Patent No. 341,792 (1934), etc.

PARTITION COEFFICIENTS.

The significance of this conception of partition coefficients and its value in estimating the relative efficiency of different solvents for the extraction of the ether-soluble resin from lac has been described in Technical Paper No. 1. That is, if the extracting solvent and the " pure lac resin " in molten form are regarded as immiscible solvents for the ether-soluble resin, the ratio of their relative solvent power can be taken to represent

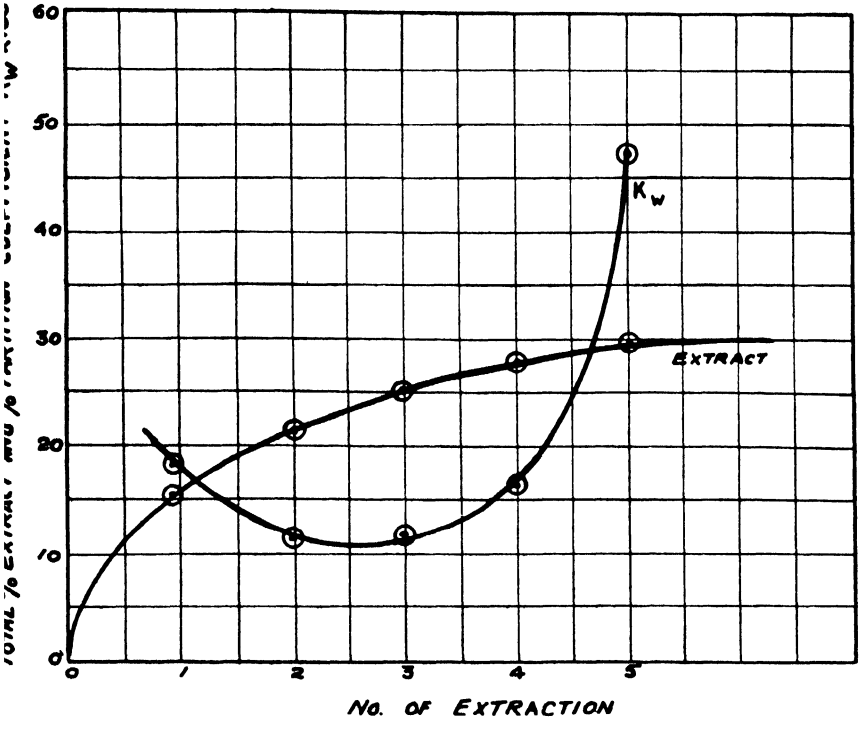

Fig. 1. Total extract and partition coefficient for toluol and " Kusmi " shellac for five repeated extractions.

the index of the excellence of the extracting solvent according to the equation :—

$$k_w = \frac{x}{\delta U} \Big/ \frac{m-x}{p} = xp \Big/ \delta U(m-x),$$

where k_w is the partition coefficient and x is the weight of ether-soluble resin (including wax, if present) extracted by U cc. of solvent of density δ from A gms. of lac containing m gms. of ether-soluble resin and p gms. of " pure lac resin."

The values for k_w given in Table I., refer only to the *initial* partition coefficients and having reached the conclusion that more than one extraction is necessary the next step is to consider whether the same k_w apply to subsequent extractions.

This has been done experimentally by making five repeated extractions (on 10 gms. of " Kusmi " lac using 50 cc.'s of extracting solvent at each extraction) and determining the amount and purity of the extract at each step. The total extract plotted against the number of extractions for toluol (see Fig. 1), shows that the total extractable matter reaches a limiting value of 30 per cent. From this curve the partition coefficients were calculated for each extraction and plotted on the same figure.

It is quite evident that the partition coefficient using toluol varies for different extractions far beyond the limits of experimental error; similar results were obtained for benzol, solvent naphtha and trichlorethylene at their respective boiling points and xylol when kept at 120°C.

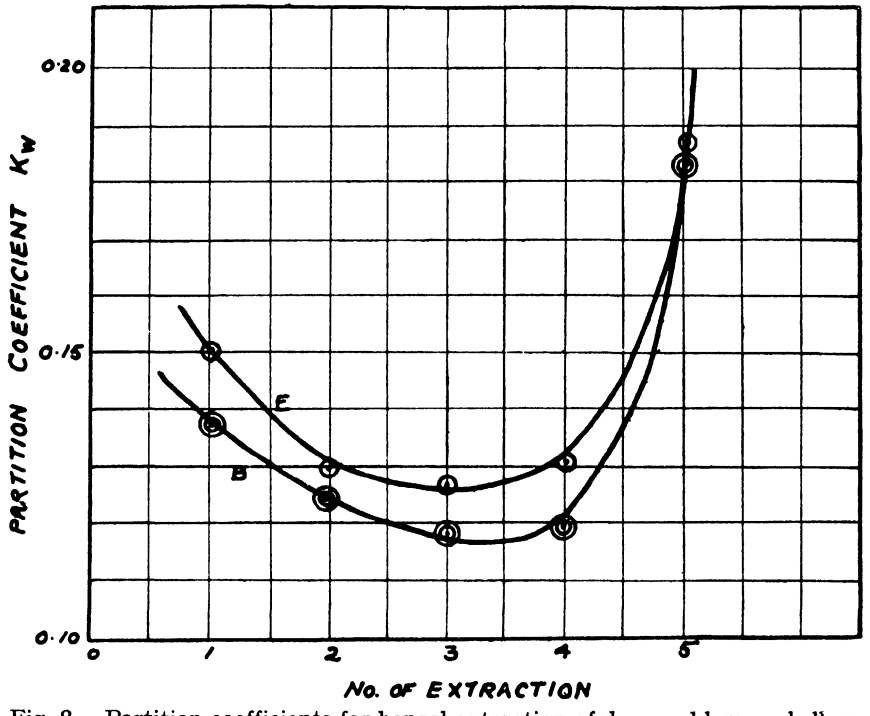

Fig. 2. Partition coefficients for benzol extraction of dewaxed lemon shellac:
Curve B is for k_w calculated for total benzol soluble extract.
Curve E is calculated for the ether-soluble portion of the extract only, making correction for the ether-insoluble resin present in the benzol extract.

Even when allowance is made for the " pure lac resin " carried over with the soft ether-soluble material the shape of the partition coefficient curve is practically unchanged. The ether extract also varies in composition at different stages according to the wax content, but corresponding experiments carried out with dewaxed lac, typical results of which are recorded in Fig. 2,

show that the form of the partition coefficient curves is unchanged. The proportion of ether-soluble to ether-insoluble matter in the extract is given in Fig. 3. There is one further point to consider in this connection, namely, the possibility of some kind of dissociation in parts of the lac complex, brought about by heat or the action of the solvent or both, but a close mathematical examination of these possibilities shows that these factors could not account for the irregularity found.

