

SPECIMENS OF SHELLAC MOULDED ARTICLES PRODUCED AT THE INDIAN LAC RESEARCH INSTITUTE, NANKUN.

# NATURAL RESINS

By

**B. S. GIDVANI**

D.I.C., Ph.D., F.R.I.C., A.M.I.Chem.E.

*Director :*

LONDON SHELLAC RESEARCH BUREAU



PLASTICS MONOGRAPH

No. 4b.

*This Monograph is the property of the Trustees of the President's Fund of the Institute of the Plastics Industry, in whom the Copyright is vested. It is issued for purposes of education to members of the Institute and to teachers, and may not be offered for sale to the public.*



The Barn on White Run

[www.donsbarn.com](http://www.donsbarn.com)

COPYRIGHT  
*All Rights Reserved*

*First Published 1946*

MADE AND PRINTED IN GREAT BRITAIN BY  
JARROLD AND SONS LIMITED, NORWICH  
AND ISSUED BY  
THE EXECUTIVE COMMITTEE OF THE PLASTICS INDUSTRY  
WINDSOR HOUSE, VICTORIA STREET, S.W.1.  
PRODUCTION BY GEORGE NEWNES LIMITED



The Barn on White Run

[www.donsbarn.com](http://www.donsbarn.com)

## PREFACE

ALTHOUGH the present-day plastics industry is based almost entirely on synthetic resins, it must not be forgotten that nature abounds in materials which have excellent plastic properties and which have been used for plastic purposes since the earliest times. The use of clay, plaster of paris, bitumens, and natural resins, especially lac, as plastic materials can be traced to several thousand years back. Synthetic resins are the result of man's efforts to copy and, if possible, to improve upon nature's work. However, even to-day, considerable quantities of natural resins are still used in the plastics and allied industries and as a matter of fact a number of synthetic resins on the market are only simple modifications of the natural materials. This monograph deals therefore, with natural resins.

The number of resins occurring naturally is so large that it would be impossible to describe them in a small monograph intended exclusively for the student of plastic industry. Moreover quite a large number of them have not been employed for plastic purposes. In this monograph, therefore, an attempt has been made to present in a simple manner, the occurrence, production, and essential characteristics of only those natural resins, which are of particular interest to the student of the plastic and allied industries.

The monograph is essentially intended for the beginner although the advanced student may find it of interest also, particularly the section dealing with lac in which a summary of the widely scattered published information arising out of research work in recent years has been included. Nevertheless, this work should not be looked upon as a reference book as no attempt has been made to deal exhaustively with any of the resins described.

B. S. G.

CHAPTER	CONTENTS	PAGE
	PREFACE - - - - -	3
I.	INTRODUCTION - - - - -	7
II.	LAC - - - - -	12
	Production and Grades—Cultivation—Lac Hosts —Crops of Lac—Preparation for Commerce— Yield and Quality—Grades of Shellac—Decolor- ised Lac—Bleached Lac—Hard Lac Resins— Exports.	
III.	COMPOSITION AND CHEMISTRY OF LAC - - -	23
	Colouring Matters—Lac Waxes—Odoriferous Sub- stance—Impurities—Lac Resin.	
IV.	CHEMICAL AND PHYSICAL PROPERTIES OF LAC	30
	Characteristics of Various Lacs—Mechanical, Thermal, Optical and Electrical Properties— Analysis—Solubility—Hydrosols.	
V.	PLASTIC PROPERTIES AND POLYMERISATION OF LAC - - - - -	41
	Polymerisation—Accelerators and Retarders of Curing—Curing under Heat and Pressure— Aggregation of Lac.	
VI.	MODIFICATIONS AND RECENT RESEARCH - - -	55
	Esters of Lac—Acyl Esters of Lac—Lac- Glycol Complexes—Electrical Properties— Modification with Sulphur—Modifications with Metallic Oxides.	
VII.	INDUSTRIAL APPLICATIONS OF LAC - - - -	62
	Plastic Industry—Shellac in Gramophone Indus- try—Shellac Mouldings—Moulding Powders— Shellac Injection Mouldings—Shellac in Rubber Mouldings—Grinding Wheels—Shellac in Elec- trical Industry—Mica Products—Laminated Paper Products—Shellac in Paints and Varnishes— Other uses of Shellac.	





VIII. ROSIN - - - - - 99

Methods of Production—Gum Rosin—Yield of Oleoresin—Wood Rosin—Removal of Colour—Grading—Chemistry—Physical and Chemical Properties — Crystallinity — Deterioration — Chemical Modifications — Soaps — Esters — Polymerised Rosin — Oxidised Rosin — Hydrogenated Rosin—Rosin Oil—Rosin in Paints and Varnishes—In Soap—In Paper Industry—In Synthetic Resins.

IX. COPALS: KAURI: DAMMARS - - - - - 112

Copals—Source, Production and Grades—Chemistry of Copals—Running—Modifications and Uses —Kauri—Dammars—Chemical Composition of Dammars — Properties — Dewaxing — Uses of Dammar Wax—Modifications of Dammar.

# NATURAL RESINS

## CHAPTER I

### INTRODUCTION

THE use of resinous materials in the preparation of moulded articles and protective and decorative coatings appears to have been known from very early times. In India and the East, shellac and lac sticks containing pigments have long been used in the manufacture of moulded ornaments and also as a plastic coating known as Indian lacquer. Shellac still is the resin *par excellence* when an alcohol soluble resin is required. Until the beginning of the present century, shellac was the only important resin used as a moulding material. Even to-day approximately 10,000 tons of shellac are used annually in the moulding of gramophone records and a similar quantity is consumed by the electrical and varnish trades.

Until the close of the past century, the term resin implied natural materials produced by vegetable or animal life, which could neither be swollen nor dissolved by water. These natural products had a number of interesting properties; for example, they could be softened by heat, could be dissolved in a number of organic solvents including alcohol to yield adhesives and could give hard, tough and glossy films which provided protection against the corrosive effect of various chemicals and weather. Consequently the natural resins found a ready outlet in various industries and as their uses grew, attention was directed to a systematic study of their physical and chemical properties.

The wide fluctuation in prices associated with all natural commodities coupled with the fact that natural resins originate under conditions which exclude the possibility of obtaining them in a state of great purity or of consistent quality led to a search for substitutes having similar properties and range of applicability as the natural products. Since shellac was the most important and the most expensive amongst all the natural resins, research was particularly directed to synthesise a cheaper substitute.





Attention was especially paid to the reaction between phenols and aldehydes which Baeyer<sup>1</sup> in 1872 had shown gave a sticky substance. Blumer<sup>2</sup> was the first to publish, in 1902, an account utilising this reaction to make a shellac-substitute, but his soluble synthetic resins which could be melted repeatedly, were not satisfactory substitutes. The objects of the work of many other investigators including Baekland<sup>3</sup> were similar, viz. to produce shellac-substitutes and the failure to attain which, incidentally resulted in Baekland's great discovery of commercially utilisable phenolic resins.

Thus the existence of the synthetic resin industry, on which the plastic industry is pivoted, may be argued to owe its existence to shellac. Even to-day, the search for a shellac-substitute is being pursued with unabated vigour because no other natural or synthetic resin possesses the combination of properties associated with it, although synthetic resins are now available which far excel shellac in particular fields of application.

The number of natural resins and their applications are both varied and wide, and it is not possible to include all of them in a small monograph. The more important natural resins are copals, rosin and shellac and of these the most important for the plastic industry is shellac. The monograph is therefore confined almost exclusively to this material although short notes have also been included on rosin, and some of the other more important natural resins.

The physical and mechanical characteristics such as the softening and melting points, solubility, elasticity, flexibility, hardness, tensile strength, etc., of resins are associated with molecular magnitude and configuration. Resinous state is caused by inhibition of crystallisation due to steric factors and all resins are not necessarily highly polymeric. Whilst synthetic resins, both of the rigid and flexible types, are obtained from simple chemically-reactive units by polymerisation through primary valencies, the formation of natural resins is due to amorphous state caused by the co-existence of homologues or isomeric organic compounds, mainly unsaturated acids of an average molecular weight of 300.

The acid and iodine values of most natural resins indicate the presence of constituent unsaturated acids in an uncombined state and such components can often be separated by selective

solvents. The hydroxyl value of those resins that are almost saturated, is usually high, suggesting that the double bonds have probably been oxidised.

Natural resins have usually a low degree of polymerisation. The association or aggregation of individual resin molecules is far short of the state of macromolecules. It is also doubtful whether any polymerisation is caused by primary valencies; polar characteristics and limited mobility of the component acid molecules would retard polymerisation in natural resins.

Most natural resins and/or their components are optically active indicating that the resinous state is due to geometrical as well as optical isomers of the principal component. Formation of anhydrides or lactones would greatly activate the secondary forces and it may be assumed that the resin molecules behave like co-ordinated compounds which can be easily resolved.

Decarboxylation on heating at high temperatures is another interesting property associated with many natural resins. Unlike the synthetic resins, natural resins decompose on heating at high temperatures and therefore are incapable of polymerisation through primary bonds. The double bonds of natural resins, unlike those of drying oils, do not readily form intermolecular complexes on oxidation or on heating.

The possibility of forming macromolecules is limited and the resins are generally brittle. An isogel structure is conceivable only if it is assumed that natural resins other than shellac, amber, and possibly hard copals are formed through weak secondary Van der Waal's forces. Useful mechanical and physical properties can be imparted to natural resins by modifying them with drying oils and other polymerisable materials, but it is doubtful whether a true chemical combination takes place. The resin is probably only dispersed and such compounds cannot be considered as true isogels or isocolloids since the compositions of the dispersed and continuous phases are not identical but different.

Such materials, when homogeneous, can only be considered as solid solutions or as a honey-comb of the polymerised component in which the slightly altered natural resin forms pockets of honey. Decarboxylation, esterification, hydrogenation and other treatments of natural resins only change their polar characteristics and improve somewhat their properties.



It is thus clear that high molecular weight polymers with acceptable physical properties such as elasticity and tensile strength cannot be obtained from natural resins by polymerisation.

Shellac, however, is an exception, and differs from other natural resins in many respects. Firstly it is formed by the condensation of polyhydroxy polybasic acids, (i.e. through primary valencies) and in its original soluble state has an average molecular weight of 1,000. Its plastic characteristics are intermediate between thermoplastic- and thermosetting resins. Though thermoplastic like other natural resins, shellac can be polymerised by heat and other treatments. Some components of low molecular weight are undoubtedly present in shellac and can be removed<sup>4</sup> leaving behind a major fraction with a molecular weight of about 1900<sup>5</sup>, which is comparable with that of many synthetic resins. For instance, the molecular weight of glyceryl phthalate at the point of gelation is believed<sup>6</sup> to be 2,100 while that of "Novolak" at the same point is between 1,200-1,500; the molecular weight of unpolymerised phenol-formaldehyde resin varies between 300 to 600. Ordinary shellac has an average molecular weight of about 1000 and the heat-polymerised shellac at the approach of "C" stage is believed to have a molecular weight of nearly 3000.

Research on natural resins has been carried out with a view mainly to improve their properties particularly for coating compositions but some work has also been directed towards their use in the plastic industries. Treatments such as mastication, hydrogenation and esterification do not materially change the nature and degree of polymerisation of the natural resins.

A natural product is normally associated with varying amounts of impurities but treatments of purification have been evolved with a view to marketing the natural resins in as uniform and as consistent a quality as possible. Rosin and shellac have actually been standardised which enables them to be purchased according to specifications.

#### REFERENCES CITED

- (1) Adolph von Baeyer, *Ber.*, 1872, 5, 25, 280, 1094.
- (2) L. Blumer, Germ. P. 172,877/1902, B.P. 12,880/1902.
- (3) L. H. Baekland, *Ind. Eng. Chem.*, 1909, 1, 149.

- (4) John, *Chemische Schriften*, Berlin, 1806, 5, 1.

- (5) S. R. Palit and G. N. Bhattacharya, *Ind. Lac Res. Inst.*, Res. Note No. 24, 1939.

- (6) H. Honel, *Paint, Oil & Chem. Rev.*, 1931, (23), 91, 19.





## CHAPTER II

### LAC

**L**AC, or shellac, as it is more commonly known, is unique amongst all the natural resins as it is the only one of animal origin.

#### PRODUCTION AND GRADES

India holds a virtual monopoly of this resin, producing about 85 per cent. of the total world output, the rest being produced in Burma, Straits Settlements, Siam, Indo-China, Ceylon and Java. Most of the lac produced in the latter countries is sent to India for refining so that the world receives supplies almost exclusively from India.

The name lac is derived from the Sanskrit word *Lakh* which means 100,000 and was probably given on account of the myriads of insects which swarm together on trees and secrete the resin. It is estimated that as many as 150,000 insects are necessary to produce enough lac for the manufacture of one pound of shellac<sup>1</sup>. Lac is almost exclusively produced by the female insects; the males take little or no part in secretion of lac, their sole function being to fertilise the females.

The lac insect called *Laccifer lacca*, KERR., is a scale insect belonging to *Coccidæ* family and the bug order Hemiptera, and lives on certain trees, shrubs and creepers known as its hosts. The insect is a parasite of these host plants feeding on their sap-juices and if proper care is not exercised in resting by rotation, the plants are injuriously affected and often die.

#### Cultivation

The lac insect begins its life cycle as a tiny red larva crawling over the tree until it finds a tender succulent shoot where it settles. It feeds on the sap-juices of the host-plant by means of a specialised hair-like proboscis inserted through the soft bark of the twig and by some unknown physiological processes produces therefrom the lac resin and waxes. The secretion

forms a cell over its body and is designed as a protection against its enemies and inclement weather. The larva grows under this cell into a full insect and continues to add fresh coats of resin and wax from inside to the cell.

Millions of larvæ settle together, generally attaching themselves to the under-surfaces of the twigs and often extending to the upper surfaces. The secretion of one insect meets that of another so that a thick continuous or semi-continuous encrustation is formed over the twigs. The insect breathes through a pair of holes on the upper surface of the lac cell, blocking of which is prevented by wax filaments; similarly, the pores of the insect are kept free of lac by wax filaments.

Soon after settling on the tree, the female insects shed their skins along with their legs. They cannot move any longer so that the protective cells become also their tombs. They, however, continue to grow rapidly feeding all the time on the sap and secreting the resin. After a few weeks the insects reach maturity and the males now come out of their cells. They have legs, and some, particularly in the winter crops, have also wings. Moving over the encrustation, they fertilise the females and soon after die.

The females now start producing lac more liberally. The females never leave their cells and their bodies act as large incubators in which the eggs develop. When the eggs are ripe, they are oviposited into the space between the lac cell and the body of the insect. Here the eggs are hatched into larvæ which afterwards emerge to start the life cycle anew. The emergence is technically known as *swarming* and continues for about three weeks. The life cycle is generally repeated twice in a period of twelve months but a strain of the lac insect in Mysore has three life cycles in thirteen months.

The lac crop is usually harvested just before swarming is due, but sometimes swarming is allowed to occur before cutting the crop. This provides a natural method of propagation but is not recommended as the host plant does not get a rest to recover from the strain of bearing the parasitic attack of the lac insects. The more favoured method of propagating lac is to tie *broodlac* (6-9 inch long lac-encrusted twigs from which the larvæ have not yet emerged) to previously prepared new host-plant so that the larvæ may at once find their new resting-place. The preparation of the host-plant consists of careful





pruning so that at the time of inoculation, the tree has sufficient new tender shoots ready.

### Lac Hosts

A large number of trees, shrubs and creepers are used as host-plants for the cultivation of lac and these may for convenience be divided into two groups, viz. major hosts and minor hosts.

The major hosts consist of BER (*Zizyphus jujuba*), KUSUM (*Schleichera trijuga*), KHAIR (*Acacia catechu*), PALAS (*Butea frondosa*).

The number of minor hosts, on the other hand, is vast but the most important of these are ARHAR (*Cajanus indicus*), BABUL (*Acacia arabica*) and GHONT (*Zizyphus Xylophra*).

The quality of lac differs with the type of host-plant, that produced on Kusum tree being superior, and having much paler colour.

It has already been stated that the lac insect has two life-cycles in a year which will mean two crops of lac each year. But actually there are four crops in a year because on the Kusum tree, the life cycle of the insect does not coincide with that on the other hosts, as can be seen from Table I.

