The London Shellac Research Bureau.

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SINCE 1929 the Indian Lac Cess Committee has maintained in London a Special Lac Inquiry Officer to provide the necessary liaison between lac producing interests in India and lac consumers in England, Europe and America. In this way a large amount of technical information, including a comprehensive bibliography, has been collected, and a number of the problems confronting consumers of lac have been examined in the light of modern conditions. It soon became apparent that the study of problems arising out of the application of lac could be best carried out near to the centres of consumption and that a research laboratory located in London would be able to provide that necessary service which consumers to-day expect. Consequently in 1933, the Indian Lac Cess Committee founded the London Shellac Research Bureau under the chairmanship of the High Commissioner with an Advisory Committee, the Special Officer, Lac Inquiry, and three Indian scientists, two of whom were chemists and one a physicist.

In the past three years the activities of the Bureau have been manifold. Some description of the work done will be found in the *Annual Reports* of the Special Officer (Mr. A. J. Gibson) but the present writer is mainly concerned with indicating and commenting upon some of the research work carried out by the staff. After a short time together at the Paint Research Station, Teddington, one of the chemists (Dr. A. Karim) was posted to Mr. Bayley Parker at the Research Laboratories of the British Thomson-Houston Co., at Rugby, and his work has been mainly concerned with the development of a buying specification for lac products in the electrical industries. to be approved by the International Electrotechnical Commission Advisory Committee No. 15, of which the Special Officer, Lac Inquiry, is chairman. This has involved a mass of research and analyses by standardised methods, work which is approaching completion. Dr. Karim has also compiled a monograph of general interest discussing the various problems of lac chemistry.[1]

The other chemist (Dr. R. Bhattacharya) and the physicist (the writer) remained at the Paint Research Station and have worked in close collaboration with each other at this Station, Teddington, of which Dr. Jordan is the Director.

The first work was to collect and consider the value of the published work on lac; in this way much valuable data have been presented in its proper perspective. Some of it has already been published in the form of critical summaries [2,3,4,5,6] but a considerable amount of material still remains to be presented in similar form. The current literature on lac has been continuously abstracted and printed as a special section of the Paint Research Station bimonthly *Review*. These abstracts are reprinted semi-annually in a collected form by the London Shellac Research Bureau.

The numerous enquiries received from lac consumers and dealt with during the three years cover a large field of application; some of the objects treated, included the preparation and testing of lacquers and finishes for various purposes such as artificial leather and leather goods, tin and aluminium foils, rubberised fabric; the study of processes for dewaxing of lac and the impregnation of cotton covered copper-wire; the production of cellulose-lac combinations; the testing and evaluation of new plasticisers and the study of problems arising out of the thickening of lac-copal solutions, and the manufacture of adhesive compositions. The general impression gained from these enquiries is that the consumer is anxiously waiting for convenient methods of increasing the softening point of lac and improving its water resisting qualities. These fundamental problems, so often referred to in lac literature, and others have received close and critical attention at the Teddington laboratories with a certain measure of success.

In dealing with any material, the first question and one of fundamental importance is "constitution," a thorough knowledge of which is absolutely necessary before any *systematic* study can be made leading to modifications showing improved and desirable properties. Some years ago Dr. Werner Nagel and his colleagues isolated and identified in lac two major acids—aleuritic and shellolic, although the correct formula for the latter is still uncertain. Dr. Bhattacharya's work[7] in this direction has revealed that the former can be easily isolated and purified, whereas the latter being very sensitive to the usual chemical reagents is difficult to obtain in a pure state. There are indications that this acid lactonises readily and indeed it has been found to exist in more than one isomeric form. He has, however, worked out a simple method[8] to isolate and purify shellolic acid, which depends on the relative solubilities of the lead salts of the lac acids in water. From the study of these comparatively pure materials it is evident that the iodine value of lac resin must be attributed to some component other than shellolic acid and not yet identified. This work and other related investigations have led to the derivation of a tentative monomeric formula for the major resinous constituent of lac—pure lac resin, which agrees with most of its known experimental constants.[9]

It has been known for a long time that shellac resin contains a hard and a soft component, the latter being ether-soluble. The work of Tschirch

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[1] A. Karim, *J. Oil & Col. Chem. Assoc.*, May 1935, **18.**

[2] R. Bhattacharya, *Lond. Shellac Res. Bur. Tech. Paper*, June 1935, No. 2.

[3] L. C. Verman, *Lond. Shellac Res. Bur. Tech. Paper*, July 1935, No. 3.

[4] L. C. Verman, *Lond. Shellac Res. Bur. Tech. Paper*, Aug. 1935, No. 4.

[5] L. C. Verman, *Lond. Shellac Res. Bur. Tech. Paper*, May 1936, No. 7.

[6] L. C. Verman, *Lond. Shellac Res. Bur. Tech. Paper*, to be published shortly.

[7] R. Bhattacharya, *J. Soc. Chem. Ind.*, March 22, 1935, **54.** Also *Lond Shellac Res. Bur. First Bull.*, March 1935.