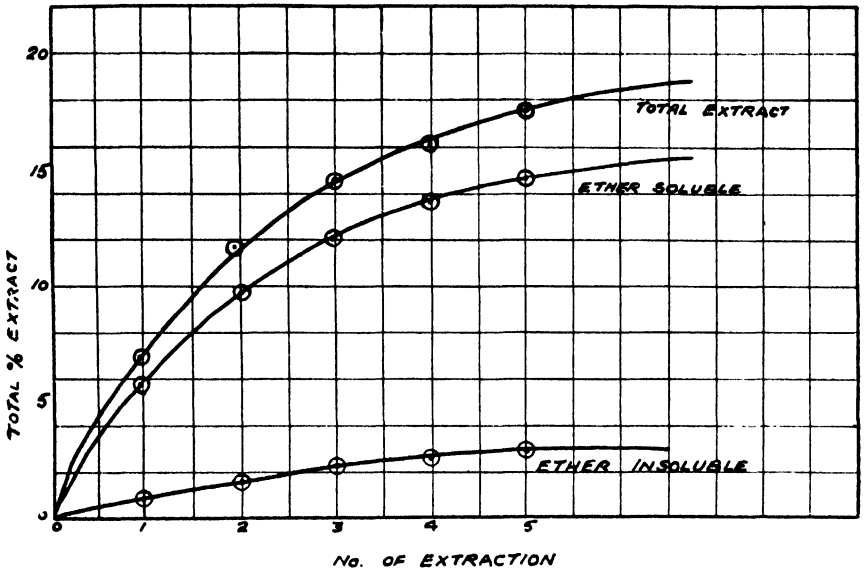

Fig. 3. Extraction of dewaxed lemon shellac by benzol, showing the total extract and the ether-soluble and insoluble portions in the extract.

EXTRACTION EQUILIBRIUM.

As, therefore, the concept of partition coefficients does not seem to be applicable to this type of lac extraction process, the extraction equilibrium must be viewed, at least for the present, on a more empirical basis.

The quantity and concentration of ether-soluble resin in the two phases (" pure lac resin " and extracting solvent) at the equilibrium of successive extractions, has been measured and the results plotted; for typical data and calculations see Table II and Figs. 4 and 5. The total amount of ether-soluble resin in the sample of lac and in the extract removed at each stage was determined by an independent ethyl ether extraction(4).

(4) Using Soxhlet extractor and a mixture of a fine mesh of powdered lac with three times the quantity of clean silver sand.

It is interesting to note (see Fig. 4) that the initial slopes of the hydrocarbon curves are practically the same, but the differences become marked later on.

Solvent naphtha behaves in a peculiar manner for the curve shows a pronounced inflexion point. A similar inflexion is only just noticeable in the benzol curve, whilst in the toluol curve it is absent. It is hardly likely that these inflexions are due to experimental error.

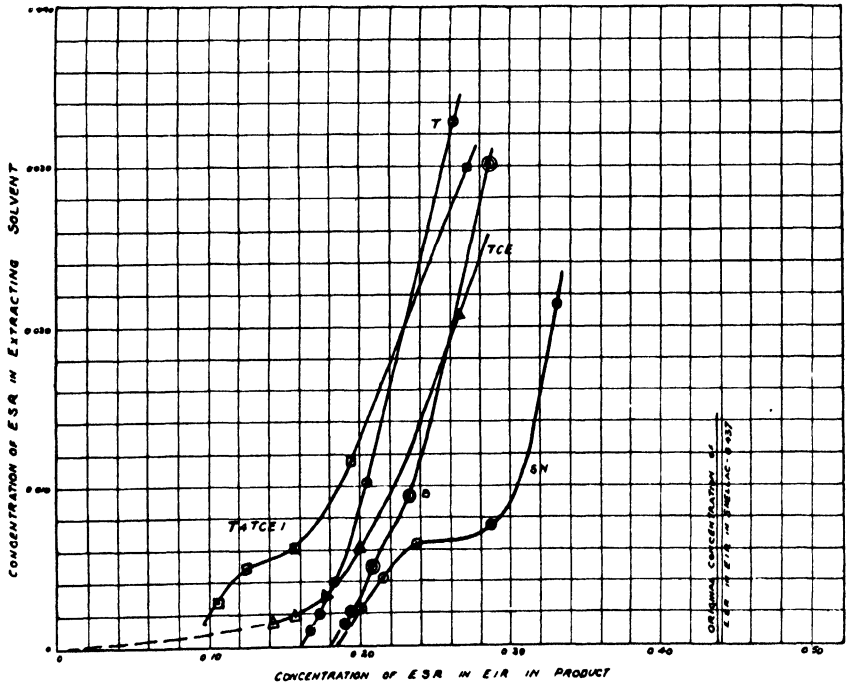

Fig. 4. Extraction equilibrium curves for Kusmi shellac with following solvents (concentrations in gms./gm.) :

Curve T—Toluol.
Curve B—Benzol.
Curve SN—Solvent Naphtha.
Curve TCE—Trichlorethylene.
Curve T4-TCE1—Mixture of 4 parts Toluol and 1 part Trichlorethylene.

The toluol curve is not only uniformly smooth and free from inflexion, but it shows that toluol extraction is the most efficient of the three hydrocarbons tested, since it reduces the concentration of the ether-soluble matter to a minimum. The curve for trichlorethylene, although it starts out with a lower efficiency of extraction than toluol and benzol, gives better results later on

TABLE II.

Extraction of "Kusmi" Shellac with Toluol.

Wt. of shellac .. .. = 10.0 gms.
Toluol used in each extraction .. .. .. = 50.0 cc.
Ether-soluble resin in shellac .. .. .. = 2.60 gms.
Lac wax in shellac .. .. = 0.44 gm.
Total ether-soluble matter (ESR) in shellac .. = 3.04 gms.
Total ether-insoluble matter (EIR) in shellac .. = 6.96 gms.

Items	No. of Extract					
	1st.	2nd.	3rd.	4th.	5th.	Totals.
ESR in each extraction ..	1.280	0.425	0.158	0.079	0.041	1.983
EIR in each extraction ..	0.250	0.165	0.110	0.063	0.035	0.623
Total extracted matter in each extraction	1.530	0.590	0.268	0.142	0.076	2.606
Concentration of ESR in extracting solvent gms/gm. ..	0.0328	0.0101	0.0039	0.0019	0.0010	—
ESR remaining in the product..	1.760	1.335	1.177	1.098	1.057	—
EIR remaining in the product..	6.710	6.546	6.436	6.373	6.337	—
Total resin remaining in the product	8.470	7.881	7.613	7.471	7.394	—
Concentration of ESR in EIR in the product gms/gm. ..	0.263	0.204	0.183	0.172	0.167	—

and tends to point towards the origin. With trichlorethylene, therefore, selective extraction would proceed until almost pure "pure lac resin" results whilst the other curves, which do not point towards the origin, set a limit to the extraction efficiency which is reached in the fifth extraction or thereabouts. The curve for a 4 to 1 mixture of toluol and trichlorethylene is

the most interesting, being parallel to the trichlorethylene curve in the initial stages, but after the inflexion it follows a path similar to the hydrocarbon curves. These variations could not be possible except for the fact that the ether-soluble resin must be an heterogeneous mixture, a portion of which is soluble in trichlorethylene but not soluble in the hydrocarbons.