TABLE I  
CROPS OF LAC

Name of Crop	Time of inoculation	Time of harvesting	YIELD App. % of the total annual lac production
Baisakhi - -	Oct.-Nov.	June-July	60
Katki - -	June-July	Oct.-Nov.	28
Kusumi (also called Aghani and Nagoli)	June-July	Dec.-Jan.	9
Jethwi - -	Dec.-Jan.	June-July	3

In practice, only the Baisakhi and Kusumi crops retain their identities, the others largely get mixed up with the Baisakhi crop. The Baisakhi and Katki crops are the major crops and

are produced by one strain of lac insect while the minor crops Kusumi and Jethwi are secreted by another strain. The main difference between these two strains of the lac insect is their different life cycle as shown in Table I.

Whereas the strain responsible for the minor crops has life of equal duration of six months in both the crops, the life cycle of the strain producing the major crops is eight months in the Baisakhi crop and only four months in the Katki crop. Another difference between the two strains is that while the Kusumi strain can be inoculated on most other host-plants and retains its Kusumi life cycle, the non-Kusumi strain does not take to Kusumi tree, either dying almost immediately or yielding a very poor crop.

### Purification and Preparation of Lac for Commerce

The lac crop is harvested by cutting off from the tree pieces of branches and twigs covered with lac encrustations. The encrustations are then scraped and form the stick-lac of commerce. Besides the woody matter, it contains the resin, colouring matter, wax and insect-bodies. The refining of stick-lac into seed-lac and shellac is mostly carried out by primitive but unique processes which have not altered during the course of several centuries.

The stick-lac is crushed in a hand stone-mill and winnowed in order to separate the woody material leaving behind the lac in a granular form. The lac is soaked in water in stone tubs for 10-12 hours and then a man known as *ghasandar* steps into the tub and rubs it with his feet against the rough bottom and sides of the stone tub. This somewhat strange but effective method breaks up the lac into smaller particles and dissolves out the water-soluble dye, which in a short time colours the water to a deep purple. By repeated changes of water, most of the dye is thus removed. The lac is then collected and dried in air. The dried product is the seed-lac of commerce.

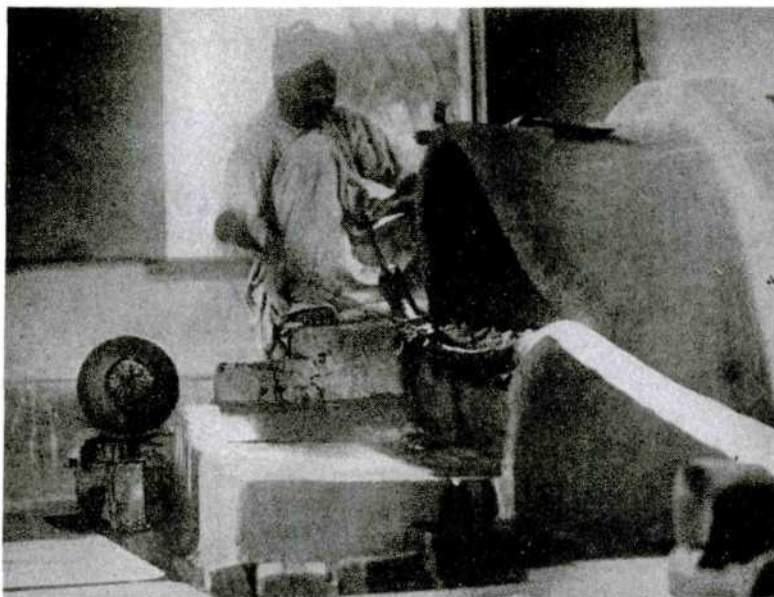
The colouring matter used to be recovered by precipitation with lime and was an important article of commerce until the advent of aniline dyes, when it quickly lost all importance. Silk and wool could be dyed directly to a brilliant orange red with this colouring matter and a wide range of beautiful colours could be obtained as lakes from it but to-day it is an





unwanted by-product of the lac industry and is simply thrown away.

The next stage in the refining of lac is to grade and mix the various qualities of seed-lac, before melting, so that a particular quality of finished product is obtained. A quantity of mixed seed-lacs (except in the case of high quality shellacs for which individual varieties are employed) is then packed into a long, narrow sausage-shaped canvas bag usually 30 feet long and 2 inches in diameter, and held by two workers in



(London Shellac Research Bureau)

FIG. 1. A CLOSE-UP OF THE MELTING-STOVE, SHOWING THE MOLTEN LAC DRIPPING FROM THE CLOTH TUBE ON TO THE HEARTH BELOW

front of an open charcoal fire of the Dutch oven type. As the lac melts, they slowly twist the bag in opposite directions so that molten lac is forced out through the walls of the bag. By this hot-filtration process, which requires great skill in order not to overheat the lac, all the impurities such as woody material, insect debris, dirt, etc., are entirely separated from the resin. The molten lac falls upon a smooth flat stone which has a sunken depression containing water to prevent sticking of the lac, and is reheated on the surface of the bag to drive off the water and to "cook" it properly. Periodically the

16

worker scrapes off the cooked lac from the surface of the bag by means of a large flat knife and when a sufficient quantity has been collected it is passed on to another worker who spreads it out on a porcelain cylindrical jar containing boiling water into a sheet approximately 2-2½ feet long and ¼ inch thick. Now holding the lower corners of the sheet by means of

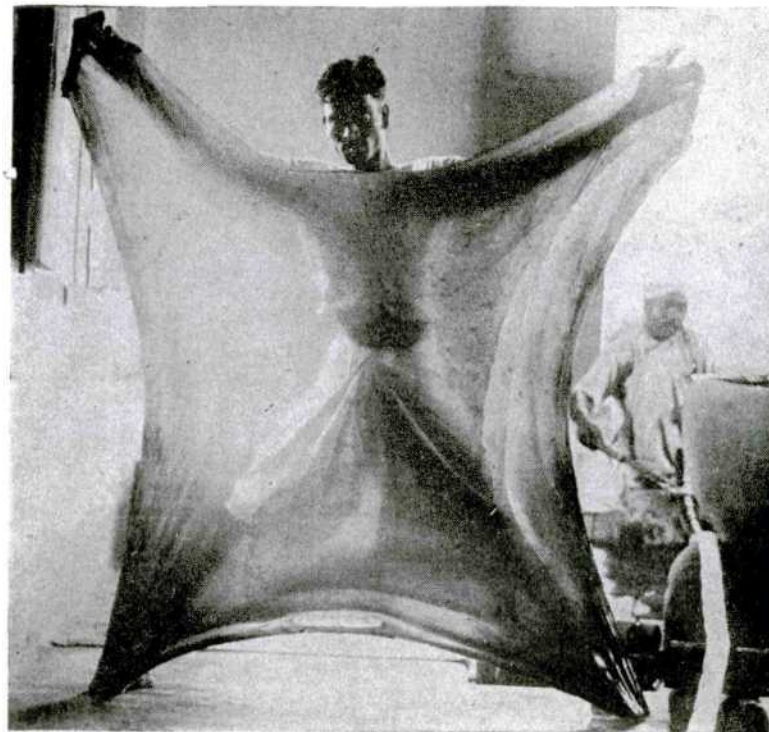


FIG. 2. STRETCHING THE LAC

Note the size and transparency of the stretched lac.

his toes and the upper ones with his hands and grasping the centre of the upper edge with his teeth, he gradually and very skilfully pulls and stretches it into a large thin sheet of the desired size. The operation is carried out in front of the fire to keep the resin plastic. The thin sheet is then broken into small pieces to form shellac flakes which are aerated in a well-ventilated room before packing.

17



The Barn on White Run

[www.donsbarn.com](http://www.donsbarn.com)



### Yield and Quality

The yield and the quality of seed-lac from stick-lac depends upon the type of host-plant, the weather conditions during the cultivation season, whether stick-lac is collected *ari* (before swarming of the larvæ) or *phunki* (after the emergence of larvæ), the extent of washing and the amount of extraneous impurities left in the seed-lac. Kusumi stick-lac, as a rule, gives higher yields than non-Kusumi types. The yield of seed-lac from Baisakhi stick-lac from a particular host-tree is said to be higher than that from Katki stick-lac from the same host.<sup>2</sup> The average yield of seed-lac from all types of stick-lac is reckoned to be about 66 per cent.

The yield of shellac varies with the quality and age of the seed-lac. Fresh seed-lac on account of its better fluidity gives more shellac than the seed-lac which has been stored for some time. Kusumi and Jethwi seed-lacs due to their better melting properties, yield a higher percentage of shellac than the non-Kusumi seed-lacs. However, the average yield of shellac from all types of seed-lacs is estimated to be about 87 per cent. In other words from every 100 tons of stick-lac, approximately 57.42 tons of shellac is obtained.

The average annual production of stick-lac for the ten-year period 1934-35 to 1943-44 is about 47,000 tons yielding some 31,000 tons of seed-lac, and a little over two-thirds of this quantity is converted into shellac.

### Grades of Shellac

There are several grades of shellac made by the native process which are based on colour, the amount of impurities, the amount of added rosin and/or orpiment. Addition of orpiment serves no useful purpose and efforts are being made to discourage the practice. Addition of rosin in limited quantities is justifiable on economic grounds so long as present production methods are retained. Rosin imparts increased fluidity to lac and keeps the polymerised lac dispersed and thus facilitates its flow from the bag. The standard grades of shellac are Pure T.N., London standard T.N. containing 3 per cent. rosin, Fine lemon, Orange, Garnet, etc. Shellacs containing rosin or orpiment are rapidly going out of favour and during the war years only pure grades of shellac have been imported.



### Garnet Shellac

Garnet shellac is made from dark coloured inferior grades of seed-lac mixed with " offals " recovered from the processing of the better grades of seed-lac. The flakes of garnet shellac are usually much thicker—about  $\frac{1}{8}$  inch thick—and are of dark ruby colour.

### Button Lac

Instead of forming sheets, the hot filtered molten lac is sometimes made into small round cakes of about three inch diameter, which are known as button lac. The buttons while still warm are impressed with the trade mark or some distinguishing symbol of the manufacturer.

### Machine-made Shellacs

Appreciable quantities of shellac are also prepared by mechanical processes employing the same principles as used in the hand-process. Another mechanical process consists of extraction of stick-lac with hot alcohol in order to separate dirt and other impurities. The solvent is then distilled off and the molten lac is sheeted on rolls to give flakes. The alcohol extraction process requires a costly plant and is beyond the reach of an average Indian shellac producer; also lac has a strong tendency to retain alcohol and alcohol-processed lacs invariably contain traces (approximately 0.5 per cent.) of this solvent. There have been cases<sup>3</sup> when this type of shellac has been rejected because of excessive flow and frothing due to the presence of a higher percentage of alcohol and such a shellac after storage and loss of residual alcohol by evaporation, has been re-accepted by the same customer. Again some consumers affirm that hand-processed shellac has superior properties which may possibly be due to the occurrence of some orientation of the lac-molecules during the stretching and pulling of the warm sheet and which would naturally be absent in machine-made shellacs.

### Dewaxed Shellac

Ordinary shellac contains about 5 per cent. of a high grade wax which is largely insoluble in alkali solutions and cold alcohol. Consequently shellac solutions in alcohol or alkali are not clear and transparent, but opaque and cloudy. For



many applications, the presence of wax in shellac is objectionable. The lac-wax can be removed by filtration and the wax-free shellac recovered from the filtered solution. The dewaxing is usually carried out *via* the alcoholic solution as when alkali is the medium, the dewaxed lac is characterised by certain undesirable properties such as poor fluidity, reduced polymerisation time, poor keeping qualities and very high colour. For some applications, e.g. moulding, the first two may not be considered as defects but as advantages, but the other two characteristics are definitely objectionable. Recently, however, a modified alkali process has been described<sup>4</sup> which overcomes these difficulties.

#### Decolorised Lac

Grades of shellac are also available from which not only the wax has been removed but also most of the colour. Decolorisation is usually carried out by treatment of the alcohol solution of lac with activated carbon and after filtration, the lac is recovered by distillation of the solvent.

#### Bleached Lac

Alternatively the colour of lac may be bleached with chlorine. The usual process consists of dissolving seed-lac or shellac in aqueous solutions of sodium carbonate, removing the impurities by straining the hot solution, and bleaching the cold strained solution with sodium hypochlorite. The bleached lac is then precipitated with dilute sulphuric acid and washed with water.

When a dewaxed bleached lac is required, the bleached lac solution before precipitation is first filtered to remove the wax. Both waxy and transparent bleached lacs are available in various grades depending upon the colour and the moisture content. Hanks or slabs of bleached lac may contain moisture up to 30 per cent. of their weight while the maximum permissible moisture content for "bone-dry" grades is 6 per cent.

#### Hard Lac Resin

In recent years, a specially treated lac has been marketed under the name of Hard Lac Resin. In a later chapter it is shown that the lac resin can be divided into two fractions by extraction with ether. The ether-soluble fraction constitutes about 30 per cent. of the total resin, is softer and more acidic than the insoluble fraction and does not harden when heated.<sup>5</sup>

The ether-insoluble fraction known as the "Pure Lac Resin" has improved properties such as higher melting point, lower acidity, faster polymerisation rate, etc., and is thus better suited for certain applications. The use of such a pure lac resin in the manufacture of laminated products has been the subject of a German patent.<sup>6</sup>

Extraction with ether, although convenient for laboratory experiments, is not suited for large-scale commercial work. Extraction with other solvents such as toluene, trichlorethylene,<sup>7, 8</sup> acetone,<sup>9</sup> ethyl acetate,<sup>10</sup> gives a product which, although not completely free from the ether-soluble components, possesses improved properties. More recently, extraction of the soft resin has been carried out with dilute alkali solutions<sup>11-14</sup>, and the insoluble part known as Hard Lac Resin is now available in commercial quantities. A range of hard lac resins can be prepared by extracting varying quantities of soft resin from the whole lac.

Grades available are waxy and dewaxed orange and bleached hard lac resins. Special grades of hard lac for use by the electrical industries have been made by removing only 3 per cent. of the soft resin. This grade does not "green" copper since the highly acidic component has been removed in its preparation.

Films from hard lac do not whiten or blush in water as readily as those of ordinary lac. Films, however, tend to crack upon complete drying and hence often require plasticisers.

#### EXPORTS

India exports nearly 90 per cent. of its total annual production, the destination of the exports being all parts of the world. In pre-war times nearly three-fourths of the total exports were shared by the United States of America, the United Kingdom and Germany. The pre-war distribution of lac exports is shown in Table II.

TABLE II

Country					Exports %
U.S.A.	..	..	..	..	39.0
U.K.	..	..	..	..	24.3
Germany	..	..	..	..	10.3
Other Countries	..	..	..	..	26.4



## REFERENCES CITED

- (1) D. Norris, P. M. Glover and R. W. Aldis, "Lac and Indian Lac Research Institute", *Ind. Lac Res. Inst.*, Namkum, Ranchi, India, 1935, p. 25.
- (2) Report on the Marketing of Lac in India, Government of India Press, Simla, 1943, p. 31.
- (3) W. H. Gardner, *Physics*, 1936, **7**, 306-10.
- (4) B. S. Gidvani and N. R. Kamath, *London Shellac Research Bureau*, Tech. Paper No. 26, 1945.
- (5) W. Nagel and M. Koernchen, *Wiss. Veröf. Siemens Konz.*, 1927, **6**, Pt. I, 235.
- (6) Germ. Patent Application No. S.116,610, published on 12th March 1936.
- (7) L. C. Verman and R. Bhattacharya, *London Shellac Research Bureau*, Tech. Paper No. 1, 1934.
- (8) L. C. Verman and R. Bhattacharya, *Ibid.*, Tech. Paper No. 5, 1935.
- (9) M. Venugopalan and H. K. Sen, *J.S.C.I.*, 1938, **57**, 371.
- (10) S. R. Palit, *Ind. Lac Res. Inst.*, Tech. Note No. 7, 1942.
- (11) R. Bhattacharya and B. S. Gidvani, *London Shellac Research Bureau*, Tech. Paper No. 13, 1938.
- (12) R. Bhattacharya and G. D. Heath, *Ibid.*, Tech. Paper No. 16, 1938.
- (13) A. F. Suter & Co., B.P. 196,124/1937.
- (14) A. F. Suter, *et al*, B.P. 515,000/1938.

## CHAPTER III

### COMPOSITION AND CHEMISTRY OF LAC

**A**PART from the lac resin, the stick-lac contains colouring matters, waxes, an odoriferous substance, albuminous matter, and woody fibres and other extraneous impurities. The actual quantity of each of these components naturally varies depending upon a number of factors such as the origin, the host, season, etc., but the following percentage compositions of various types of lacs recorded by Hatchett,<sup>1</sup> are typical.