[8] R. Bhattacharya, *Chem. and Ind.*, April 17, 1936, **55, 309.**

[9] L. C. Verman and R. Bhattacharya, *Lond. Shellac Res. Bur. Tech. Paper*, to be published shortly.

and Schæffer, Harries and Nagel and others has, in a general way, indicated that the harder ether-insoluble component is chiefly responsible for the excellent properties of shellac. Our recent work has substantiated this view,[10] and the various means of isolating this hard component, which constitutes about 75 to 80% of lac, have been investigated[11]: of the methods available it has been found that a direct solvent extraction process is not only practicable and advantageous in several respects but is also likely to be a commercial possibility.[12] A semi-industrial scale pilot plant was constructed last year and the experience gained has brought the process to a stage where it can well be taken up by an industrial organisation.

The properties of this material, which has been named " Hard Lac Resin " in preference to the term "Reinharz," have been investigated in great detail[13] and it has been found to be superior to the parent lac in almost all respects. For example it is higher melting, is much more water-resistant, much quicker heat-hardening, possesses a higher degree of adhesive properties, yields harder and more flexible films, whilst the solvent retention of its films is negligibly small. In one respect, colour, it is inferior to whole lac; it can, however, be decolorised to a considerably greater extent than lac by means of a little oxalic acid or the like. It can also be bleached like ordinary lac, although this process has not yet been fully investigated. Furthermore, as it does not react with copper, no green discoloration is produced as is the case with lac under certain conditions. Other properties which make this material highly suitable for electrical insulation work are its higher breakdown voltage and its capacity to withstand high temperatures for prolonged periods of heating.

A general survey of the known physical properties of lac has indicated the need for a more detailed and systematic examination of most of them, especially those properties that are immediately important from the point of view of industrial application of lac. Investigations in this direction have yielded extremely interesting results of technical as well as theoretical importance. The following subjects have thus far reached the first stage of publication :—

(1) DARKENING OF LAC SOLUTIONS AND THE EFFECT OF OXALIC ACID THEREON.[14]

It is well known that lac solutions stored in tinned iron containers have a tendency to discolour with time and it is also well known that a small proportion of oxalic acid added to the solution has an inhibiting effect on this process. So far, no satisfactory explanation has been known for this phenomenon, nor has it been possible to determine the necessary amount of acid required to produce the effect. Our studies have revealed that on addition of acid to lac solutions the electrical conductivity of the latter decreases at first, passes through a minimum and then slowly rises. By a complicated series of conductivity measurements it has been shown that the minimum conductivity point, which varies from sample to sample between concentrations of about 0.025 and 0.25% of acid on lac, is definitely related to the anti-corrosive action of oxalic acid. The mechanism appears to be that the addition of acid precipitates the inorganic impurities in shellac as oxalates, which causes a depression in conductivity. A slight excess of acid over and above the minimum conductivity point helps to establish an equilibrium between the corroding iron surface, oxalic acid and iron oxalate, which is formed in preference to iron-shellac salts. Such an equilibrium prevents the weaker shellac acids from reacting with iron and thus preventing the darkening of the solution. This mechanism seems to explain the known facts for example of conductivity, but the necessity for further work in this direction still exists. It may also be mentioned that the amount of oxalic acid required to give the minimum conductivity to shellac solutions is also the amount necessary to cause the maximum possible decoloration of the solution, so that either electrometric or colorimetric methods can be used to determine the necessary amount of acid for the purpose of inhibiting the darkening of solutions in tinned iron containers.

(2) PLASTICISING OF LAC FILMS.[15]

The problem of finding a suitable plasticiser and that of comparing various available plasticisers for lac films has been a subject of controversy for some time. A preliminary study of the literature at once indicated that the chief reason for this controversy had been the lack of a systematic study. A comprehensive plan was drawn up, therefore, to study ten well-known and commonly employed plasticisers. The underlying idea of the scheme was to investigate all the properties dependent on plasticising action and to compare the results with the control as well as among themselves. The properties of the film so far studied are :—

1. Tensile strength.
2. Extensibility.
3. Adhesion to metal surfaces.
4. Water-sensitivity including blushing and amount of water absorbed by
   (a) detached films,
   (b) films on metal supports.
5. Effect of baking on these properties.

Other properties that may be included in the scheme are :—

6. Permeability to water and water vapour.
7. Durability under alternative exposure to dry and moist atmospheres.
8. Durability under normal as well as artificial weathering.

A good plasticiser should prove satisfactory in all these respects. So far, it has been found that among those tested sextol phthalate is the most satisfactory all-round plasticiser for lac.

(3) HARDENING OF LAC.[13]

In moulding practice, knowledge of the hardening properties of the material is essential and it

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[10] L. C. Verman, *J. Soc. Chem. Ind.*, March 22, 1935, **54**. Also *Lond. Shellac Res. Bur. First Bull.*, March 1935.

[11] L. C. Verman and R. Bhattacharya, *Lond. Shellac Res. Bur. Tech. Paper*, Dec. 1934, No. 1.

[12] L. C. Verman and R. Bhattacharya, *Lond. Shellac Res. Bur. Tech. Paper*, Aug. 1935, No. 5.