Similar extraction equilibrium curves for dewaxed lemon shellac are given in Fig. 5. The curves take the same general form, with toluol as the most efficient material..

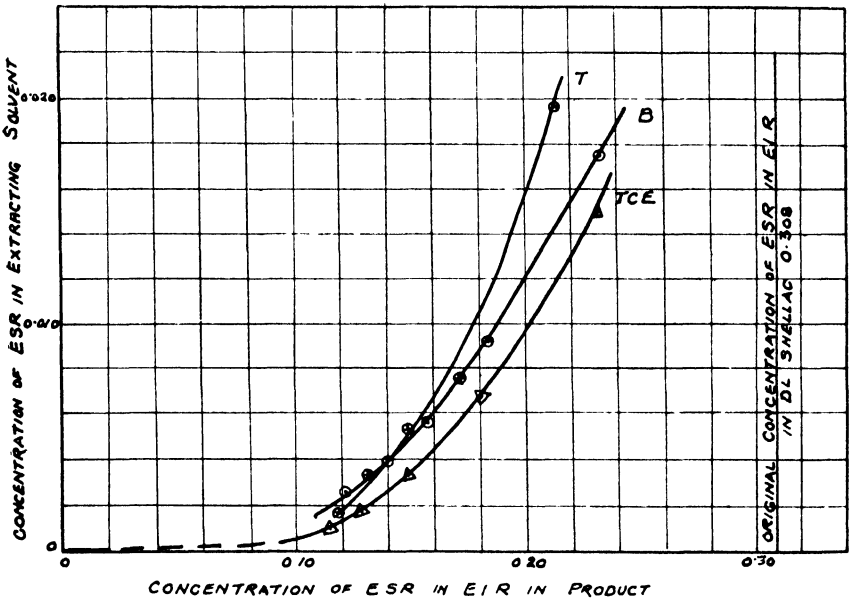

Fig. 5. Extraction equilibrium curves for dewaxed lemon shellac with following solvents (concentrations in gms./gm.) :

Curve T—Toluol.
Curve B—Benzol.
Curve TCE—Trichlorethylene.

As a matter of comparative interest the results of ethyl ether extractions(5) on dewaxed lemon shellac are plotted in Fig. 6, and except for the low efficiency in comparison with the higher boiling materials already described above, the form of the

(5) Ten of these extractions were made by shaking an 80 mesh mixture of one part lac and three parts by weight of silver sand with eight parts by volume of ether for 50 minutes.

curve is similar to the others. As an example of the relative efficiency of toluol and ether as extracting liquids, five repeated extractions on 10 gms. of lac, gave a product containing a concentration of 0.12 ESR with 250 cc's. of toluol; with ether the requirement for the same quality of extraction was more than double this amount.

If the data relating to some of the extraction experiments above described are plotted on a logarithmic graph paper as in

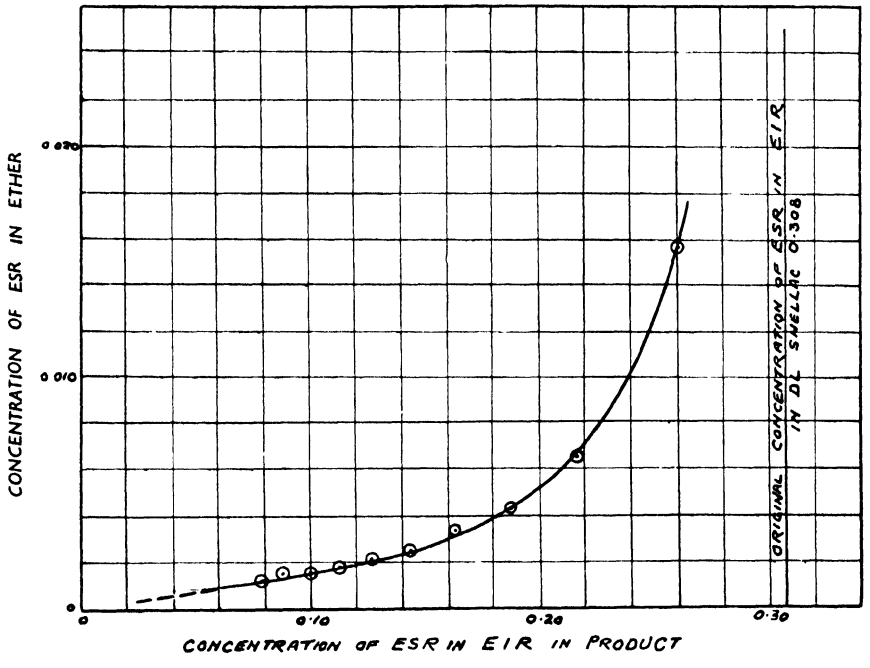

Fig. 6. Extraction equilibrium curve for dewaxed lemon shellac with ethyl ether (concentrations in gms./gm.).

Fig. 7, the curves all become straight lines showing that the extraction follows a power law of the form

$$y = ax^n, \tag{1}$$

where the concentration in gms. per gm. of ether-soluble resin in the extracting solvent and in the ether-insoluble resin is represented by y and x respectively and the constants for the particular set of extracting conditions are represented by a and n.