TABLE III  
COMPOSITION OF VARIOUS LACS

Percentage Composition	Stick-lac	Seed-lac	Shellac
Resin .. ..	68.0	88.5	90.9
Wax .. ..	6.0	4.5	4.0
Colouring matter ..	10.0	2.5	0.5
Gluten .. ..	5.5	2.0	2.8
Impurities .. ..	6.5	—	—
Loss (moisture) ..	4.0	2.5	1.8

### CHEMISTRY OF LAC

Although lac has been known and used for over 2,000 years, its exact composition and the chemistry of its constituents is not yet fully known. The work carried out particularly in the present century is briefly given below.

#### Colouring Matters

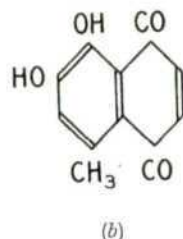
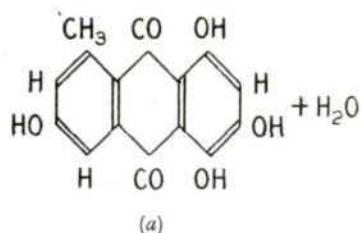
The colouring matter is derived from the bodies of the lac insects and consists of two distinct dye-stuffs one of which is soluble in water and is almost entirely washed out during the conversion of stick-lac to seed-lac. Thus, the colour of seed-lac and shellac is almost exclusively due to the water-insoluble dye-stuff called erythrolaccin. Both the dye-stuffs are soluble in alcohols and in aqueous alkali solutions.





Laccaic acid, the water-soluble dye was first examined by Schmidt<sup>2</sup> in 1887 and later by other investigators.<sup>3-7</sup> It is known to be a hydroxy quinone, but whether it is an anthra-, a benza-, or a naphtha-quinone has still to be settled.

Erythrolaccin, the water-insoluble dye, has also received some attention, but its structure also remains to be ascertained. Tschirch and his collaborators<sup>3,5</sup> believe it to be a tetra-hydroxy methyl anthraquinone with one molecule of water of crystallisation (a), but Spoerri<sup>7</sup> could not obtain an anthracene from it and considers it to be a dihydroxy methyl naphtha-quinone (b).



#### Lac Waxes

The chemistry of lac wax has received more attention<sup>5, 8-16</sup> than that of any other component of lac. In appearance it is not unlike beeswax but is somewhat harder and has a higher melting point. The lac wax is practically insoluble in cold ethyl alcohol but can be separated into two parts by extraction with boiling alcohol in which a larger part is soluble. Both fractions are insoluble in alkalis. The hot alcohol soluble fraction is a mixture of even-number primary alcohols from C<sub>26</sub> to C<sub>34</sub> while the hot alcohol insoluble part is a mixture of esters from which on hydrolysis, even-number primary alcohols C<sub>30</sub>-C<sub>36</sub> and even-number normal fatty acids C<sub>30</sub>-C<sub>34</sub> are obtained.<sup>16</sup>

#### Odoriferous Substance

Lac, on heating gives a characteristic odour which is due to the presence of an odoriferous substance. Tschirch and Lüdy<sup>5</sup> isolated a small quantity of this material in the form of a colourless tablet but its composition has not yet been determined.

#### Albuminous Matter and Other Impurities

Little information is available about the albuminous matter which is derived from the insect-bodies. Some sugars, acids, salts and similar substances, presumably obtained from the sap of the host-plants are also believed to be associated with stick-lac<sup>5</sup>; other impurities are mostly woody matter on which lac has been secreted, insect debris and some sand.

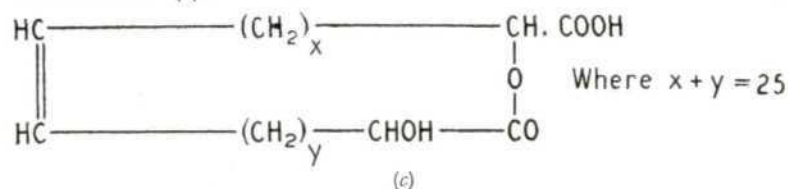
#### Lac Resin

The lac resin is considered<sup>17, 18</sup> to be a mixture of lactones, lactides, inter esters and ethers of a number of hydroxy aliphatic and hydro-aromatic acids. The acidity of lac is attributed to such carboxyl or a portion of carboxyl group which has not inter-reacted due to its positional relationship between the reacting carboxyl and hydroxyl groups.<sup>19</sup>

John,<sup>20</sup> Funk,<sup>21</sup> Unverdoben,<sup>22</sup> Farner,<sup>23</sup> and Endemann<sup>24</sup> are amongst the earliest workers associated with the chemistry of lac. John separated the lac resin into two parts by extraction with ether in which about 30 per cent. is soluble.

#### Ether-Soluble Fraction

According to Tschirch and Lüdy,<sup>5</sup> the ether-soluble fraction on hydrolysis gives a mixture of acids in which aleuritic acid, C<sub>16</sub>H<sub>32</sub>O<sub>5</sub> (a trihydroxy palmitic acid) predominates. From the remaining mixture a monohydroxy palmitic acid has been isolated and the presence of a dihydroxy palmitic acid is also suspected. The structures of the mono- and the dihydroxy acids have not been established so far. Recent investigations<sup>25</sup> however, have not confirmed the presence of either aleuritic acid or other hydroxy palmitic acids in the ether-soluble lac resin.<sup>26</sup> It has been suggested that this material is a lactone with a molecular weight between 510 and 560 having probably the formula (c).



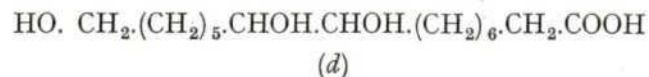
#### Ether-Insoluble Fraction

Harries, Nagel, and co-workers<sup>27-33</sup> have examined the composition of ether-insoluble fraction which constitutes some 70

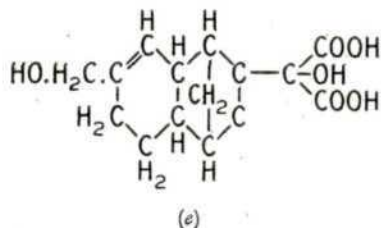




per cent. of the total lac resin. By hydrolysis with caustic alkalis, they obtained a mixture of acids from which two crystalline acids were isolated. One of them was the water-white aleuritic acid, m.p. 101° C. The structure of which was established as,<sup>27, 28, 30</sup>



The other acid called shellolic acid,  $\text{C}_{15}\text{H}_{20}\text{O}_6$ , was found<sup>28</sup> to be a hydro-aromatic acid, m.p. 200–201° C., the constitution of which has not been definitely settled, although Nagel and Mertens<sup>31, 32</sup> have assigned the oxidised tricyclic sesquiterpene structure to it.



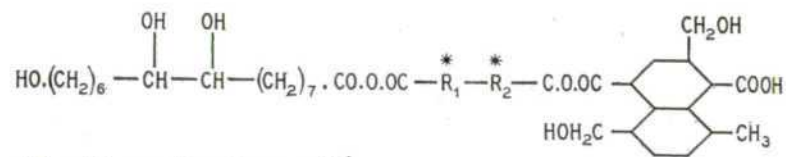
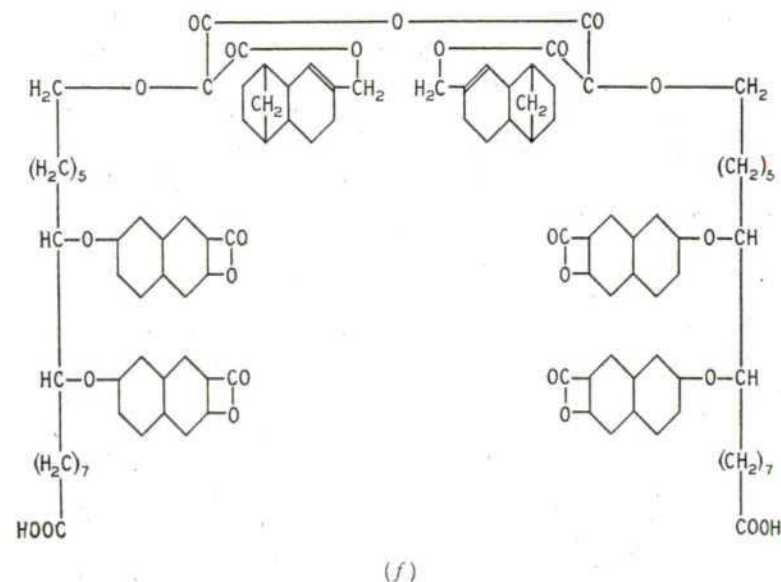
The yield of aleuritic acid obtained by Nagel was 30 per cent. of the "pure lac resin" or about 20 per cent. of the whole lac resin. Recently, however, Gidvani<sup>34</sup> has isolated this acid in a yield of nearly 43 per cent. of the total lac resin and considers that probably it constitutes 50 per cent. of the resin. Shellolic acid on the other hand is always isolated in variable yields (never exceeding 8–10 per cent. of the "pure lac resin"), depending upon the method of separating it from the gummy mixture of acids obtained on hydrolysis of lac. Gidvani believes that this acid is not a primary product of hydrolysis of the lac resin but is formed from unidentified acids or possibly from aleuritic acid itself.

Besides these two acids, American investigators<sup>35–37</sup> have claimed to have isolated kerrolic acid which is a tetrahydroxy acid,  $\text{C}_{15}\text{H}_{27}(\text{OH})_4\text{COOH}$ , m.p. 132° C. and a lactone called laccolic lactone  $\text{C}_{14}\text{H}_{22}(\text{OH})(\text{COO})\text{COOH}$ , m.p. 90–91° C. The lactone is said<sup>36</sup> to consist largely of two crystalline isomers of a  $\text{CH}_2$  homologue of dihydroshellolic acid  $\text{C}_{16}\text{H}_{24}\text{O}_6$ ,

26

which melt at 166° C. and 226° C. respectively. In addition to these two homologues of dihydroshellolic acid, two isomers of dihydroshellolic acid, m.p. 226° and 245° C., and two isomers of shellolic acid, m.p. 206° and 238° C. have also been reported.<sup>37, 38</sup>

It is clear from the foregoing description that lac is a far more complex resin than any other natural or synthetic resin. Since the complete composition of lac is still unknown, a structural formula cannot be assigned to the resin molecule with any certainty. Nevertheless, various formulæ have been postulated for the hypothetical molecule of lac resin,<sup>32, 39–42</sup>



\*  $\text{R}_1$  and  $\text{R}_2$  are the unknown acids.

chief amongst which are formula (f) by Nagel and Mertens<sup>32</sup> and formula (g) by Bhattacharya.<sup>42</sup>

Gardner,<sup>37</sup> on the other hand, does not consider that lac

27



The Barn on White Run

www.donsbarn.com

resin is a chemical entity as would be implied by the above formulæ. He believes it to be a mixture of several different compounds of polyhydroxy acids, the resinous state being caused by the existence in a state of solid solution of the various constituents, which individually lack film forming properties. According to him no single formula can even approximately indicate all its chemical properties. The other postulation<sup>42</sup> is that lac like many synthetic resins, is an isogel in which the molecular weight of individual molecules varies from 300 to 3,000. Nevertheless for all practical purposes, lac behaves like a fairly uniform substance and formula (g) (after modifying to account for increased yield of aleuritic acid isolated by Gidvani<sup>34</sup> and for the other acids isolated by the Americans<sup>35-38</sup>) explains many of its reactions.

Whether the molecule of lac is globular or a chain is uncertain, although recent investigations<sup>43</sup> would indicate it to be of the latter type. The chain is believed to be neither absolutely straight and rigid nor completely kinked and curled, but is intermediate between these two extreme cases.

#### REFERENCES CITED

- (1) C. Hatchett, *Philosophical Trans.*, 1804, 191.
- (2) R. E. Schmidt, *Diss.* Zurich, 1887.
- (3) A. Farner, *Diss.* Bern, 1899.
- (4) O. Dimroth and S. Goldschmidt, *Annal.*, 1913, Bd. 399, 62.
- (5) A. Tschirch and F. Lüdy, *Helv. Chim. Acta.*, 1923, 6, 994.
- (6) H. Mitrea, *Diss.* Bern, 1934.
- (7) P. Spoerri *et al.*, Second Semi-Annual Rept. of Shellac Res. Bureau, Polytechnic Inst., Brooklyn, 1936-37, pp. 46-47.
- (8) A. Kauffmann, *Diss.* Bern, 1887.
- (9) R. Benedikt and F. Ulzer, *Monats. Chem.*, 1888, 9, 579.
- (10) A. Gascard, *J. Pharm. Chim.*, 1893, 365.
- (11) A. Gascard, *Comp. Rend.*, 1914, 159, 258.
- (12) A. Gascard, *Ann. Chim.*, 1921, 15, 332.
- (13) A. Gascard and Damoy, *Comp. Rend. Acad. Sci.*, 1923, 177, 1224, 1442.
- (14) H. H. Schäfer, *Diss.* Bern, 1926.
- (15) A. Tschirch and H. H. Schäfer, *Helv. Pharm. Acta*, 1926, 1, 9.
- (16) A. C. Chibnall *et al.*, *Biochem. J.*, 1934, 28, 2189.
- (17) C. Harries and W. Nagel, *Kolloid Zeit.*, 1923, 33, 248.
- (18) W. Nagel and M. Koernchen, *Wiss. Veröf. Siemens Konz.*, 1927, 6, Pt. 1.

- (19) H. K. Sen, *Science and Culture*, India, 1937.
- (20) John, *Chemische Schriften*, Berlin, 1806, 5, 1.
- (21) Funk, *Buchners Rep. d. Pharm.*, 1819, 5, 338.
- (22) Unverdoben, *Pogg. Annalen*, 1828, 14, 16.
- (23) A. Tschirch and A. Farner, *Arch. Pharm.*, 1899, 23, 35.
- (24) H. Endemann, *Ztschr. Ange. Chem.*, 1907, 20, 1776; 1909, 22, 676.
- (25) *Ind. Lac Res. Inst.*, Annual Report, 1939-40, p. 6.
- (26) S. R. Palit and G. N. Bhattacharya, *J. Ind. Chem. Soc.*, 1939, 16, 258.
- (27) C. Harries and W. Nagel, *Wiss. Veröf. Siemens Konz.*, 1922, 1, Pt. 3, 178.
- (28) C. Harries and W. Nagel, *Ber.*, 1922, 55, 3833.
- (29) W. Nagel, *Ibid.*, 1927, 60, 605.
- (30) W. Nagel, *Wiss. Veröf. Siemens Konz.*, 1931, 10, Pt. 2, 108.
- (31) W. Nagel, and W. Mertens, *Ber.*, 1936, 69, 2050.
- (32) W. Nagel, and W. Mertens, *Ibid.*, 1937, 70, 2173.
- (33) W. Nagel, and W. Mertens, *Ibid.*, 1939, 72, 985.
- (34) B. S. Gidvani, *J. Chem. Soc.*, 1944, 306.
- (35) B. B. Schaeffer and W. H. Gardner, *Ind. Eng. Chem.*, 1938, 30, 333.
- (36) H. Weinberger and W. H. Gardner, *Ibid.*, 1938, 30, 454.
- (37) W. H. Gardner, Chapter on Shellac in "Protective and Decorative Coatings", Vol. I., edited by J. J. Mattiello, published by John Wiley & Sons, New York, 1941, p. 268.
- (38) P. Kirk, "Shellolic Acid and Allied Acids", Thesis, Shellac Res. Bureau, Polytech. Inst., Brooklyn, 1939.
- (39) W. Nagel and E. Baumann, *Wiss. Veröf. Siemens Konz.*, 1932, 11, 99.
- (40) R. Bhattacharya and B. S. Gidvani, *J.S.C.I.*, 1938, 57, 285.
- (41) R. Bhattacharya and L. C. Verman, unpublished information.
- (42) R. Bhattacharya, *Chem. and Ind.*, 1940, 18, 327, cf. B. S. Gidvani, *London Shellac Research Bureau*, Tech. Paper No. 17, 1939.
- (43) A. Bartovics, W. H. Gardner and H. Mark, paper presented before *Amer. Chem. Soc.* at Memphis, April, 1942.





# CHAPTER IV

## CHEMICAL AND PHYSICAL PROPERTIES OF LAC

THE chemical, physical and electrical properties of various types of lacs are recorded and analysed in Tables IV-IX for ease of reference.