[13] L. C. Verman, *Lond. Shellac Res. Bur. Tech. Paper*, to be published shortly.

[14] L. C. Verman and R. Bhattacharya, *Lond. Shellac Res. Bur. Tech. Paper*, May 1936, No. 8.

[15] L. C. Verman and R. Bhattacharya, *Lond. Shellac Res. Bur. Tech. Paper*, June 1936, No. 9.

is to be noted with regret that very little is known about lac in this respect. Our efforts so far have been confined to the study of time and temperature relationships in respect of hardening. It has been found that "Life of Lac under Heat" which means the time of heating necessary to reach the beginning of the "B" stage of polymerisation or rubbery, highly elastic state, can be expressed by the equation :—

$$l = ae^{-\alpha\theta} \quad \cdots \quad (1)$$

where l is the "life" in minutes,
θ is the temperature in °C.,
and a and α are characteristic constants.

The constant a seems to vary from sample to sample, while α is found to be more or less the same for most lac samples and even for hard lac resin it is only slightly different.

Furthermore, no appreciable insolubility of lac in alcohol takes place before the "life" has been spent; thereafter insolubilisation proceeds at a rather rapid rate reaching a maximum of about 70-75%, corresponding to the proportion of the pure or hard lac resin component of lac. Then the rate again becomes very slow.

Data obtained by other investigators have also been analysed in the light of the above discoveries. The splitting away of water during the hardening of lac has been connected with the fact that the chemical reactions that take place are chiefly of the condensation type.

(4) VISCOSITY OF LAC AND HARD LAC RESIN SOLUTIONS.[16]

Studies of viscosity also leads to a simple empirical relationship between viscosity and concentration, *i.e.*,

$$\eta = \eta_0 e^{kc} \quad \cdots \quad (2)$$

where η is the viscosity of the solution at a given temperature,
η_0 is the viscosity of the solvent at the same temperature,
c is the concentration in terms of gm. of lac per c.c. of solvent,
and k is a characteristic constant.

The constant k is found to vary very slightly from sample to sample but appreciably with temperature. It is slightly greater for hard lac resin than for whole lac, the theoretical implications of equation (2) are unknown, but the variation of k with temperature indicates the formation of aggregates in solution. Equation (2) applies from the lowest concentration to the highest investigated (*i.e.*, from 0.5 to 50%).

Another useful relationship that emerged from these studies was the simple correlation of densities of solutions with their concentrations, expressed as :—

$$\text{Density} = \frac{\text{Wt. of lac} + \text{wt. of solvent}}{\text{Vol. of lac} + \text{vol. of solvent}} \quad \cdots (3)$$

[16] L. C. Verman, *Lond. Shellac Res. Bur. Tech. Paper*, to be published shortly.

The practical usefulness of equations (2) and (3) is self-evident.

Among the numerous chemical modifications studied, two of them have so far proved to be of considerable technical importance: sulphitation of lac[17] and drying oil-lac compositions.[18]

It has been found that lac can be dispersed in water by the aid of sulphurous acid and alkaline bisulphites. Sulphurous acid dispersions yield water-proof films in which lac appears to be in the "B" stage of polymerisation, while bisulphite-dispersions may be made water-proof by pigmentation to form distempers. In both cases, a reaction appears to take place between the dispersing agent and the hard lac resin component. Large-scale experiments are in progress to test the utility of distempers thus prepared.

Since no other natural or synthetic resin reacts in this manner with sulphurous acid, it appears that the sulphitation process may be successfully developed as an identification test for lac.

The difficulties of dispersing lac in drying oils have long been known but they have been overcome by an ingenious process developed by Dr. Bhattacharya. Lac, bleached lac and even polymerised lac have been found to be easily soluble in fatty acids at moderate temperatures. Such solutions esterified with glycerol yield low acid value and normally drying oil-lac varnishes, which may be pigmented and tinted to give normal oil paints. One most important feature of lac-oil varnish is that it can be combined with cellulose lacquers in any proportion. Thus it is possible to combine in one vehicle the properties of cellulose (high gloss, quick drying, etc.) of lac (hardness, good adhesion, etc.), and of oils (flexibility, weathering, etc). Paints made from such combinations have been found to be highly satisfactory.

The completely esterified product of lac and fatty acids yields a product which, when neutralised with aqueous ammonia, provides a basis for emulsion paints and varnishes. Such emulsions have been used as binding media with various materials to prepare special surfaces.

In conclusion, it may be added that the work of the London Shellac Research Bureau has only just begun and judging from the present state of developments it is not unreasonable to conclude that the future holds unknown and great possibilities. The programme of researches in hand is very comprehensive and with the co-operation of the Indian Lac Research Institute and the United States Shellac Research Bureau, effected through the office of the Special Officer, Lac Inquiry, considerable progress may be expected in the near future.

[17] R. Bhattacharya and L. C. Verman, *Lond. Shellac Res. Bur. Tech. Paper*, Jan. 1936, No. 6.

[18] R. Bhattacharya, *Lond. Shellac Res. Bur. Tech. Paper*, to be published shortly.