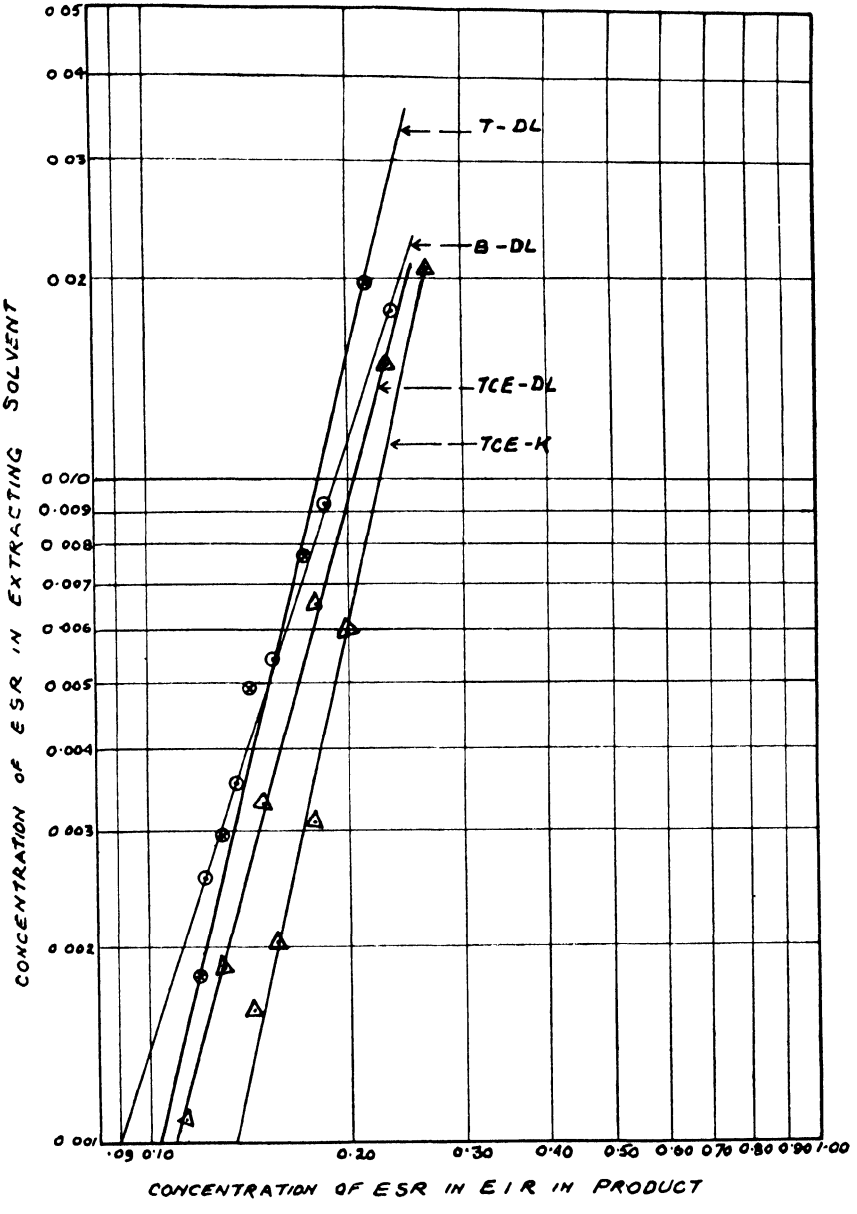

Fig. 7. Extraction equilibrium curves for DL and " Kusmi " shellacs (concentrations in gms /gm.) :

Curve T-DL—Dewaxed lemon shellac with Toluol.

Curve B-DL—Dewaxed lemon shellac with Benzol

Curve TCE-DL—Dewaxed lemon shellac with Trichlorethylene.

Curve TCE-K—" Kusmi " shellac with Trichlorethylene.

This form of equation suggests that a sufficient number of repeated extractions should reduce the concentration of ether-soluble resin in the product to zero where this equation applies. Obviously in practice it will be quicker to reach zero concentration with some solvents than with others as is clear from the linear co-ordinate graphs in Figs. 4 and 5.

The values of the constants *a* and *n* for the above examples have been calculated as follows:—

TABLE III.

Extraction Constants of Shellac with Various Solvents.

Shellac	Solvent	*a*	*n*
Dewaxed Lemon	Toluol	10.45	4.03
,, ,,	Benzol	1.43	3.01
,, ,,	Trichlorethylene	3.25	3.65
Kusmi Orange	,,	6.61	4.35

On the other hand, the records of some of the extraction experiments, particularly the extraction of " Kusmi " lac with aromatic hydrocarbons, when plotted on the logarithmic graph paper as in Fig. 8, do not yield straight lines and therefore equation (1) does not apply. It is suggested that the presence of wax may be the cause of this divergence because after the first one or two extractions (one in the case of toluol, two for benzol, three for solvent naphtha), by which time it is reasonable to assume that the wax has been removed, the curves appear to follow the normal straight line course. It is interesting to note that trichlorethylene does not discriminate against wax as do the hydrocarbon solvents, the curves for extractions of " Kusmi " and dewaxed lemon shellac with trichlorethylene being perfectly rectilinear (see Fig. 7). On the other hand, the 4 to 1 mixture of toluol and trichlorethylene (see Fig. 8) shows discrimination against wax similar to that shown by the hydrocarbons, in spite of its relatively high efficiency of extraction.

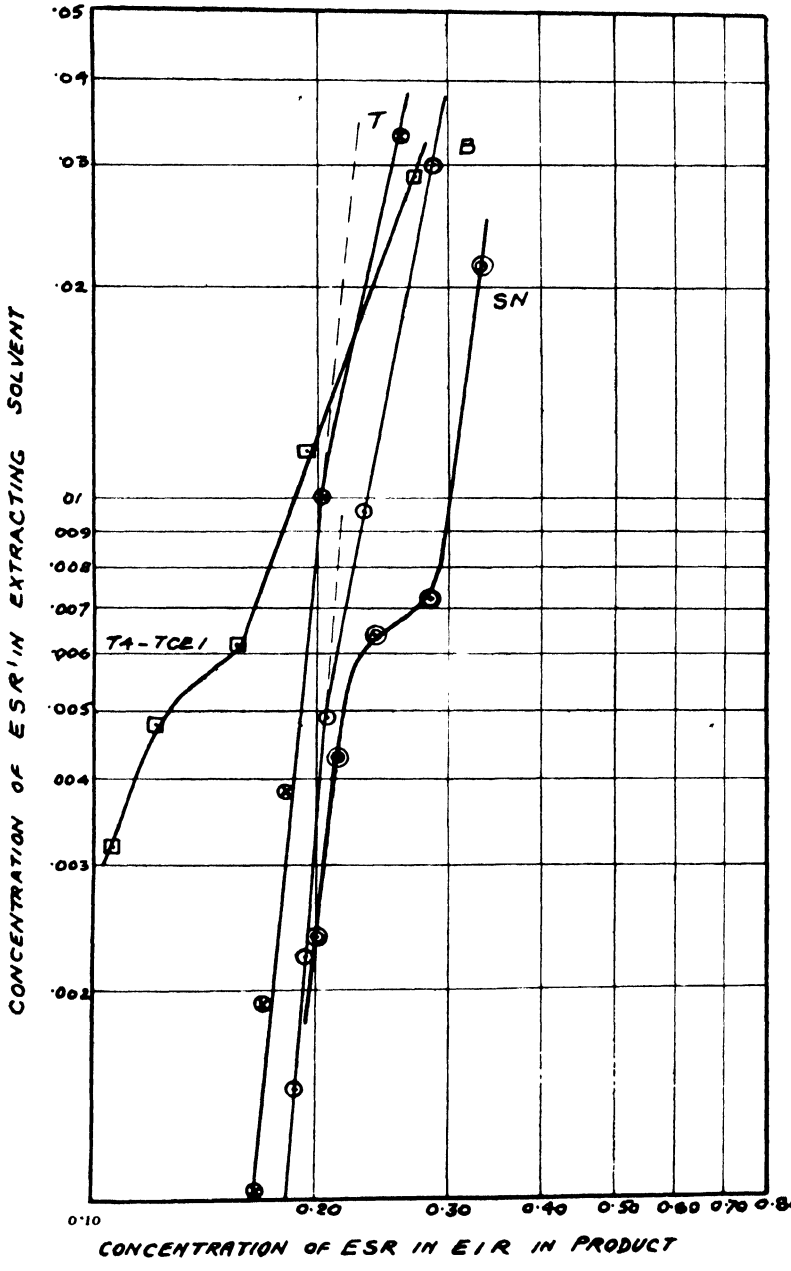

Fig. 8. Extraction equilibria curves for "Kusmi" shellac and hydrocarbon solvents (concentrations in gms./gm.) :

Curve T—Toluol.
Curve B—Benzol.
Curve SN—Solvent-Naphtha.
CurveT4-TCE1.—Mixture of 4 parts of Toluol and 1 part of Trichlorethylene.