TABLE IV  
CHARACTERISTICS OF VARIOUS LACS  
(All analysis on moisture-free basis)

	Seed Lac	Shellac	Garnet Lac	Button Lac	Dewaxed Shellac	Bleached Lacs	
						Trans-parent	Cloudy
Moisture % (max.)	3	2	2	2	2	5-30	5-30
Matter soluble in water % (max.)	1	0.5	0.5	0.3	0.3	0.3-1.0	0.3-1.0
Matter soluble in cold alcohol %	80-95	90-96	90-98	93-96	98-99	98-99	93-95
Wax %	3-7	3-6	0.5	3-4	> 0.2	> 0.2	3-6
Ash % (max.)	2.0	1.0	0.5	0.3	0.3	0.3	1.0
Rosin %	None	0-15	0-25	None	None	None	None

TABLE V  
CHEMICAL CONSTANTS OF VARIOUS LACS  
(All analysis on moisture-free basis)

	Seed Lac	Shellac	Garnet Lac	Button Lac	Dewaxed Shellac	Bleached Lacs
Acid value	60-70	65-75	65-75	65-70	68-75	65-100
Saponification value	210-225	225-230	190-225	200-225	225-230	260-275*
Ester number	140-165	150-165	115-160	130-160	150-162	160-210*
Hydroxyl value	250-270	260-280	270-280	220-270	260-280	—
Iodine value (Wijs' 1 hour)	10-18	16-25	18-40	16-18	12-16	8-12
Thiocyanogen number	—	18-20	—	—	—	9-11

\* Apparent, not corrected for combined chlorine.



TABLE VI  
MECHANICAL PROPERTIES

Property	Type of Lac	Value
Specific gravity (15.5° C./15.5° C.)	Various	1.196-1.217
Ultimate tensile strength	Shellac at 20° C.	132 Kg/cm <sup>2</sup>
Modulus of elasticity	Bleached lac	11.5 × 10 <sup>3</sup> Kg/cm <sup>2</sup>
	T.N. Shellac	13.5 × 10 <sup>3</sup> Kg/cm <sup>2</sup>
	T.N. Shellac heated at 110° C. for 20 hrs.	26.0 × 10 <sup>3</sup> Kg/cm <sup>2</sup>
Adhesion to steel	Shellac	(a) to ordinary plane surfaces, 225 Kg/cm <sup>2</sup>
		(b) to optically plane surfaces, 450 Kg/cm <sup>2</sup>

TABLE VII  
THERMAL PROPERTIES

Property	Type of lac	Numerical value and units
Conductivity	Shellac at 35° C.	2.42 MW/cm/° C.
	Shellac at 63° C.	2.09 „
	Shellac at 25-35° C.	60.5 × 10 <sup>-8</sup> C.G.S. units
	Dewaxed shellac at 25-35° C.	56 × 10 <sup>-8</sup> „
Resistivity	Shellac at 25-35° C.	397 C.G.S. units
	Dewaxed shellac at 25-35° C.	429 „
Specific heat (10-40° C.)	Shellac	0.36-0.38
	Seed lac	0.40-0.41
Coefficient of cubical expansion	Shellac (-80° C. to 46° C.)	$\alpha = 2.73 \times 10^{-4}$ per ° C. $\beta = 0.39 \times 10^{-6}$ per (° C.) <sup>2</sup>
	Shellac (46° C. to 200° C.)	$\alpha = 13.10 \times 10^{-4}$ per ° C. $\beta = 0.62 \times 10^{-6}$ per (° C.) <sup>2</sup>
Softening point	Various	60-70° C.
Melting point	Various	70-90° C.
Fluidity	Various, at 70° C.	2-100 × 10 <sup>-8</sup> Rhe



TABLE VIII  
OPTICAL PROPERTIES

Property		Type of lac	Value
Optical activity ( $\alpha$ ) <sup>25</sup>		Dewaxed, decolourised lac	60.71°
Colour	Intensity	Various	Light to deep
	Hue		Yellow-orange-red (no blue component)
	Tone		Dull to bright
Refractive index		Various	1.515-1.519
Double refraction		Shellac—original	Isotropic
		Shellac—in tension	Negative
Photo-electric long-wave limit		Shellac	2150-2200 Å
X-ray analysis	5 rings	Shellac	
	Medium		6.37 Å
	Strong		5.31 Å
	Strong		5.03 Å
	Medium		4.88 Å
	Weak		4.84 Å
	2 rings	Shellac at 28° C. (11.0 Å ring disappears on further heating)	11.0 Å 4.76 Å
Yellowing index		Bleached lac—original	0.037
		Bleached lac—after 48 hours U.V. irradiation	0.039

TABLE IX  
ELECTRICAL PROPERTIES

Property	Type of lac	Value
Dielectric constant	Shellac	3.6 C.G.S. electro-magnetic units
Dielectric strength	Various	200-500 × 10 <sup>3</sup> V/cm.
Surface resistivity	Shellac film from alcoholic soln.	2.2 × 10 <sup>14</sup> ohms cm. @ 20° C. and 20% R.H.
		1.1 × 10 <sup>14</sup> ohms cm. @ 20° C. and 40% R.H.
Volume resistivity	" "	1.8 × 10 <sup>16</sup> ohms cm. @ 20° C.
		1.2 × 10 <sup>16</sup> ohms cm. @ 30° C.
Permittivity	Shellac	2.3-3.8 C.G.S. electro-magnetic units
Magnetic susceptibility	"	-0.30 × 10 <sup>-6</sup> C.G.S. electro-magnetic units
Dipole moment at 25° C.	Ether soluble portion of dewaxed lac	4.61 Debye units
	Ether insoluble portion of dewaxed lac	7.45 Debye units

Polymerisation time or the "life under heat" of different types of lacs at various temperatures as measured by some investigators<sup>1,2</sup> is graphically shown in Fig. 3.

#### Analysis

A number of methods are available for determining each important property of lac, most of which have been collected together in a recently issued book.<sup>3</sup>

A reference to this book shows that as yet there is no uniformity on test-details on an international basis, although the differences are trifling. There should not be, therefore, any undue difficulties to get international agreement and consolidation of the testing methods. The British Standards Specifications on lac<sup>4</sup> and bleached lac<sup>4a</sup> with slight modifications could easily form the basis of international specifications.



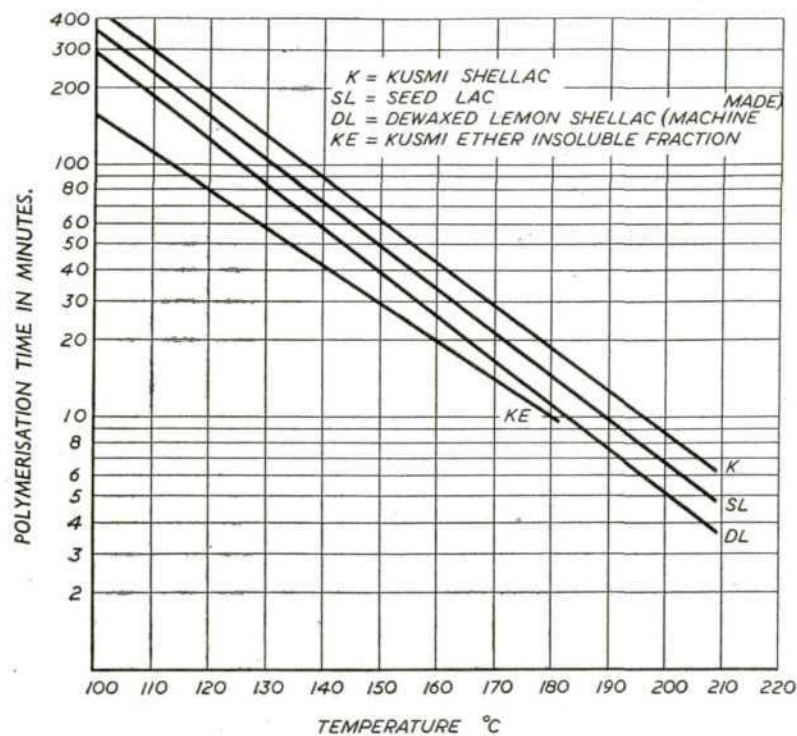


FIG. 3. POLYMERISATION OF VARIOUS LACS

### Solubility

Starting from theoretical considerations that the best solvents for any particular substance are those with the closest chemical resemblance to the latter, Gardner and Whitmore<sup>5</sup> determined the solubility of lac in a number of widely differing solvents. The solubility was qualitatively determined by treating about 0.5–1 g. of lac with 15–20 c.c. of solvent, shaken at intervals for forty-eight hours. The results are shown in Table X, pp. 35 and 36.

Depending upon their solvent power upon lac, solvents can be classified into four groups: hydroxyl containing liquids, solvents with a carboxyl group, solvents with carbonyl group and basic amines. The best solvents are alcohols and related substances containing alcoholic groups. It is seen from the table that hydroxylated solvents invariably dissolved lac even when other free groups were present. This group of solvents is designated the alcoholic group and includes the esters of hydroxy

TABLE X  
SOLUBILITY OF LAC

No.	Solvent	Formula	Boiling Point <sup>1</sup> , °C	Solubility		
				Stick lac	T.N.	Bleached
1.	Methyl alcohol	CH <sub>3</sub> OH	64.57	S	S	S
*2.	Ethyl alcohol (anhydrous)	C <sub>2</sub> H <sub>5</sub> OH	78.4	S	S	S
3.	Ethyl alcohol, 95%	CH <sub>3</sub> CH(OH)CH <sub>3</sub>	82.85	S	S	S
4.	Isopropyl alcohol	C <sub>3</sub> H <sub>7</sub> OH	117.02	S	S	S
5.	n-Butyl alcohol	C <sub>4</sub> H <sub>9</sub> OH	117.02	S	S	S
6.	s-Butyl alcohol	C <sub>4</sub> H <sub>9</sub> (OH)CH <sub>3</sub>	99.8	S	S	S
7.	Isobutyl alcohol	(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> OH	107.9	S	S	S
8.	t-Butyl alcohol	(CH <sub>3</sub> ) <sub>3</sub> COH	83	S	S	S
9.	n-prim.-Amyl alcohol	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> OH	137	S	S	S
10.	Methylpropyl carbinol	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> CH(OH)CH <sub>3</sub>	118.5	S	S	S
11.	sec-Butyl carbinol	CH <sub>3</sub> CH <sub>2</sub> CH(CH <sub>3</sub> )CH <sub>2</sub> OH	128.7	S	S	S
12.	Isobutyl carbinol	(CH <sub>3</sub> ) <sub>2</sub> CH(CH <sub>2</sub> ) <sub>2</sub> OH	131.4	S	S	S
13.	Diethyl carbinol	C <sub>2</sub> H <sub>5</sub> CH(OH)C <sub>2</sub> H <sub>5</sub>	116	S	S	S
14.	Dimethyl ethyl carbinol	(CH <sub>3</sub> ) <sub>2</sub> C(OH)C <sub>2</sub> H <sub>5</sub>	102.5	FS	FS	FS
15.	Fused oil (refined)		110–130	S	S	S
16.	Citronellol	CH <sub>3</sub> C(CH <sub>3</sub> )(CH <sub>2</sub> ) <sub>2</sub> CH(OH)CH <sub>3</sub>	222	SS	SS	SS
17.	Geraniol	(CH <sub>3</sub> ) <sub>2</sub> C(CH <sub>2</sub> ) <sub>2</sub> CH(OH)CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	230	FS	SS	SS
*18.	Diacetone alcohol	(CH <sub>3</sub> ) <sub>2</sub> C(OH)CH <sub>2</sub> COCH <sub>3</sub>	164	S	S	S
*19.	Ethyl lactate	CH <sub>3</sub> CH(OH)COO-C <sub>2</sub> H <sub>5</sub>	154.5	S	S	S
*20.	Ethyl oxybutyrate	(CH <sub>3</sub> ) <sub>2</sub> C(OH)COOC-C <sub>2</sub> H <sub>5</sub>	145.5	FS	FS	FS
21.	Diethylene glycol	HOC <sub>2</sub> H <sub>4</sub> OC <sub>2</sub> H <sub>4</sub> OH	245	S	S	S
22.	Ethylene glycol	HOC <sub>2</sub> H <sub>4</sub> OH	197.37	I	I	I
23.	Propylene glycol	CH <sub>3</sub> CH(OH)CH <sub>2</sub> OH	188	FS	FS	FS
24.	Glycerol	HOCH <sub>2</sub> CH(OH)CH <sub>2</sub> OH	290	I	I	I
25.	Ethylene glycol methyl ether	CH <sub>3</sub> OC <sub>2</sub> H <sub>4</sub> OH	124*	S	S	S
*26.	Ethylene glycol ethyl ether	C <sub>2</sub> H <sub>5</sub> OC <sub>2</sub> H <sub>4</sub> OH	134.8	S	S	S
*27.	Ethylene glycol butyl ether	C <sub>4</sub> H <sub>9</sub> OC <sub>2</sub> H <sub>4</sub> OH	170.6	S	S	S
28.	Ethylene chlorohydrin	ClC <sub>2</sub> H <sub>4</sub> OH	128	S	..	..
*29.	Acetate of ethylene glycol ethyl ether (commercial)	..	..	FS	FS	SS
30.	Acetate of ethylene glycol ethyl ether (distilled)	C <sub>2</sub> H <sub>5</sub> OC <sub>2</sub> H <sub>4</sub> OCOCCH <sub>3</sub>	154	I	I	SS
31.	Ethylene diacetate	CH <sub>3</sub> COOC <sub>2</sub> H <sub>4</sub> OCOCCH <sub>3</sub>	186.7	I	..	..
32.	Diethylene glycol methyl ether	CH <sub>3</sub> OC <sub>2</sub> H <sub>4</sub> OC <sub>2</sub> H <sub>4</sub> OH	189*	S	S	S
*33.	Diethylene glycol ethyl ether	C <sub>2</sub> H <sub>5</sub> OC <sub>2</sub> H <sub>4</sub> OC <sub>2</sub> H <sub>4</sub> OH	186	S	S	S
*34.	Diethylene glycol butyl ether	C <sub>4</sub> H <sub>9</sub> OC <sub>2</sub> H <sub>4</sub> OC <sub>2</sub> H <sub>4</sub> OH	222	S	S	S
35.	Propylene glycol methyl ether (mixture)	CH <sub>3</sub> OCH(CH <sub>3</sub> )CH <sub>2</sub> OH	119–130*	S	S	S
36.	Propylene glycol ethyl ether (mixture)	C <sub>2</sub> H <sub>5</sub> OCH(CH <sub>3</sub> )CH <sub>2</sub> OH	125–136*	S	S	S
*37.	Acetic acid (glacial)	CH <sub>3</sub> COOH	118.1	S	S	S
38.	Formic acid, 85%	HCOOH	100.47*	S	S	S