Extraction with ethyl ether is characteristically different from extraction with other solvents. The data for ether extraction of dewaxed lemon shellac is plotted on semi-logarithmic paper as in Fig. 9. Except for the bend at the beginning of the curve, which may be explained by the initial absorption and adsorption of ether by lac, the record of Fig. 9 corresponds to the equation

$$y = be^{mx}, \tag{2}$$

where y and x have the same meaning as in equation (1) and b and m are characteristic constants for the particular extraction.

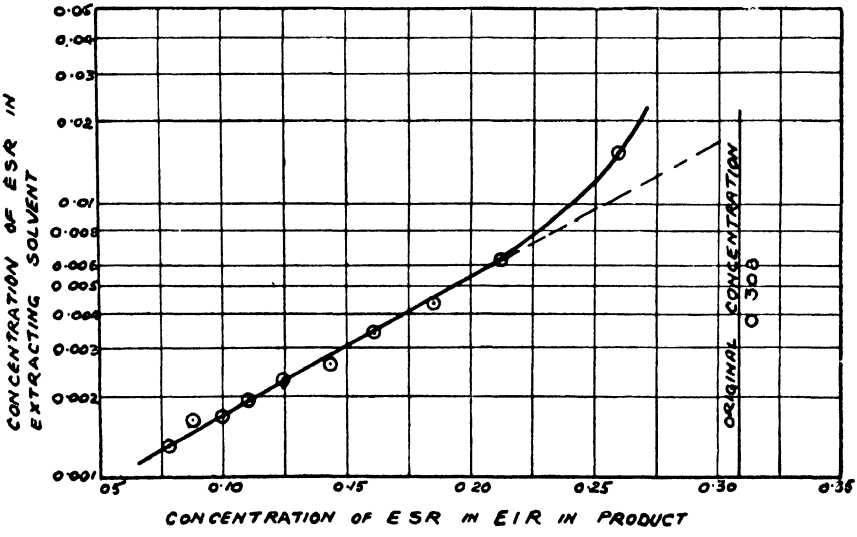

Fig. 9. Extraction equilibrium curve for dewaxed lemon shellac with ethyl ether (concentrations in gms./gm.)

The values of these constants for the experimental conditions described are

$$b = 5.29 \times 10^{-4}$$
$$m = 11.55$$

It is interesting to note that according to equation (2), when $x = 0$, y has a definite and positive value equal to b, which means that the end point will not be sharply approached. This fact in a considerable measure explains why it has been so difficult to obtain consistent results for ether-soluble content of lac([1]).

The application of extraction equilibrium curves for determination of extractive efficiencies, etc., will be discussed in the Appendix.

SOLVENT DISTRIBUTION.

There are certain secondary factors which have some effect on the economy and efficiency of the extraction process which have not been taken into account in the above discussion. These factors are :—

(1) Loss of pure lac resin by dispersion in the extracting solvent.

(2) Adsorption, absorption and mechanical occlusion of extracting solvent by the product, all of which may be termed as solvent retention.

(3) Loss of solvent by evaporation.

Some experimentally determined figures touching these matters are presented in Table IV. It is seen that the hydro-

TABLE IV.

Distribution of Solvent after Five Successive Extractions.

Total of 25 parts by volume of solvent used for each part by wt. of lac.

Shellac	Solvent	Total EIR dispersed Per cent.	Per cent. Solvent Distribution			
			Retained	Lost	Total un-recovered	Recovered in extract
Kusmi	Toluol	6 23	1.9	3.2	5.1	94.9
Kusmi	Benzol	7.48	1.2	4.4	5 6	94.4
Kusmi	Solvent Naphtha	4.97	1.6	5.3	6.9	93.1
Kusmi	Trichlor-ethylene	11.03	—	—	3.6	96.4
Dewaxed Lemon	Toluol	3.26	2.8	3.3	6.1	93.9
Dewaxed Lemon	Benzol	2.92	2 4	5.2	7.6	92.4
Dewaxed Lemon	Trichlor-ethylene	7.00	—	—	4.1	95.9

carbon solvents have less tendency to disperse " pure lac resin " than trichlorethylene, while solvent recovery in the case of this latter material is more than in the case of the hydrocarbons.

On the whole, the loss and retention of solvent is not very serious, but the loss of " pure lac resin " is definitely more than

can be tolerated in a commercial process, particularly with trichlorethylene treatments of Kusmi lac. The extent of this loss depends on the temperature at which the liquid is removed, that is the lower the temperature the smaller the loss, but there is a lower limit set by the fact that at too low a temperature, the soft resin itself would be partially deposited. Obviously there will be an optimum temperature for the processes, but the value of this has not yet been determined. In a commercial unit where maximum efficiency is desirable provision would have to be made for cooling the extract to the optimum temperature before removal.

' In the experiments described above, a period of one minute was allowed for the trichlorethylene extracts to cool before removal. Evidently this period of cooling was insufficient to minimise the loss of lac resin as can be seen from the figures in Table IV. On the other hand, when the hydrocarbon solvents were used the losses were extremely small in spite of the fact that the separation was made without delay and, therefore, without cooling.

QUALITY OF FILMS AND EXTRACTION EFFICIENCY.

The investigations already made show that so-called " pure lac resin " from which only a part of the ether-soluble material has been removed gives quite remarkable improvement in certain qualities of the films produced therefrom. Whilst it may be expected that the greater the purity of the " pure lac resin," the better will be the performance of the films, it is obviously uneconomic to pursue the ideal of purity beyond the point at which further improvement in performance is not evident. To correlate these factors of purity and performance value, films produced from " pure lac resin " at different stages of extraction have been examined. To facilitate the preparation of samples, extraction experiments were made in duplicate and careful adjustments made after the removal of each sample in order to maintain the pre-determined ratios of extracting solvent and lac.

The separated samples of " pure lac resin " were then dissolved in alcohol (at 20 per cent. solid) and applied by flowing on to copper panels, drying and baking directly at 120°C. for 1 hour. The panels were judged for general appearance and tested for scratch hardness and resistance to bending over a rod 1 mm. diameter in order to determine the relative flexibility and adhesion([2]) of the specimens. It was found that as the number of extractions was increased from 1 to 5 under the general conditions of extraction already described, the properties of the films improved. This general improvement is indicated in Table V. The smooth and glossy appearance improved progressively with a concurrent increase in adhesion and flexibility; and, at the same time, the scratch hardness increased from about 1 kg. to

considerably over 2 kgs(6). In some cases as for example, when making extractions of " Kusmi " lac with solvent naphtha, the product became partially insoluble in alcohol. The danger of premature polymerisation with high boiling solvents is so

TABLE V.

Properties of Films Obtained from Extraction Products of Lac at Various Stages of Extraction Process.

Films on copper baked at 120°C. for one hour.