No.	Solvent	Formula	Boiling Point <sup>1</sup> °C.	Solubility		
				Stick lac	T.N.	Bleached
39.	Propionic acid	C <sub>2</sub> H <sub>5</sub> COOH	140.7	S	S	S
40.	Butyric acid	C <sub>3</sub> H <sub>7</sub> COOH	162.3	S	FS	FS
41.	Palmitic acid	C <sub>15</sub> H <sub>31</sub> COOH	390	I	I	I
42.	Lactic acid	CH <sub>3</sub> CH(OH)COOH	119/12 mm.	FS	FS	FS
43.	Ethyl acetate (pure)	C <sub>2</sub> H <sub>5</sub> COOCH <sub>3</sub>	77.15	I	I	I
44.	Ethyl acetate, 85%	..	..	FS	FS	FS
45.	n-Butyl acetate (pure)	C <sub>4</sub> H <sub>9</sub> COOCH <sub>3</sub>	125.1	I	I	I
46.	n-Butyl acetate 85%	C <sub>4</sub> H <sub>9</sub> COOCH <sub>3</sub>	148	FS	FS	FS
47.	n-Amyl acetate	C <sub>5</sub> H <sub>11</sub> COOCH <sub>3</sub>	137	I	I	I
48.	Isobutyl propionate	C <sub>4</sub> H <sub>9</sub> COOC <sub>2</sub> H <sub>5</sub>	125.8	I	I	I
49.	Diethyl carbonate	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> CO <sub>3</sub>	290.4	I	I	I
50.	Diethyl phthalate	(C <sub>2</sub> H <sub>5</sub> COO) <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	340	I	I	I
51.	Dibutyl phthalate	(C <sub>4</sub> H <sub>9</sub> COO) <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	222.2	I	..	..
52.	Methyl salicylate	OH.C <sub>6</sub> H <sub>4</sub> COOCH <sub>3</sub>	186.1	I	I	SS
53.	Ethyl oxalate	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	208.4	S	FS	I
54.	Ethyl sulfate	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> SO <sub>4</sub>	56.48	I	FS	FS
55.	Acetone	CH <sub>3</sub> COCH <sub>3</sub>	128.39	S	..	..
56.	Mesityl oxide	CH <sub>3</sub> COCH : C(CH <sub>3</sub> ) <sub>2</sub>	202	FS	FS	FS
57.	Acetophenone	CH <sub>3</sub> COC <sub>6</sub> H <sub>5</sub>	79.6	FS	FS	FS
58.	Methyl ethyl ketone	CH <sub>3</sub> COC <sub>2</sub> H <sub>5</sub>	181	SS	SS	SS
59.	Ethyl acetoacetone	C <sub>2</sub> H <sub>5</sub> COCH <sub>2</sub> COCH <sub>3</sub>	..	S	FS	FS
60.	Cyclohexones	C <sub>6</sub> H <sub>10</sub>	184.4	S	S	S
61.	Aniline	C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	198.8	FS	I	SS
62.	Monomethylaniline	C <sub>6</sub> H <sub>4</sub> NH(CH <sub>3</sub> )	206	SS	..	..
63.	Monoethylaniline	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> NHNC <sub>6</sub> H <sub>5</sub>	192.5	I	I	I
64.	Dimethylaniline	(CH <sub>3</sub> ) <sub>2</sub> NC <sub>6</sub> H <sub>5</sub>	215.0	I	I	I
65.	Diethylaniline	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> NC <sub>6</sub> H <sub>5</sub>	115.5	VS	VS	VS
66.	Pyridine	C <sub>5</sub> H <sub>5</sub> N	..	SS	..	..
67.	o-Nitraniline in ethyl acetate	NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	..	FS	..	..
68.	p-Phenylene diamine in ethyl acetate	C <sub>6</sub> H <sub>4</sub> (NH <sub>2</sub> ) <sub>2</sub>	..	SS	SS	SS
69.	Diethyl ether	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O	34.97	S	S	S
70.	Acetaldehyde	CH <sub>3</sub> CHO	20.8	SS	I	I
71.	Butaldehyde	C <sub>4</sub> H <sub>7</sub> CHO	73.4	I	..	..
72.	Acetaldoi	CH <sub>3</sub> CHOHCH <sub>2</sub> CHO	83/20 mm	I	I	I SW
73.	Benzene	C <sub>6</sub> H <sub>6</sub>	79.7	I	I	I SW
74.	Toluene	C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	110.7	I	I	I SW
75.	Xylene	C <sub>6</sub> H <sub>4</sub> (CH <sub>3</sub> ) <sub>2</sub>	142.6	I	I	I
76.	Petroleum ether	C <sub>6</sub> H <sub>14</sub>	156.15	I	I	I SW
77.	Bromobenzene	C <sub>6</sub> H <sub>5</sub> Br	210.85	I SW	I SW	SS SW
78.	Nitrobenzene	C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>	106.6	I	I	I
79.	Amyl chloride	C <sub>5</sub> H <sub>11</sub> Cl	83-84.5	I SW	I SW	I SW
80.	Ethylene dichloride	C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>	..	I	..	..
81.	Cyclochlorohexanes	C <sub>6</sub> H <sub>11</sub> Cl	61.2	I SW	I SW	I SW
82.	Chloroform	CHCl <sub>3</sub>	76.74	I	I	I
83.	Carbon tetrachloride	CCl <sub>4</sub>	46.2	I	I	I SW
84.	Carbon disulfide	CS <sub>2</sub>	..	..	..	..

\* = Common solvents for nitrocellulose.  
 VS = Very rapidly dissolved.  
 S = Soluble.  
 FS = Fairly soluble.  
 SS = Slightly soluble.  
 I = Insoluble.  
 SW = Swells.

<sup>1</sup> As given by varied authorities.  
<sup>2</sup> Approximate.  
<sup>3</sup> For pure formic acid.  
<sup>4</sup> Decomposes at this temperature.

acids, such as those of lactic acid, the polyglycols and their monoethers. The monoalkyl ethers of ethylene glycol are solvents for shellac but if both hydroxyl groups are substituted the alcoholic characteristics disappear and the solvent power is lost. Furthermore, the chain length of the molecule influences the solvent power of a particular solvent.

Variations in solvent action are elegantly demonstrated by the following example: The two poly-hydroxy compounds, ethylene glycol and glycerol, are non-solvents for shellac, whereas propylene glycol, 1, 2- dihydroxy propane, readily dissolves it. It is assumed that the first-named substances closely resemble water in their properties in that they contain several hydroxyl groups close to one another in a relatively small molecule. This, however, does not explain why a mixture of such liquids as acetone and ethylene glycol or acetone and water, which individually do not dissolve shellac, should be a solvent for it.<sup>6</sup> The synergism of shellac may probably explain the latent solvency of pure solvents towards it.

A mixture of two solvents such as methyl and ethyl alcohols is stated<sup>7</sup> to be more efficient than each alcohol individually.

In a study of the solubility of colloidal substances such as shellac, many phenomena which would otherwise be considered abnormal, can readily be explained on the assumption that the solutions obtained are not true but colloidal in nature. The swelling that accompanies preliminary solution with most solvents, the rapid rise in the viscosity with increasing concentration and the adhesive properties of these solutions are manifestation of the colloidal nature of shellac and its solutions. Colloidal substances rarely follow the solubility rules for crystalline solids. The presence of traces of impurities may bring about surprising alterations in their solubility. Thus the importance of the colloidal phase in the solubility of shellac should not be overlooked.

The porosity and flexibility of shellac films is influenced by the solvent. For instance the films produced from methyl alcohol solutions are more porous and brittle than those from ethyl alcohol which in turn are more porous and brittle than the films from propyl and butyl alcohols.

Shellac is also soluble in ketones and organic acids. It readily dissolves in lower fatty acids while solubility in higher fatty acids can be obtained only by heating.



### Solubility in Alkalis

Basic amines as well as aqueous solutions of inorganic alkalis dissolve shellac easily but here too it is doubtful whether true solutions are obtained. Neutralisation of shellac with alkalis is not accompanied by evolution of the theoretical quantity of carbon dioxide.<sup>8</sup> It appears that approximately 25 per cent. of the shellac acids are neutralised and the resulting soap peptises the remaining resin. This would explain the high viscosity of the shellac-acqueous solutions when compared with alcoholic solutions of the same concentration.

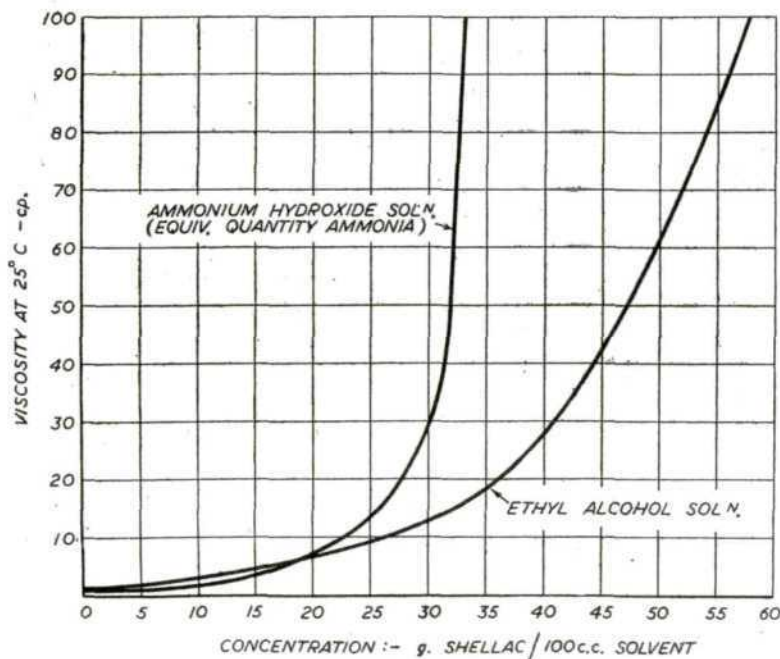


FIG. 4

Soap-formation undoubtedly occurs when most grades of rosin are neutralised with alkalis. The dry soap swells in water and will completely dissolve if a sufficient excess of water is added. With shellac, on the other hand, if a neutralised solution is evaporated to dryness, the residue does not redissolve but swells only, and the degree of swelling steadily decreases with repeated evaporations until it is no longer affected by water.



Again, if shellac dispersions in ammonia are heated in the open, ammonia volatilises, leaving behind a colloidal solution of shellac in water, which is quite stable at pH values down to about 4.8. Thin films from this solution, when baked, are exceedingly hard and compact and show surprising resistance to acids.

### Hydrosols

Another method of forming hydrosols of shellac is to carefully pour with stirring a small quantity of an alcoholic solution of lac in a large excess of water and to concentrate the resulting solution under reduced pressure. The residue obtained is free from alcohol and has a low-water content. A recently developed method for preparing shellac-hydrosols consists of dialysing an ammoniacal solution.<sup>9</sup> Thin transparent films are obtained from these hydrosols by air-drying for about two hours and such films are hard, tough and water-resistant.

Thus it is clear that solubility and solubility-changes of shellac can be explained on the assumption of colloidal nature of shellac, and cannot be accounted for on a purely chemical theory, although some investigators firmly believe that solutions of shellac particularly in organic solvents, like alcohol, acetones, etc., are non-colloidal.<sup>10</sup>

Shellac is also soluble in aqueous solutions of alkaline sulphites and bisulphites as well as sulphurous acid.<sup>11</sup>

### REFERENCES CITED

- (1) S. Ranganathan and R. W. Aldis, *Ind. Lac. Res. Inst.*, Bull. No. 14, 1933.
- (2) L. C. Verman and R. Bhattacharya, *unpublished data*.
- (3) M. Rangaswami and H. K. Sen, "A Handbook of Shellac Analysis", *Ind. Lac Res. Inst.*, 1942.
- (4) B.S.S., 954/1941.
- (4a) B.S.S., 1284/1946.
- (5) W. H. Gardner and W. F. Whitmore, *Ind. Eng. Chem.*, 1929, 21, 226.
- (6) S. R. Palit, *Ind. Lac Res. Inst.*, Bull. Nos. 39, 1940 and No. 46, 1942.
- (7) M. Rangaswami and M. Venugopalan, *Ind. Lac Assoc. for Res.*, Bull. No. 2, 1929.
- (8) H. Wolff, *Farben-Ztg.*, 1922, 27, 3130.



- (9) S. R. Palit, *J. Ind. Chem. Soc.*, 1940, **17**, 375.  
 (10) S. R. Palit, *Ind. Lac Res. Inst.*, Bull. No. 41, 1940.  
 (11) R. Bhattacharya and L. C. Verman, *London Shellac Research Bureau*, Tech. Paper No. 6, 1936.

## CHAPTER V

### PLASTIC PROPERTIES AND POLYMERISATION OF LAC

**S**HELLAC is generally classified as a thermoplastic material since it can be repeatedly re-softened by heat and re-moulded. But shellac is not a true thermoplastic resin since the phenomenon of heat-hardening or "curing" which is characteristic of thermo-setting resins is apparent also in shellac.

Normally the lac resin melts at about 70° C. and is completely soluble in alcohol. When heated at or above its melting point over prolonged periods, it gradually becomes more and more viscous and is converted through a rubbery stage to a tough horny mass that is mostly insoluble in alcohol; hence the practice of "heat-curing" wherein shellac mouldings are baked for a considerable time just below their softening points. The length of the thermoplastic "life" of lac depends upon a number of factors, but particularly on temperature and is generally so long as to preclude its use as a thermosetting resin for compression-mouldings. Incidentally, because of its lengthy life or "polymerisation time" shellac mouldings have a definite scrap value.

#### Polymerisation

The polymerisation time or "life" of lac can be calculated from the equation  $t = Ae^{-\alpha\theta}$ , where  $t$  is the polymerisation time,  $\theta$  the temperature in degrees centigrade,  $e$  the Naperian logarithmic base, and  $A$  and  $\alpha$  the characteristic constants. The constants for three types of lac are as given in Table XI.<sup>1</sup>

Using the common terminology of the plastic industry, the ordinary shellac, which has not been heated, is in A stage; the rubbery lac which is still almost completely soluble in alcohol, but, which has no flow under atmospheric pressure, is in B stage while the fully cured hard horny lac is in the final C stage being approximately 90 per cent. insoluble in alcohol. A distinguishing feature of the C stage lac



is that unlike true thermosetting resins, it can be resoftened by heating at a higher temperature than that at which it has been cured. This explains why shellac mouldings are subjected to a gradual baking schedule. As the softening point of the moulding rises with the time of baking, the temperature of curing is gradually raised till the desired heat-resistance has been obtained. This process is naturally slow and costly and can have but a limited application. The phenomena of heat-hardening of lac has, therefore, been studied in order to devise methods of speeding up the curing.

TABLE XI

	A	$\alpha$
Seed lac ..	$19.5 \times 10^3$	0.0397
Machine made Dewaxed Lemon Shellac ..	$16.23 \times 10^3$	0.0401
Kusumi Shellac	$22.52 \times 10^3$	0.0393

During the polymerisation of lac under the influence of heat, there is a small but steady loss of water resulting from an internal chemical reaction and no other volatile matter is lost.<sup>2-5</sup> With continued heating, increasing proportions of the lac resin become progressively insoluble in alcohol but complete insolubility is not obtained even when temperatures up to decomposition point of lac (about 300° C.) are employed.<sup>6-8</sup> Some 5-10 per cent. of the total lac resin does not harden but remains permanently fusible. The presence of this material which acts as a plasticiser for the rest of the cured lac may account for the lack of true thermosetting properties in shellac. Alcohol insolubility may also be induced by aggregation of lac molecules into miscelles and is discussed later.

The loss of water from shellac when heated at 100° C. for a number of hours and the accompanying reduction in alcohol-solubility is shown in Fig. 5, while Fig. 6 gives the loss on heating for two hours at various temperatures. At 200-220° C. shellac loses 5.3 per cent. water in two hours and on further heating more water is evolved without reaching a constant.<sup>2</sup>

Evolution of water from lac on heating indicates that some

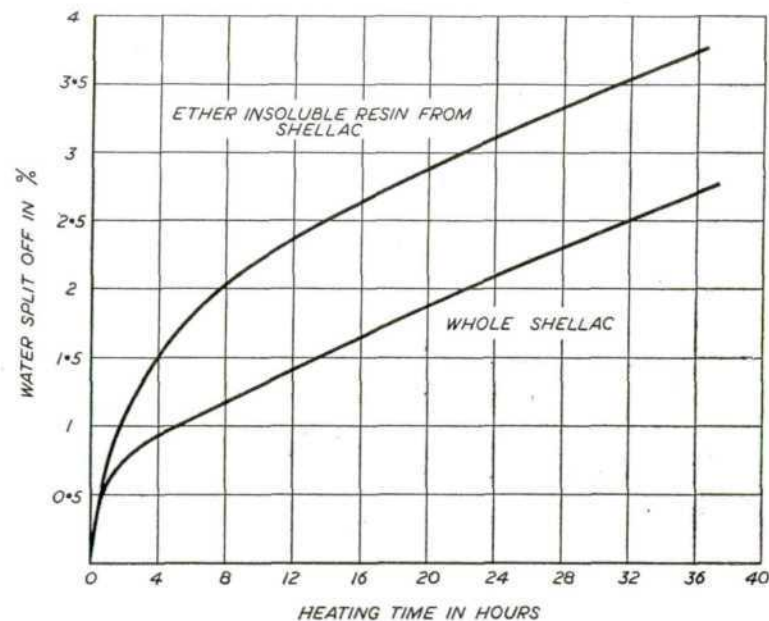


FIG. 5. LOSS OF WATER AT 100° C. (after H. Stäger<sup>9</sup>)

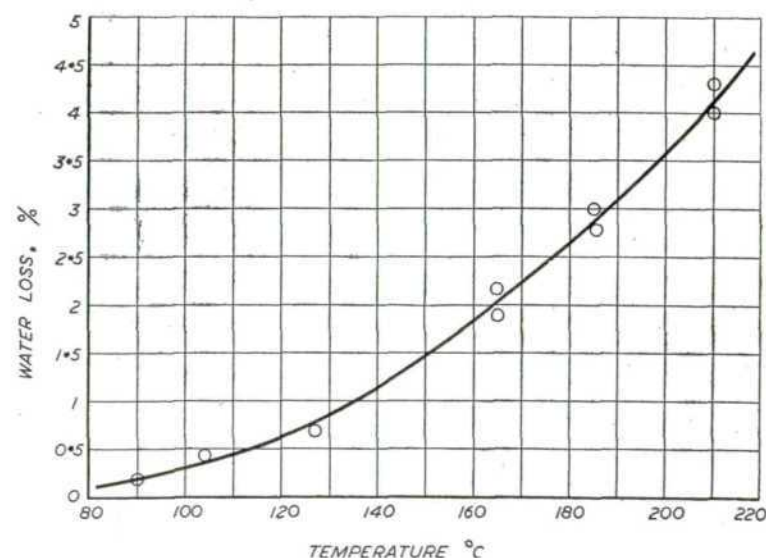


FIG. 6. LOSS OF WATER ON HEATING SHELLAC FOR 2 HOURS AT VARIOUS TEMPERATURES CORRECTED FOR ABSORBED MOISTURE GIVEN OFF AT 38° C. (after Nagel and Koernchen<sup>3</sup>)



inter- and intra-condensation is taking place. An average molecule of the lac resin has five hydroxyl and one carboxyl groups and the following three types of condensation reactions can occur.<sup>10</sup>

- (a) Reaction between a carboxyl and a hydroxyl to give a lactone or a lactide.
- (b) Reaction between two carboxyl groups producing an anhydride.
- (c) Reaction between two hydroxyls to form an ether.

There is also the possibility that the hydroxyl group and a hydrogen atom held to adjacent carbon atoms may combine to produce water and generate a double bond, but since increased unsaturation has not been observed in the polymerised lac, this reaction may be safely excluded.

Although some investigators<sup>5,11</sup> believe that formation of anhydrides is the main reaction responsible for evolution of water from shellac, Gidvani's<sup>10</sup> work clearly precludes such a reaction. He has shown that when all the hydroxyl groups of lac have been blocked by esterification with saturated fatty acids such as acetic, butyric or caprylic acids, the resulting products cannot be hardened even after curing for fourteen days at 175°C. Hence the anhydride-formation alone plays only a small part in the polymerisation of lac and it may be argued that heat-curing of lac leads to the formation of inter- or intramolecular lactones, lactides and ethers. Nagel and Koernchen's<sup>3</sup> study of the reduction in alcohol-solubility when lac is heated for three hours at various temperatures throws further light on the mechanism of polymerisation of lac (Fig. 7).

They have established that no appreciable polymerisation, as judged by the solubility in alcohol, occurs when lac is heated below or just above its melting point for three hours. Between 120°C. and 135°C., hardening is completed in a relatively short time and when approximately 70 per cent. of the resin has become insoluble, the rate of polymerisation is considerably reduced. Polymerisation of lac can take place at lower temperatures if heating is continued for sufficiently long time and can actually begin at 85–90°C., but the rate is so slow that the curing is only half complete after treatment for ten times as long.<sup>9</sup> It is well known that the reactions involving ester and

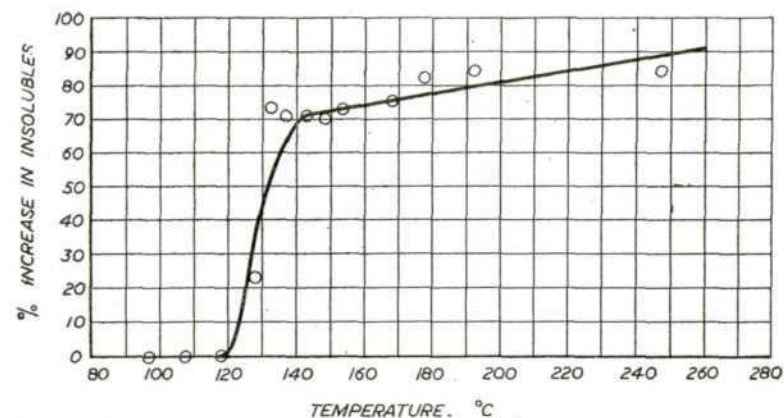


FIG. 7. EFFECT OF HEATING LAC FOR THREE HOURS AT VARIOUS TEMPERATURES (after Nagel and Koernchen<sup>3</sup>)

ether formations are more readily carried out at higher temperatures; the reduced rate of polymerisation after 70 per cent. curing has been achieved, would be due to decreased mobility of the resulting larger molecules so that the active groups can no longer come in contact with each other. Considering the size of the original molecule and the number of centres where condensation can take place, it is highly improbable that there can be any very great increase in molecular weight before a state of immobility is reached. At this stage, condensation will probably cease or at any rate the rate of reaction will be considerably slowed down. A gel structure would be formed, most probably by the same processes which occur in the heating of alkyd resins where a limited reaction between polyreactive substances brings about gelation.<sup>12</sup> The union of only two molecules could produce a gel structure, although it is believed that at least three molecules are involved in the conversion of lac to the rubbery B stage.

It is clear from Fig. 8 that the alcohol solubility of lac remains unaffected so long as it is not heated more than its "life" or the polymerisation time at any particular temperature, i.e. just before reaching the B stage.<sup>1</sup> When heated beyond this stage, the solubility in alcohol is first rapidly reduced and after a certain degree of polymerisation has been reached, the velocity of the reaction slows down considerably. It is apparent, therefore, that the increased molecular magnitude associated with conversion from A to B stage lac does not





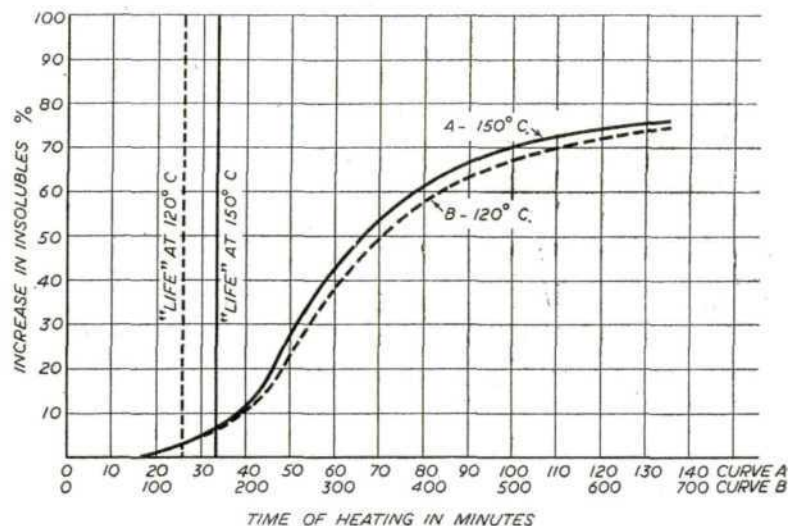


FIG. 8. EFFECT OF HEAT ON ALCOHOL-SOLUBILITY OF KUSUMI SHELLAC

involve any cross linkages, and to obtain a fully cured lac of C stage, probably three molecules of lac will be required to inter-condense. The molecular weight of the fully polymerised lac would, therefore, be of the order of 3,000.

According to Houwink,<sup>13</sup> the high elasticity associated with B stage lac is due to the formation of primary linkages during polymerisation, together with the presence of some secondary linkages, and the existence of a certain amount of soft unpolymerised resin in the interstices of the polymer. The B stage lac has no appreciable flow but can be moulded when subjected to a pressure of  $\frac{3}{4}$ – $1\frac{1}{2}$  tons per sq. inch at 120–160°C. Further heating would not necessarily increase the molecular weight of the polymer but would probably result in cross linkages and the polymer would be of a more compact structure. This explains why the cured lac resin crumbles when subjected to further heat and pressure. The brittleness of the cured lac is thus due to the comparatively low molecular weight of the polymer.

By preventing the early formation of cross linkages, a fairly long chain polymer with rubbery properties can be obtained. This is achieved by reducing the reactivity of the hydroxyl groups as for example by condensing them with ethylene glycol. The lac-ethylene glycol compound which has the same

number of hydroxyl groups as the original lac takes 260 minutes at 150°C. to reach B stage as against 40 minutes in the case of lac.<sup>10</sup> Under certain conditions of polymerisation, a tough, flexible rubber-like material with a molecular weight of nearly 22,000 is obtained from this compound.

### Accelerators and Retarders of Curing

The polymerisation time of lac can be considerably varied by the use of certain materials which can be classified into two groups, viz. (a) accelerators and (b) retarders. The accelerators include most inorganic and organic acids, acid salts, and certain nitrogenous compounds such as hexamine, urea, thiourea and some ammonium salts. On the other hand, alkalis, fatty acids including formic and acetic acids and substituted ureas and thioureas such as dimethyl-, diethyl-, or diphenyl urea or thiourea are retarders.<sup>11</sup>

The efficiency of the accelerator has been measured by determining the ratio of the polymerisation times with and

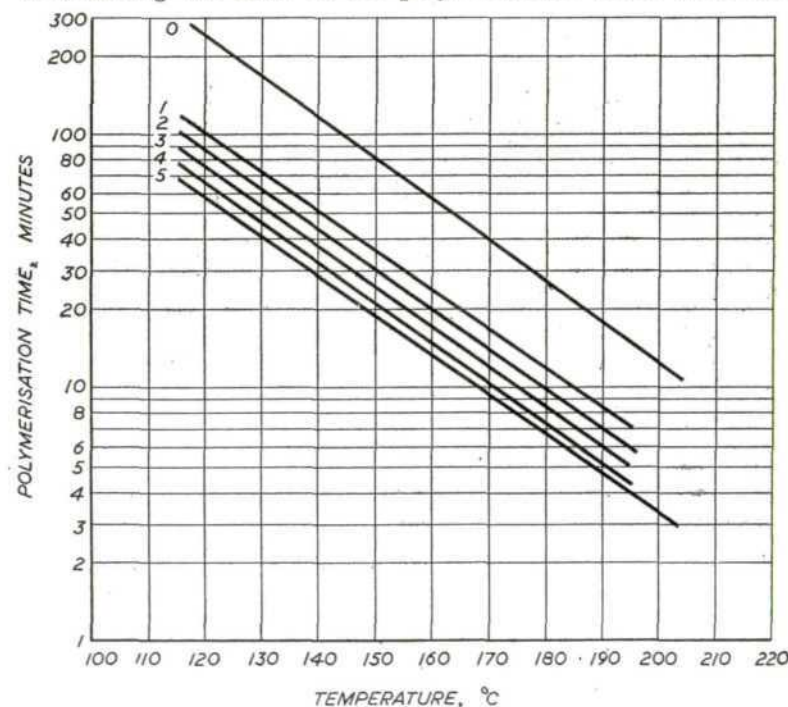


FIG. 9. EFFECT OF TARTARIC ACID (0-5 PER CENT.) ON POLYMERISATION TIME





without the catalyst and it has been possible to distinguish three different types of accelerators.

(A) Those which show the same accelerating efficiency at all temperatures, indicating that the basic processes involved in the heat-curing of lac are not chemically altered but only the rate of reaction is accelerated. Referring to the equation on page 41, the effect of this type of accelerator is to reduce the value of A without affecting  $\alpha$ . Tartaric acid belongs to this group.

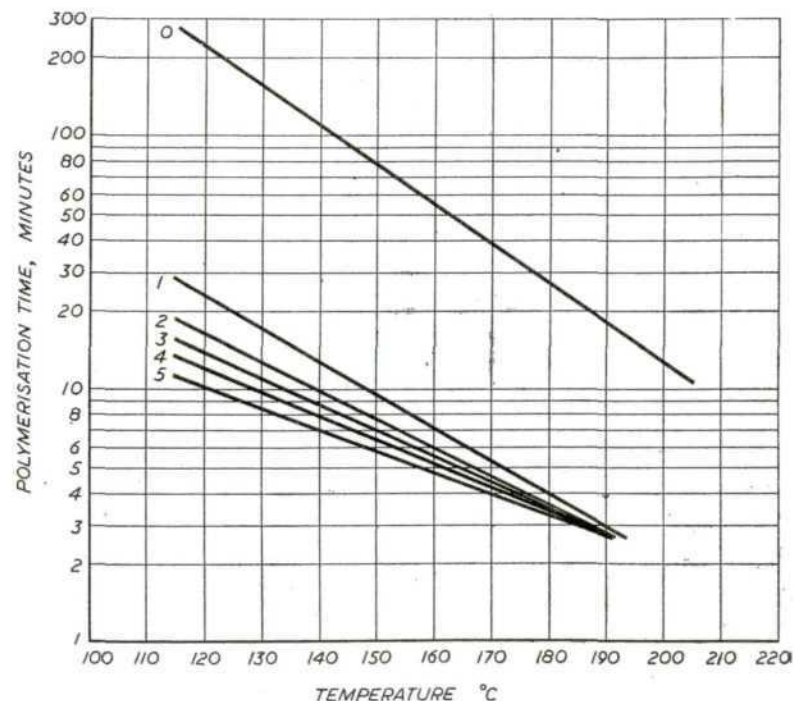


FIG. 10. EFFECT OF OXALIC ACID (0-5 PER CENT.) ON POLYMERISATION TIME

(B) The second type of accelerator is exemplified by oxalic and citric acids which alter the values of both A and  $\alpha$ , showing that some modification of the polymerisation reaction is taking place. The fact that the effect of oxalic acid at low temperature is much more pronounced than at high temperatures may be due to the decomposition of oxalic acid or shellac-oxalic acid compound at the higher temperatures.

(C) The effect of urea, shown in Fig. 11, on the other hand, appears to be entirely different from either of the above cases. The polymerisation time in this case is only slightly affected when 3 per cent. or more of the accelerator is employed, although with less than 3 per cent., the reaction appears to be similar to that with oxalic acid. Aluminium chloride gives similar curves but much more crowded together.

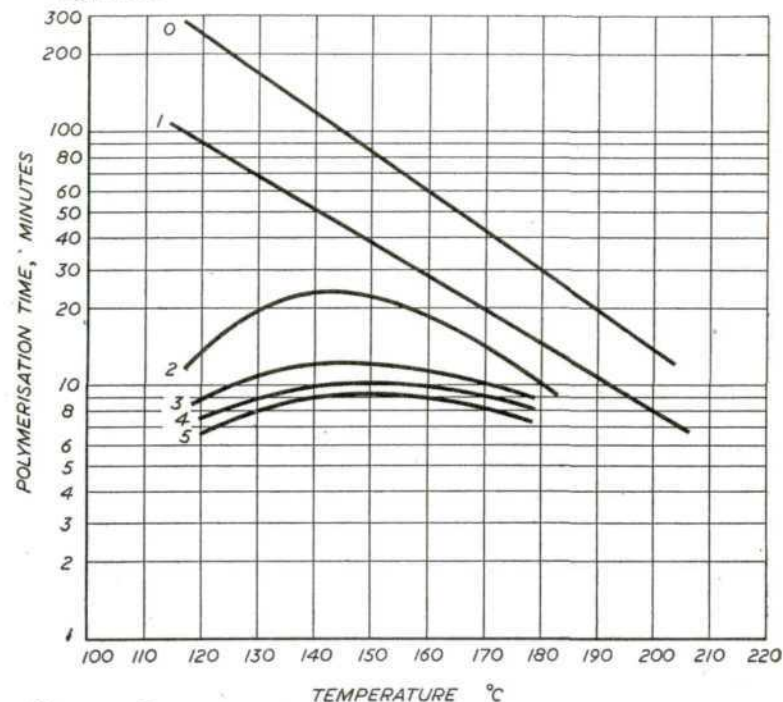


FIG. 11. EFFECT OF UREA (0-5 PER CENT.) ON POLYMERISATION TIME

A probable explanation of this peculiar behaviour of urea is that when melted with shellac it forms an additive compound. It is also known<sup>14</sup> that an additive compound containing 2.8 per cent. urea is formed when urea is added to a concentrated solution of lac in alcohol or acetone.

If it is presumed that two molecules of lac (mol. wt. 1,000) combine with one of urea, the complex would contain 2.91 per cent. urea, and it becomes clear why the polymerisation reaction is not further accelerated when more than 3 per cent. urea is employed.



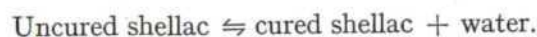
Gardner and Gross<sup>15</sup> consider that a chemical reaction takes place between lac and the added chemical. Alkalis combine with the acids of lac to form salts and thus retard the rate of curing. Accelerators having functionality of more than one are more reactive and combine with two or more lac molecules, giving a product where the chemical acts as a bridge in binding the lac molecules together.

On the other hand, if the accelerator has only one reactive group, it will combine with only one molecule of lac. The molecular weight of the complex in such a case would be increased only by that of the added substance while in the case of polyreactive accelerators, reacting with more than one lac molecule, the size of the polymer is theoretically at least infinite. Thus it seems not unreasonable to state that the key to the production of a true thermosetting shellac may lie in the discovery of a suitable bridging material.

#### Curing Heat and Pressure

The behaviour of shellac under the joint effect of heat and pressure is quite different. The exponential law expressed by the equation on page 41 no longer holds, and the curing is retarded rather than accelerated. Aldis and his collaborators<sup>16, 17</sup> have shown that polymerised lac can be depolymerised by heating it with water under pressure (Fig. 12).