Shellac-Extracting Solvent	Number of Extraction before test	Properties			
		Appearance	Bending Test		Scratch hardness, kgs.
			Adhesion	Flexibility	
Kusmi-Toluol	1	Mottled ..	Poor	Poor	2.0
	2	Slightly Mottled	Poor	Poor	2.0
	3	Slightly Mottled	Fair	Good	2.0
	4	Slightly Mottled	Good	Good	> 2.0
	5	Smooth, Glossy	Good	Good	> 2.0
Kusmi-Benzol	1	Mottled ..	Poor	Good	2.0
	2	Glossy ..	Fair	Good	1.0
	3	Glossy ..	Fair	Good	1.0
	4	Glossy ..	Good	Good	1.5
	5	Glossy ..	Good	Good	> 2.0
Kusmi-Solvent Naphtha	1	Mottled ..	Good	Good	> 2.0
	2	Fairly Smooth	Good	Good	> 2.0
Kusmi-Trichlor-ethylene	5	Smooth, Glossy	Good	Good	> 2.0

marked that it is inadvisable to use them under reflux conditions, but if operated at temperatures lower than the boiling point, the extraction efficiency is never satisfactory. It is, therefore, advisable in practice to use relatively low boiling solvents, such as toluol, benzol and trichlorethylene.

(6) Unfortunately at the time these measurements were made scratch hardness apparatus was not adopted for higher loads than 2 kgs. Scratch hardness values published here are, therefore, not comparable with those published in L.S.R.B. Tech. Paper No. 3. For relative scratch hardness of lac and pure lac resin films as a function of baking time, see L.S.R.B. First Bulletin (Figs. 1 and 2).

EXTRACTION APPARATUS.

The provision of laboratory apparatus for the quantitative extraction of lac with hydrocarbon solvents according to the general requirements outlined, presents no serious problem. A short-necked flask fitted with a cork carrying a condenser suffices for the refluxing of a mixture of lac and extracting solvent, the flask being frequently shaken to provide the necessary stirring. If the solvent is lighter than the lac it can be decanted when required, but when heavier solvents on which the lac floats are used, a suitable separating device must be provided so that the separation can be made quickly without disturbing the lac layer. For this purpose a separating funnel maintained at the required temperature by an electrically heated jacket has been successfully used. For dealing with small quantities of material the experimental procedure described above was adequate ; but when it was desired to obtain larger quantities of the product a modified form of apparatus was employed.

The details of construction of such laboratory extraction apparatus with which approximately 1 lb. batches of " pure lac resin " can be prepared are illustrated diagrammatically in Fig. 10. The vessel F is a 5-litre pyrex flask with a 2 in. diameter neck fitted with a condenser C, a thermometer T, and a mercury seal M, through which passes the shaft of a collapsible stirrer S. The details of the stirrer and the seal are shown at 1A ; the former is composed of a short bearing piece at the end of the shaft, through which passes a smaller shaft carrying two blades of the stirrer diametrically opposed. The stirrer passes through the neck of the flask in the folded position and spreads out inside the flask under centrifugal force. Through a flexible rubber coupling, the stirrer is connected through a suitable reduction gear to a 1/10 h.p. motor E. Heating of the flask F is carried out by means of an oil bath O set on the gas ring G.

600 gms. of lac are put into the flask with 3 litres of extracting solvent and the temperature quickly raised to the boiling point. As soon as the resin becomes soft enough to allow passage of the metal paddles stirring is commenced. Half an hour is allowed for each extraction after the contents of the flask have been brought to the boil. At the end of each boiling period, the flask is detached and the solvent containing the soft resin poured off while still hot. At this stage a good deal of occluded solvent can be freed by vigorous shaking of the flask. Another 3 litres of solvent, preferably preheated, is then added and the process repeated five times, *i.e.*, until 15 litres in all of the solvent has been used. This amount of extraction is identical with that obtained in the previously described small scale quantitative experiments and suffices to produce sufficiently pure " pure lac resin" for technical purposes. The number of extractions may have to be increased for

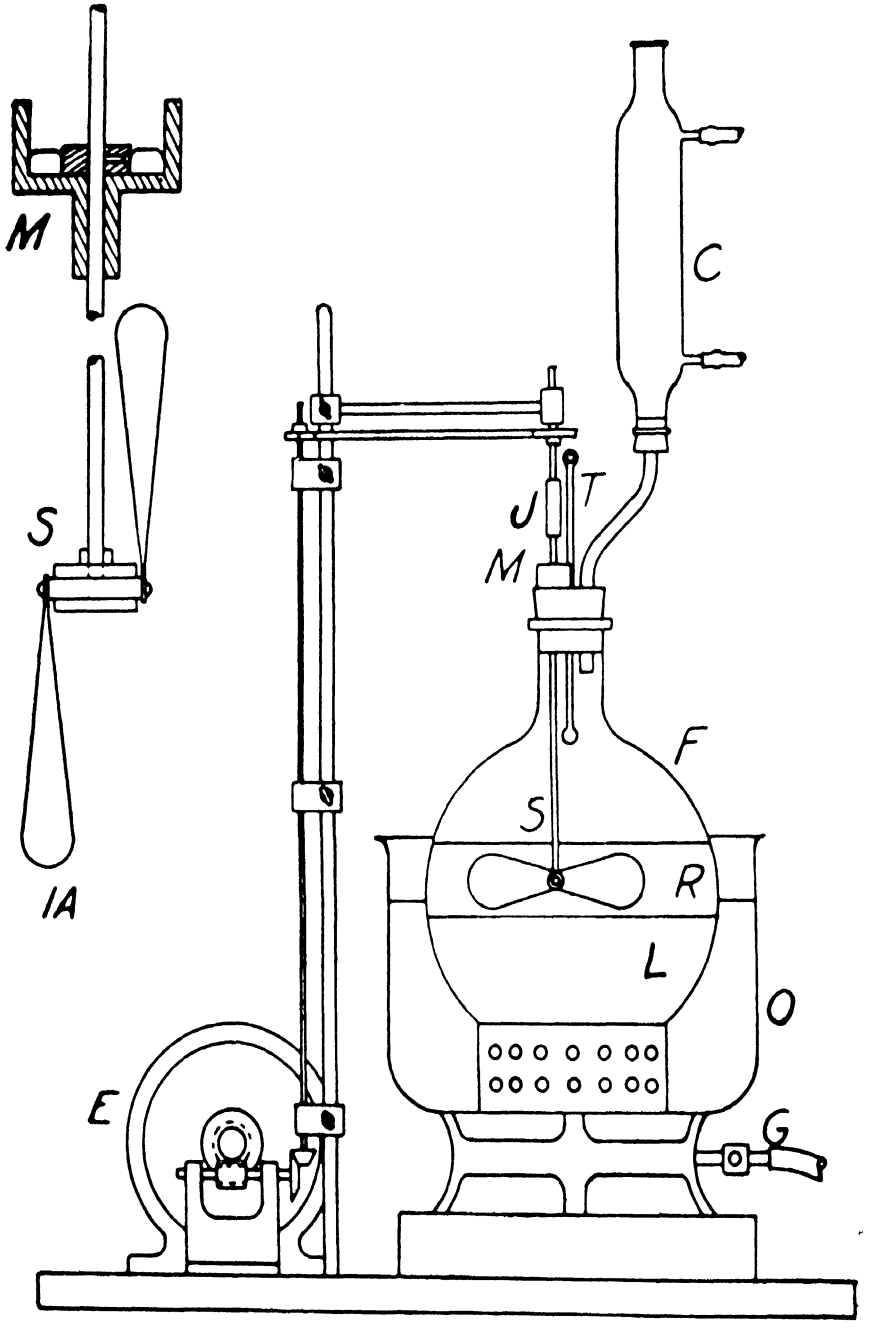

Fig. 10. Apparatus for large scale laboratory extraction of lac.

some very low grade lacs, but on the other hand good grades such as dewaxed lemon may only need about four extractions of the type described.