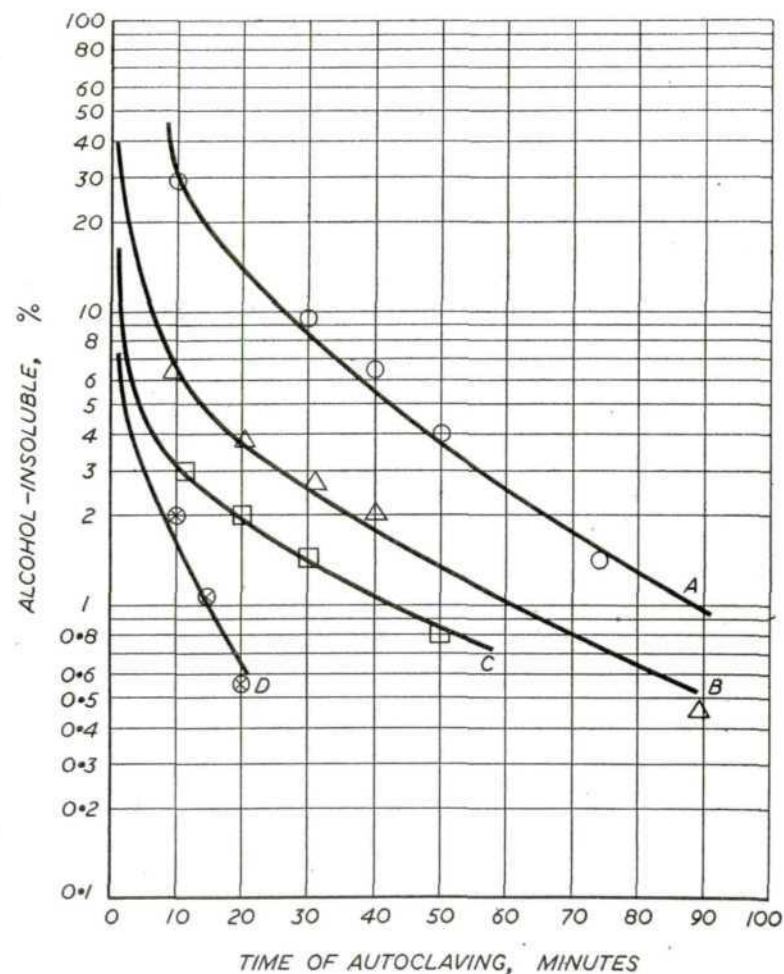
The polymerisation of lac is, therefore, a reversible reaction, viz.,



The reversible nature of the reaction means that shellac cannot be thermohardened under pressure since the water evolved by the condensation reaction of the hardening process would depolymerise the cured portion. To overcome this difficulty, Gardner<sup>18</sup> has suggested that shellac moulding compositions should be precured to the B stage so that most of the water of condensation is already evolved and removed. Such precured compositions can be easily moulded under pressure and have adequate flow.

#### Aggregation of Lac

The polymerisation, accompanied by loss of water when lac is heated, should be distinguished from aggregation described



CURVE	STEAM TEMPERATURE	STEAM PRESSURE kg. sq. cm.
A	148°	3.6
B	174°	7.8
C	193°	12.6
D	208°	17.6

FIG. 12. DEPOLYMERISATION OF "B" STAGE SHELLAC





by Harries and Nagel<sup>2</sup> that results when shellac is treated, as for example, with ether containing a little hydrochloric acid or when it is stored under adverse conditions. The aggregated and the heat-polymerised products are both practically insoluble in alcohol and are more or less infusible,<sup>6</sup> but there is considerable difference in their properties. For example, the aggregated material has the same empirical formula as the original lac, while that of the polymerised lac is somewhat altered due to the loss of water. Whereas the ordinary shellac is completely hydrolysed by 5N caustic potash in 12 hours and aleuritic acid in a yield of about 20 per cent. is obtained, the aggregated material is but slightly hydrolysed in the same period and the yield of aleuritic is considerably diminished.

The properties of the aggregated lac depend upon the degree of aggregation. For instance "pure" lac resin (i.e. ether-insoluble portion of lac) becomes aggregated when shaken with ether containing a little hydrochloric acid. This aggregated form is chemically identical with the parent resin but differs from it in as much as it is infusible even at 240° C., is completely insoluble in boiling alcohol and although soluble in caustic potash, it is difficult to hydrolyse, the hydrolysis being only 12 per cent. in twelve hours with 5N KOH. Dissolution in glacial acetic acid or formic acid, yields a modification of the aggregated lac which is soluble in alcohol and in caustic potash but still slow to hydrolyse and gives in the same period only 3 per cent. aleuritic acid as against 22 per cent. in the case of original "pure" lac resin. If this alcohol-soluble aggregated lac is dissolved in alcohol and precipitated with water, a product is obtained which corresponds to the original pure lac resin, i.e. it is not only soluble in alcohol and alkalis but is also readily hydrolysed to yield normal amounts of aleuritic acid.

In aggregation, a chemical reaction or the primary valencies are not involved. The secondary valencies or the Van der Waal's forces will hold together a number of lac molecules in bundles or miscelles. These aggregates consequently show different properties from the heat-polymerised lac and may be broken up by peptisation into simpler disperse phase. The alcohol-insoluble aggregate may be presumed to be a compact bundle of a number of lac molecules in which no adequate points of attack for chemical action are available. Peptisation

results in dispersion of the aggregates and reformation of the active phase.<sup>9</sup>

A more physical explanation is offered by Harries and Nagel who point out that peptisation occurs through the medium of a hydroxyl carrier, in other words, alcohol. This suggests the loss or redistribution of electrical charges which alter the degree of dispersion and so pave the way for the mutual absorption of the various disperse phases.

The heat-polymerised lac, on the other hand, cannot be restored to its original form by successive solution and precipitation from acetic acid and alcohol. It must be depolymerised by heat, moisture and pressure.<sup>15</sup> Recent investigations<sup>20</sup> have, however, established that both the polymerised and the aggregated lacs can be reconditioned to original state by treatment with aqueous alkali solutions and subsequent precipitation with dilute acids.

#### REFERENCES CITED

- (1) L. C. Verman and R. Bhattacharya, *London Shellac Research Bureau*, unpublished information, cf. A. J. Gibson, *J.S.C.I.*, 1938, **57**, 169T.
- (2) C. Harries and W. Nagel, *Kolloid Zeit.*, 1923, **33**, 248.
- (3) W. Nagel and M. Koernchen, *Wiss. Veröff. Siemens Konz.*, 1927, **6**, Pt. 1, 236.
- (4) T. V. Townend and W. R. Clayton, *Ind. Eng. Chem.*, (Anal. Ed.), 1936, **8**, 108.
- (5) W. Nagel and E. Baumann, *Wiss. Veröff. Siemens Konz.*, 1932, **11**, 99.
- (6) W. Nagel, *Metallborse*, 1930, **20**, 2133, 2190.
- (7) H. Stäger, "Kolloidchemische Technologie", Th. Steinkopff, Dresden und Leipzig, 1927, p. 292.
- (8) W. H. Gardner, *Physics*, 1936, **7**, pp. 306-310.
- (9) H. Stäger, "Elektrotechnische Isoliermaterialien", Wissenschaftliche Verlagsgesellschaft M.B.H., Stuttgart, 1931, p.p. 206-9.
- (10) B. S. Gidvani, *London Shellac Research Bureau*, Tech. Paper No. 17, 1939.
- (11) S. Ranganathan and R. W. Aldis, *Ind. Lac Res. Inst.*, Bull. No. 14, 1933.
- (12) R. H. Kienle, *Ind. Eng. Chem.*, 1931, **23**, 1260.
- (13) R. Houwink, *J.S.C.I.*, 1936, **55**, 247T.
- (14) M. Sarma and M. Sreenivasaya, *Current Science*, India, 1939, **8**, 165.



- (15) W. H. Gardner and B. Gross, *British Plastics*, 1934-35, **6**, 514.  
 (16) S. Ranganathan and R. W. Aldis, *Ind. Lac Res. Inst.*, Res. Note No. 13, 1933.  
 (17) M. Rangaswami and R. W. Aldis, *Ibid.*, Bull. No. 19, 1934.  
 (18) W. H. Gardner, B. Gross, C. C. Whipple and M. Fasig, *British Plastics*, 1934-35, **6**, 571.  
 (19) N. R. Kamath and B. S. Gidvani, *London Shellac Research Bureau*, Tech. Paper No. 25, 1944.



## CHAPTER VI

## MODIFICATIONS AND RECENT RESEARCH

THE meagre knowledge of the chemistry of lac as reviewed in a previous chapter has already proved most invaluable in suggesting ways and means for modifying the lac resin to improve its properties and adopt it for new applications.

For example, formula (g), shows that an average molecule of lac has one carboxyl and five hydroxyl groups; the latter groups have been shown to be alcoholic in nature. Thus lac is both an alcohol as well as an acid and can, therefore, be esterified in two ways, (1) by esterifying the  $\text{-COOH}$  group with an alcohol and (2) by reacting an acid with the  $\text{-OH}$  groups of lac. Both types of reactions have been studied.

**Esters of Lac**

In the first group are the alkyl esters of lac.<sup>1-3</sup> Depending upon the esterifying alcohol, the esters vary from viscous liquids to balsams and hard resins. Thus methyl, ethyl and butyl esters of lac are viscous liquids with increasing viscosity in the named order. They are soluble in most common organic solvents except the aliphatic hydrocarbons and are particularly useful as resin-plasticisers for nitrocellulose lacquers.<sup>4</sup>

Esters with polyalcohols such as glycols<sup>5</sup> and glycerol<sup>4,6</sup> have also been described. Generally speaking, their properties are similar to mono-alcohol esters except that they are more viscous, less volatile and give more flexible films. Shellac-glycerol ester is a tacky solid, but produces non-tacky films on air-drying.

Recent work on these lines is the esterification of hydrolysed lac with ethylene glycol.<sup>7</sup> The product is particularly suitable for plasticising shellac films when flexibility at such low temperatures as *minus* 25° C. is required. When copolymerised with some more shellac, the product gives extremely flexible films. Fabrics coated with this material have remained flexible down to *minus* 40° C. and have successfully withstood the action of various hydrocarbon solvent mixtures. This copoly-



mer has been recommended for coating flexible fuel tanks and the risk of leaching out of the plasticiser in the fuel associated with the presently-employed plasticised vinyl compounds can thus be eliminated.<sup>8</sup>

The glycol ester of hydrolysed lac may also be used in the formulation of lacquers for vulcanised natural and synthetic rubbers and as a component of cements and adhesives. For example, an excellent cement to replace de Khotinsky's cement can be made by heating 80 parts lac with 20 of the ester at 90–100° C. until homogeneous. By altering the proportion of the two constituents, cements with varying properties and to withstand boiling water can be obtained.

#### Acyl Esters of Lac

The esterification of the OH groups of lac with both saturated and unsaturated acids has also been carried out and a range of new materials with quite different properties from those of lac have been produced.<sup>9</sup> For instance shellac is insoluble in hydrocarbon solvents, while shellac-fatty acid esters show increasing hydrocarbon-solubility and alcohol-insolubility, depending upon the degree of esterification. The esters of lower saturated fatty acids can be used as resin-plasticisers in cellulose lacquers, while with unsaturated acids, synthetic drying oils are obtained. Thus, lac-oleic acid ester gives films which can be either air-dried or stoved. The stearic acid ester of lac is a wax-like material and is compatible with paraffin and other waxes. This ester can be used in the formulation of polishes, and waterproofing compositions.

Fatty acids of drying oils and resin acids have also been esterified with lac; the linseed oil fatty acid esters are sticky balsams and may be useful in the manufacture of linoleum. The rosin esters, on the other hand, are hard resins and may be cooked with drying oils to give excellent oil varnishes. When the reaction between rosin and lac is carried out in the presence of phenol, castor oil,<sup>10</sup> or cashew nut shell oil,<sup>11</sup> interesting compositions having excellent weather resisting properties are obtained. These products after pigmenting may be used as outdoor paints without adding any drying oil.

Esterification in the presence of solvents and non-solvents of lac with various organic and inorganic acids such as maleic, phthalic, succinic, adipic, butyric, malic, boric, phosphoric,

etc., has led to the development of a number of new products which have improved gloss, water resistance, elasticity and adhesion.<sup>12</sup> The malic and tartaric acid treated varnishes are particularly suitable for formulation of adhesives, for bonding metal to metal, especially copper to copper and steel to steel.<sup>13</sup>

#### Lac-Glycol Complexes

Instead of esterification, the OH groups of lac may, under certain circumstances, be reacted with OH groups of an alcohol. For example, ethylene glycol and lac can be reacted in such a way that one OH group of each reactant combine together with elimination of water and the resulting complex has the same number of hydroxyl groups as the original lac.<sup>14</sup> Incidentally, it may be mentioned that recent work, as yet unpublished, has shown that the reaction between lac and ethylene glycol may be more complex than simple etherification.

The electrical properties of the lac-glycol compound are excellent, its dielectric strength being 1,100 volts per mil. as against approximately 550 volts per mil. of the unmodified shellac. The optimum properties of the films are only developed when the compound is first heat-polymerised prior to dissolving it in a mixture of solvents for making a varnish. The films from this varnish need baking, although air-drying films can be produced by incorporation of a small quantity of nitrocellulose in the varnish. Adhesion of the varnish films to various surfaces is excellent and when properly cured, they provide very good protection against the attack of various common solvents, mineral and vegetable oils, greases, dilute acids, inorganic salt solutions and other corroding chemicals.<sup>15</sup> The air-drying lacquer has excellent adhesion to vulcanised natural and synthetic rubbers and may be employed for increasing their oil-resistance.

Ordinarily when lac is heated, it results into a rigid, horn-like brittle material of approximately 3,000 molecular weight. Lac-glycol compound, on the other hand, can be heat-polymerised to an elastic rubber-like material having a molecular weight of about 22,000. This rubbery material may be used for the production of such articles as rubberised cloth, artificial leather, etc. Its incorporation in rubber improves the resistance of the vulcanisate to simultaneous action of tension and light. A product claimed to be unaffected by water





and hydrocarbon solvents is obtained by milling together four parts of the lac-glycol compound with one of rubber and small quantities of sulphur, zinc oxide and hexamethylene tetramine.<sup>16</sup>

The lac-glycol compound may be further modified by esterifying its hydroxyl groups with various resin- and fatty acids.<sup>14, 17, 18</sup> The properties of the resulting esters depend upon the type and the proportion of the esterifying acids. The esters with lower fatty acids, though not lacking in film-forming properties, are mostly suitable as resin-plasticisers in cellulose lacquer formulations. The higher saturated fatty acid esters are waxy products which give soft tacky films and cannot be hardened even after prolonged baking. The esters with unsaturated acids such as oleic, crotonic and cinnamic acids, and particularly with the fatty acids of drying oils have interesting properties and may be used to advantage for replacing oil modified alkyds of stoving type. The electrical properties, retention of flexibility on prolonged exposure to high temperatures of the order of 150° C., durability and other ageing characteristics of the lac-glycol-fatty acid complexes are as good as, if not superior to, oil modified alkyds containing the same type and quantity of acid. Table XII shows the comparative electrical properties.