To overcome the difficulties associated with trichlorethylene already outlined it is necessary to provide the special arrangement shown in Fig. 11 for draining the extract. A wide U-tube with limbs the height of the flask and a straight tube with a ground glass stopper are inserted into the flask as shown in Fig. 11A. With the tap closed the flask is slowly inverted as in position 11B the tap is then opened and the solvent is allowed to flow out. Alternatively, the solvent may be removed by applying air pressure to the straight tube or it may be sucked out through the U-tube by slight evacuation.

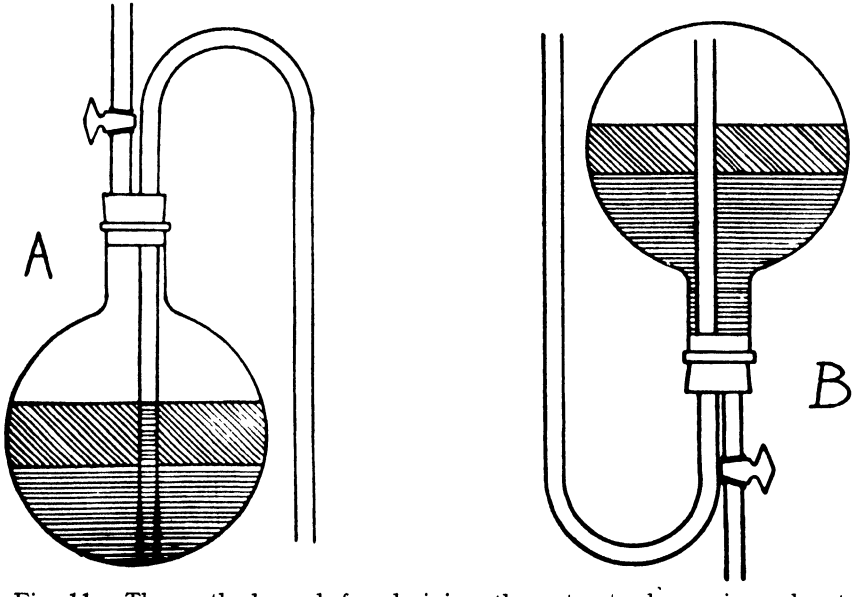

Fig. 11. The method used for draining the extract when using solvents heavier than lac.

After the final extraction, " pure lac resin " is poured out while still in the molten condition, allowed to cool slightly until it assumes a soft, rubber-like form and then broken up into small pieces by passage through a meat mincer or similar device in order to help the drying and liberation of the excess solvent.

Material dried by exposure to air will be found suitable for varnish making and for general purposes, but to obtain perfectly solvent-free material special treatment is necessary. Drying under a light vacuum is to be recommended.

A large number of samples were prepared in one-pound batches by the use of this apparatus, employing various grades of lac and different types of solvents. A simplified notation has been adopted to designate each of these products in relation to the original lac

sample, the type of solvent used and the number of extractions given with the usual proportions of solvents to lac (*i.e.* five parts by volume of solvent to one part by weight of lac in each extraction). So that K-T5 indicates Kusmi shellac extracted with toluol five times, DL-TCE5 applies to dewaxed lemon shellac extracted five times with trichlorethylene and SL-B4 designates seedlac extracted four times with benzol, and so on. A number of these large-scale products have been examined for their chemical and physical properties as well as for possible technological applications. The results of these investigations will form the subject matter of separate publications but it may be mentioned here that the degree of purity of the " pure lac resin " obtained by this apparatus suffices to improve lac properties to a considerable extent so that it becomes a very valuable product, having a large number of applications (2).

In order to gain some indication of relative extraction efficiencies and to investigate the purity of the products obtained, two samples of " pure lac resin " obtained by this method were analysed for their ether-soluble resin content, by ether soxhlet extractions of lac in admixture with sand (4). The results are given in Table VI.

TABLE VI.

Ether-soluble Resin Content of "Pure Lac Resin" Samples Prepared by Large Scale Laboratory Apparatus.

Product	Per Cent. Ether-Soluble Resin	Concentration of ESR in EIR
K - T5	11.2	0.126
K - TCE5	8.9	0.098

Comparing the concentration figures with those obtained by quantitative systematic extraction as shown in Fig. 4, it becomes clear that the large-scale apparatus is slightly more efficient than the smaller device, due, no doubt, to the more efficient stirring mechanism employed.

In one of the large-scale extraction experiments (K-T5) close check was kept on the solvent recovery. Total recovery amounted to about 94 per cent., which figure compares favourably with 95 per cent. recovered in the small-scale extraction for K-T5, as shown in Table IV.

Encouraged by these results and the published (2) and unpublished results concerning the properties of the " pure lac resin," it was thought justifiable to take a further step and to develop a semi-industrial scale pilot plant in order to obtain sufficient experience to be able to design an industrial scale apparatus. A semi-continuous ten-pound extraction plant has been designed and is now in the course of construction.

APPENDIX I.

Application of Extraction Equilibrium Curves.

The utility of the extraction equilibrium curves and the method (7) of using them for the investigation of an extraction process and the design of an extraction plant will be here illustrated by the extraction equilibrium curve for dewaxed lemon shellac with benzol reproduced in Fig. 12. The marked points lying on or near this curve are experimental determinations,

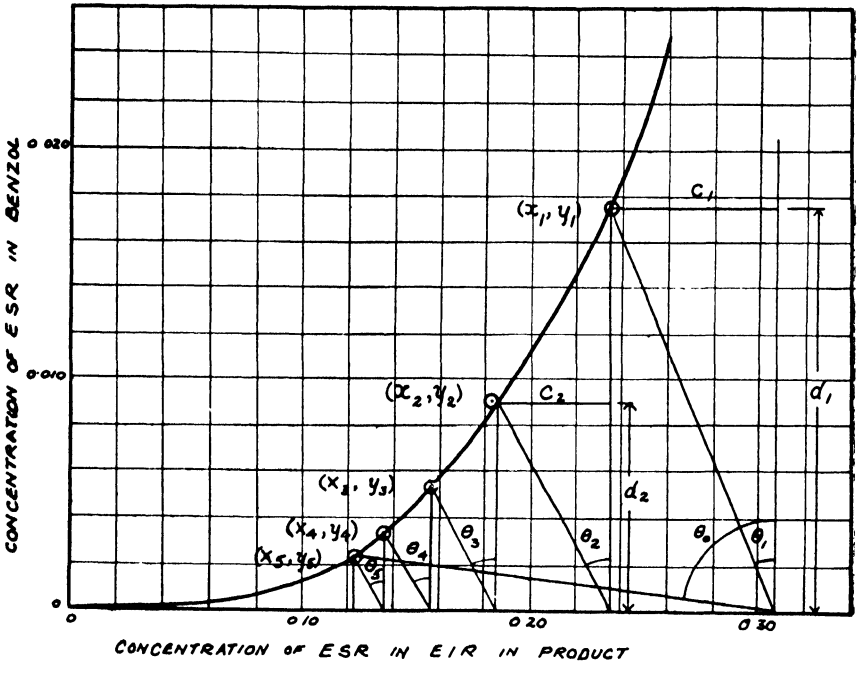

Fig. 12. Extraction equilibrium curve for the extraction of dewaxed lemon shellac with benzol. Points are experimental and the curve is computed from the empirical equation (1) with constants from Table III. Construction lines show how the amount of solvent necessary to extract a certain amount of ether-soluble resin can be determined by five repeated extractions or one single extraction (See text).

but the curve as drawn is computed from equation (1) by the use of the appropriate constants given in Table III. In the following calculations the dispersion of ether-soluble resin in the extracting solvent is neglected, since it is comparatively small and does not affect the general principles involved.

(7) T. W. Evans, "Countercurrent and Multiple Extraction", Ind Eng. Chem., 1934, *26*, 860.

Now, consider a given quantity of shellac containing s gms. of ether-soluble resin (ESR) dissolved or associated with p gms. of pure lac resin (EIR). The initial concentration of ESR in EIR is therefore

$$x_0' = \frac{s}{p}$$

As in the experiment 10 gms. of shellac were used, containing 23.6 per cent. of ether-soluble resin,

$$x_0 = \frac{2.36}{7.64} = 0.31.$$

Now assume that this shellac is successively extracted with $b_1, b_2 \ldots b_5$ gms. of benzol, and the successive concentrations in the extracts are $y_1, y_2 \ldots y_5$. After each extraction let the concentration of ether-soluble resin remaining in the product be represented by $x_1, x_2 \ldots x_5$. Then at each stage, the material balance equations become

$$\begin{aligned} px_1 + b_1y_1 &= px_0 \\ px_2 + b_2y_2 &= px_1 \\ &\ldots\ldots\ldots\ldots \\ px_5 + b_2y_5 &= px_4 \end{aligned}$$

These relationships are independent of the form of extraction equilibrium curves. Rearranging the terms we get

$$\begin{aligned} \frac{x_0 - x_1}{y_1} &= \frac{b_1}{p} = \frac{\triangle_1 x}{y_1} \\ \frac{x_1 - x_2}{y_2} &= \frac{b_2}{p} = \frac{\triangle_2 x}{y_2} \\ &\ldots\ldots\ldots\ldots \text{ etc.} \end{aligned} \qquad (3)$$

where $\triangle_1 x$, $\triangle_2 x \ldots$ etc. represent the change in concentration of the product during first, second and successive extractions respectively. In other words the ratio of the amount of extracting solvent to the amount of " pure lac resin " in any given extraction is equal to the ratio between the change in the concentration of the product and the concentration of the extract obtained in that particular extraction. This relationship, together with knowledge of the concentration equilibrium curve, enables one to determine in a relatively simple manner the concentration of the product, x, at any given step of the extraction process.

Referring again to Fig. 12, the point $(x_0, 0)$, *i.e.* (0.31, 0) is joined to the first experimental point on the equilibrium curve, thus making a line at an angle θ_1 to the normal. Now

the distance c_1, which is also $\triangle_1 x$, corresponds to the change in concentration of the product, and d_1 is the concentration of ether-soluble resin in the extract; thus, the angle θ_1 can be defined as

$$\tan\theta_1 = \frac{c_1}{d_1} = \frac{\triangle_1 x}{10 y_1} \quad .$$

The necessity of introducing the factor 10 arises from the fact that the scale of ordinates is ten times that of the abscissae. Now from the set of equations (3) already given

$$\frac{\triangle_1 x}{y_1} = \frac{b_1}{p}$$

$$\therefore \tan\theta_1 = \frac{c_1}{d_1} = \frac{\triangle_1 x}{10 y_1} = \frac{b_1}{10p} \qquad (4)$$

Therefore, from equation (4) the amount of solvent necessary to reach the concentration x_1 is given by the equation

$$b_1 = \frac{10 p c_1}{d_1} = 10 p \tan\theta_1 \qquad (5)$$

On the other hand if the amount of solvent b_1 used is known, then the resulting concentration of the product can be found by drawing a line through $(x_0, 0)$ at an angle to the normal, the tangent of which is given by the equation

$$\tan\theta_1 = \frac{b_1}{10p}$$

The point at which this line cuts the equilibrium curve (x_1, y_1) determines the concentration of the product as well as that of the extract.

The same construction can be repeated after the point (x_1, y_1) has been determined by making angles θ_2, θ_3, etc., corresponding to the amount of solvent used at each step, finally reaching the point (x_5, y_5) which gives the concentration of the product obtained after the fifth extraction.

From the experimental data available these steps have been worked out for five extractions as shown in Fig. 12. They show that the total quantity of solvent used in five extractions should be from these theoretical considerations 201 gms. while experimentally a total of 202 gms. of solvent was actually recovered from the various extracts.

If it is desired to obtain a product of the same final purity, *i.e.* a concentration x_5 by means of only one extraction instead of five, the quantity of solvent required for this purpose can be calculated as follows : Join the point (x_5, y_5) to the point $(x_0, 0)$, determine the tangent of the angle θ_0 (see Fig. 12), and apply equation (5). The calculated amount of solvent necessary is found to be 563 gms., in comparison with the 201 gms. necessary when five extractions are made. From these figures the advantage of repeated extractions becomes evident. It follows that calculations can be made for any number of extractions and, further, that extraction efficiencies to fit the requirements of any proposed scheme of operation may be determined.

APPENDIX II.

Analysis of Solvent Naphtha Used.

Light solvent naphtha, being a product of coal tar, varies considerably in its composition, depending upon the origin of the tar. The naphtha used in the experiments described before had the following characteristics as submitted by the manufacturer :—

Specific gravity	0.876
Distillation range :	
Initial boiling point	130°C.
34 per cent.	140°C.
85 per cent.	150°C.
96 per cent.	160°C.
Final boiling point	170°C.

The solvent was practically free from paraffins, naphthenes and olefines, and consisted almost exclusively of aromatic hydrocarbons, in the following approximate proportions :—

Toluols	15 per cent.
Xylols	50 per cent.
Higher Homologues ..	35 per cent.

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