#### Modification with Sulphur

Hardness and resistance to abrasion and water of lac is improved by treatment with sulphur<sup>19, 20</sup> and sulphur monochloride.<sup>21</sup> Mouldings from sulphur treated lacs show superior impact and heat resistance. Treatment with sulphurous acid or alkaline bisulphites gives stable dispersions which have oil-emulsifying properties.<sup>22</sup> When suitably pigmented, quick-drying aqueous paints are obtained. The painted surfaces after a few days' drying can be scrubbed with soap and water. These compositions have also been used in the formulation of white line road paints.<sup>23</sup>

#### Modifications with Metallic Oxides

Metallic derivatives of lac can be prepared by heating lac with a metallic oxide, either alone or in the presence of a high or low boiling liquid, which may or may not be a solvent for lac, and also by adding a solution of metallic salt to an alkaline

solution of lac. Lac derivatives of alkali metals (and also of ammonia) are fully discussed elsewhere. Among the derivatives of other metals, those of calcium, lead and zinc, have been investigated in some detail. In many cases the derivative is not prepared as such, but the modification is carried out in the presence of various other materials to meet individual

TABLE XII

No.	Composition	Con- ditions of stoving	Film thick- ness mils	B.D.V./Mil.			
				In air at 20° C. after ½ hr. in air at 90° C.	In air at 90° C. after ½ hr. in air at 90° C.	In air at 20° C. after condition- ing for 1 tropical cycle *	In air at 20° C. after ½ hr. at -40° C.
1	D.L.-Ethylene glycol-linseed oil fatty acids	0.5 hr. @ 180° C.	3.9	1790	1300	295	1700
2	" "	"	5.6	1740	1220	610	1600
3	D.L.-Ethylene glycol-crotonic acid	1.5 hrs. @ 200° C.	2.5	5700	3500	—	—
4	D.L.-Ethylene glycol-cinnamic acid	2.0 hrs. @ 200° C.	2.5	5700	4300	—	—
5	Commercial alkyd containing the same percentage of linseed oil fatty acid as No. 1	0.5 hr. @ 180° C.	3.6	2060	1030	443	2000

\* One tropical cycle consists of 7 hours in air at 60° C. with a relative humidity of 95-100%, after which the air is allowed to cool to 20° C. overnight.

requirements. For example a casein-lac complex containing calcium oxide is used in the preparation of moulding powders,<sup>24</sup> and lac-lead oxide-linseed oil derivative is used for quick drying oil varnishes suitable for coach-builders, japans, etc.<sup>25, 26</sup> The zinc derivative prepared by heating lac with 30-50 per cent. zinc oxide at a temperature of 120-200° C. has been suggested for bonding micanite.<sup>27</sup>

Materials suitable for the preparation of coating compositions are obtained by carrying out the reaction between lac and the metallic oxide in the presence of a solvent for lac,





usually industrial methylated spirits. Kamath and Bhattacharya<sup>28</sup> have studied the reactions involved, particularly in the case of zinc oxide, and came to the conclusion that in addition to the salt formation with the more acidic portion of lac, coordinate complexes involving the reactive hydroxyl groups are also produced. Such derivatives are different from the many metal soaps described by Simonson and Blair,<sup>29, 30</sup> and Gardner.<sup>31</sup>

Thus it becomes clear that shellac is not only a natural resin with an excellent combination of useful properties but that it can also be used as a raw material for the production of various synthetic resins having properties widely different from those of the parent lac.

#### REFERENCES CITED

- (1) W. Nagel and M. Koernchen, *Wiss. Veröf. Siemens Konz.*, 1927, **6**, 235.
- (2) W. H. Gardner, U.S.P., 1,910,100/1933.
- (3) B. S. Gidvani and N. R. Kamath, *Paint Technology*, 1945, **10**, 35.
- (4) B. S. Gidvani and N. R. Kamath, *Paint Manufacture*, 1945, **15**, 93.
- (5) O. Schmidt and E. Meyer, U.S.P., 1,845,198/1932.
- (6) W. F. Stirling, U.S.P., 1,395,874/1921.
- (7) N. R. Kamath, *London Shellac Research Bureau*, Bull. No. 6, 1944.
- (8) B. S. Gidvani, *J. Oil Col. Chem. Assoc.*, 1945, **28**, 83.
- (9) R. Bhattacharya and B. S. Gidvani, *London Shellac Research Bureau*, Tech. Paper No. 15, 1938.
- (10) R. Bhattacharya, *J. Oil Col. Chem. Assoc.*, 1940, **23**, 145.
- (11) G. M. Ajmani, *J. Sci. Ind. Res.*, India, 1945, **3**, 354.
- (12) M. Venugopalan, *Current Science*, India, 1939, **8**, 14.
- (13) N. N. Murty, *Plastics*, 1945, **9**, 585.
- (14) B. S. Gidvani, *London Shellac Research Bureau*, Tech. Paper No. 17, 1939.
- (15) B. S. Gidvani and N. R. Kamath, *Ibid.* Tech. Paper No. 23, 1944.
- (16) S. Caplan, U.S.P., 2,301,253/1942.
- (17) B. S. Gidvani and N. R. Kamath, *London Shellac Research Bureau*, Tech. Paper No. 28, 1945.
- (18) B. S. Gidvani and N. R. Kamath, *Paint Manufacture*, 1944, **14**, 304.

- (19) M. Venugopalan, *Ind. Lac Res. Inst.*, Res. Note No. 10, 1933.
- (20) M. Venugopalan, *Ibid.*, Bull. No. 18, 1934.
- (21) M. Venugopalan, *Ibid.*, Res. Note No. 12, 1933.
- (22) R. Bhattacharya and L. C. Verman, *London Shellac Research Bureau*, Tech. Paper No. 6, 1936.
- (23) B. S. Gidvani and N. R. Kamath, *Oil & Col. Trades J.*, 1944, **106**, 590.
- (24) *Ind. Lac Res. Inst.*, Annual Repts., 1939-40, p. 12; 1940-41, p. 15.
- (25) H. K. Sen and S. Ranganathan, "Uses of Lac", *Ind. Lac Res. Inst.*, 1939, p. 33.
- (26) A. K. Thakur and G. N. Bhattacharya, *Ind. Lac Res. Inst.*, Res. Note No. 32, 1943.
- (27) W. A. Broughton, U.S.P., 1,953,950/1934 and 1,953,951/1934.
- (28) N. R. Kamath and R. Bhattacharya, *London Shellac Research Bureau*, Tech. Paper No. 22, 1942.
- (29) W. W. Simonson and L. P. Blair, B.P. 127,825/1919.
- (30) W. W. Simonson, U.S.P. 1,309,967/1919.
- (31) W. H. Gardner, W. F. Whitmore and H. J. Harris, *Ind. Eng. Chem.*, 1933, **25**, 696.



## INDUSTRIAL APPLICATIONS OF LAC

THE number of industries using lac is truly astonishing and it will not be an exaggeration to state that no other natural or synthetic resin has proved useful for so many widely different applications. The extensive use of lac in various industries has been due to a remarkable combination of physical properties which characterise this plastic material and which as yet has not been produced in any other individual resin. The various applications of lac are based upon one or more of its following properties :

(1) High dielectric strength (2) Relatively low dielectric constant (3) Non-tracking properties (4) Excellent adhesion on various types of surfaces (5) Excellent bonding properties (6) Low thermal conductivity (7) Small coefficient of expansion and contraction (8) Ease of fusibility and moulding (9) Scrap value due to its thermoplasticity (10) Ability to wet fillers (11) Hardness coupled with resiliency (12) High gloss (13) Production of smooth and durable films from its alcohol solutions by air-drying (14) Solubility in aqueous alkaline solutions and production of good films therefrom and (15) Resistance to a wide range of industrial solvents, particularly petroleum products.

It will be beyond the scope of this monograph to describe in detail all the manifold uses of lac and only the principal uses will be discussed. For convenience, these are grouped together under six headings in Table XIII which also shows the approximate consumption of lac in each of the various industries.

**Plastic Industry**

The employment of resins for plastic purposes is not a modern discovery as many may have been led to believe from the recent advances in this field, but has an antiquity of several thousand years. For example, plastic nature of shellac has been known and exploited in India since prehistoric days, as is



TABLE XIII

Industry	Proportionate consumption of the annual lac production %
Mouldings, including gramophone records .. ..	35-40
Electrical Industries .. ..	15-20
Paints, Varnishes and Lacquers	10-15
Hat Industry .. ..	8-10
Sealing Wax .. ..	3-4
Miscellaneous .. ..	The rest

clear from the following description by John Huyglin von Linschoten who was the first European to undertake a scientific mission to India in 1596 at the instance of the King of Portugal<sup>1</sup>:

“ Thence they dresse their bedsteds withall, that is to say, in turning of the woode, they take a peece of Lac of what colour they will, and as they turne it when it commeth to his fashion they spread the Lac upon the whole peece of woode which presently, with the heat of the turning (melteth the waxe) so that it entreth into the crestes and cleaveth unto it, about the thicknesse of a man's naile : then they burnish it (over) with a broad straw or dry Rushes so (cunningly) that all the woode is covered withall, and it shineth like glasse, most pleasant to behold, and continueth as long as the woode being well looked unto : in this sort they cover all kind of household stufte in India, as Bedsteddes, Chaires, stooles, etc., and all their turned wood worke which is wonderful common and much used throughout all India : the fayrest workemanshippe thereof commeth from China, as it may be seene, from all the things that come from thence, as Desks, Targets, Tables, Cubbordes, Boxes, and a thousand such like thinges, that are all covered and wrought with Lac of all colours and fashions so that it maketh men to wonder at the beautie and brightness of the colour, which is altogether Lac : They likewise use Lac to fill their Golde and Silver workes, that is to say, haftes or knives, and other things, which they make very fayre outwardly of Silver, and inwardly full of Lac. The Indians likewise are so cunning,



that they make Ringes of Gold, which (to man's sight) seem (very) fayre and bright, as though they were all of massy Gold, inwardly they are hollow and stopt with Lac, and cannot be perceyved, unlesse a man bee advertised (thereof)."

This process which is known as Indian turnery is still practised in various parts of India.

Early records also indicate that the ancient Indians used shellac for moulding various articles by casting. However, the modern plastic moulding industry may be considered to date from the close of the last century when the pioneer work with shellac developed into large-scale industry. As early as 1868, patents were filed in the U.S.A. by Gardner<sup>2</sup> and Merrick<sup>3</sup> for shellac moulding compositions. In Europe the use of shellac in the manufacture of sealing waxes can be traced to the Middle Ages while example of elaborately engraved shellac mouldings produced in England in 1876 have been recorded by Rowell.<sup>4</sup> Somewhat later the work of Hyatt,<sup>5</sup> Petit,<sup>6</sup> Marks,<sup>7</sup> Macdonald,<sup>8</sup> James,<sup>9</sup> and others led to the development of what is even to-day the most accurate of mouldings, the gramophone record.

The early work on the moulding of gramophone records has had an important influence on the plastic industry in general. For instance, Macdonald was the first to produce a laminated paper record in 1907 which consisted of a core of a cheap material pressed in-between two sheets of shellac-coated paper. The modern processes of lamination are only extensions of the same principle. Shellac may, therefore, aptly claim to be the parent of modern plastic industry.

From these early foundations the plastics industry has made such a rapid progress during the past two decades that it has come to be generally acclaimed as a wonder of the modern age. The industry has developed in numerous directions. Many new resinous materials have been man-evolved which in many instances have replaced shellac, particularly in the field of general mouldings. Nevertheless, shellac has succeeded in holding a valued place in a number of branches of the moulding industry, viz., in the manufacture of gramophone records, electrical insulators, mica products, paper laminated tubes for insulation, moulded rubber goods, grinding wheels, etc.



The largest outlet for shellac in any single industry is for the manufacture of gramophone records, wherein nearly one third of the total annual production of shellac is consumed.

The early gramophone records were moulded from hard rubber and were not only expensive but also prone to excessive scratching noises.<sup>10</sup> From 1877 onwards numerous attempts were made to overcome these difficulties by the use of other materials but it was not until 1888 that Hyatt succeeded in producing a flat or disc record from celluloid and demonstrated that accurate duplicates could be produced from plastic materials by simple processes.

The record, however, had poor sonorous qualities and the industry did not succeed until several years later when Berliner<sup>11</sup> after having experimented unsuccessfully with several plastic materials, found the advantage of using shellac for this purpose. Since then attempts have repeatedly been made to use practically every known natural and synthetic plastic material for gramophone records but even to-day shellac is the preferred plastic in this field. The reasons for this preference are that shellac combines toughness, flow and heat-stability with hardness and water-resistance. Moreover, due to its low coefficient of expansion, absolute accuracy of the moulding is assured and faithful reproduction of high-tones, without distortion, becomes possible. The industry has also developed techniques which minimise shellac's defects and which are considered as "high-water" mark of moulding technique.<sup>12</sup>

Two types of gramophone records were developed ; one, the common solid record and the other a laminated paper record consisting of a core of some cheap thermoplastic material sandwiched between two sheets of paper coated with shellac.

#### Solid Shellac Record

The composition used for the production of the solid record contains in addition to shellac, manila copal, rosin, cotton flock, carbon black, nigrosine dye and mineral fillers such as barytes, kaolin, slate dust, or silica. The plastic content of the composition is usually between 22-30 per cent. of which the main component is shellac. Cotton flock is usually about



3 per cent. of the total composition, the blacks vary from 2 to 10 per cent. depending upon the quality and grade, and the mineral fillers between 45 to 70 per cent. Great care is taken that all the components are free from dirt, dust and any other coarse and hard particles. The finely ground ingredients are mixed in correct proportion in a large mixer in the cold and the mixture is then hot rolled in small batches on heated rolls until homogeneous.

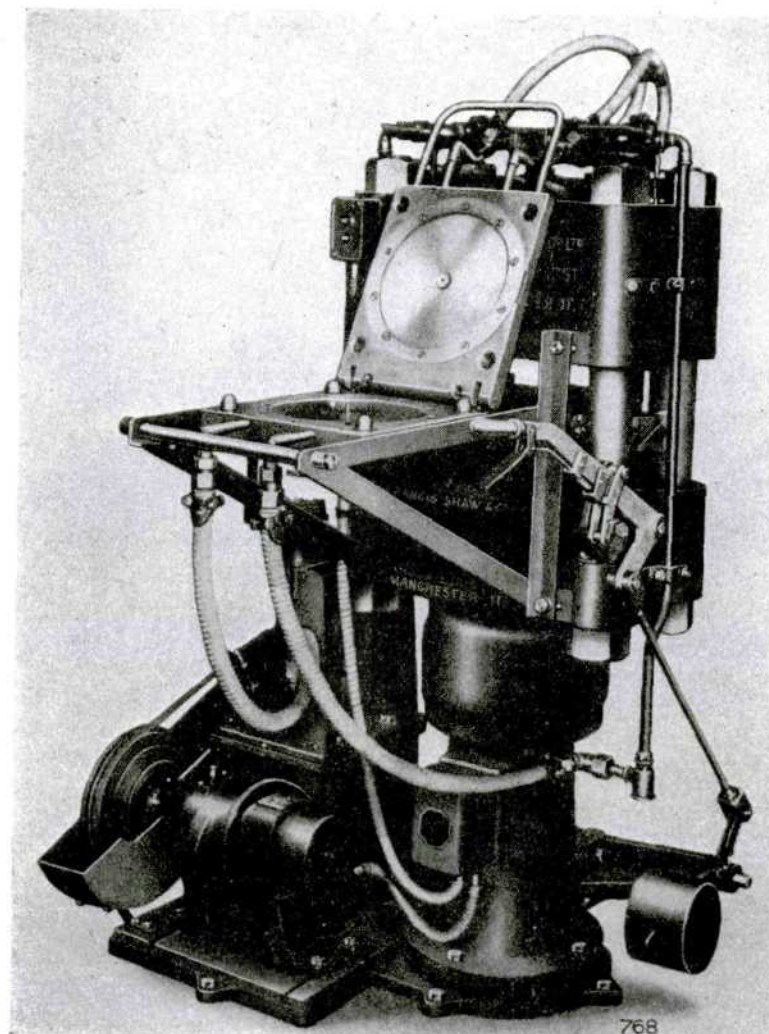
After cooling, the composition is ground finely. This powder is either re-worked on heated rolls and slabbed out into "biscuits" of the correct weight to make a record or the powder is spread out on paper sheets which are subsequently used in the production of laminated records.

### Pressing

The actual moulding is usually carried out in an 80-100 ton hydraulic press which has a hinged counter balanced head. Flash type steel moulds channelled internally for heating and cooling, are permanently attached, one to each platen. A nickel-plated copper "Matrix" or "Stamper" prepared by electrolytic deposition on a wax blank containing the original recording is fixed to each die with a ring which also serves as the edge of the die and controls the thickness of the record.

The system of working the press is quite simple and is usually made semi-automatic. The moulds are heated to 80-100° C. by circulating steam at 90 lbs. pressure, paper labels are placed in position on label pins, and a biscuit that has been previously heated on a hot-table to the correct temperature and rolled into a ball, placed on the centre of the bottom stamper and top of the press is lowered. On locking the press, hydraulic valve opens pushing up the ram to exert a pressure of  $\frac{3}{4}$ -1 ton per sq. inch on the whole of the record surface. The steam is shut off and cold water is circulated through the same channels in the mould blocks until the temperature is reduced to 30-40° C. This takes about 20 seconds. The hydraulic valve then closes and the ram recedes. The press is now opened and the record with its adhering flash is removed. On opening the head, the cold water valve and the relief valve operating the hydraulic ram are cut off and the steam valve opens to heat the mould and thus the cycle is repeated. This system of operation is automatic, so that the operator has only

to load the press with the heated plastic composition and start the cycle by depressing a lever. A complete cycle of all these operations producing one record takes about 30 seconds. The operator removes the flash from each record while the next is being pressed. After trimming and polishing the edges on a lathe, the records are passed on for inspection and packing.



(Francis Shaw & Co. Ltd.)

FIG. 13. AN AUTOMATIC GRAMOPHONE RECORD PRESS





### Laminated Records

These records are prepared, as already stated, by laminating a cheap thermoplastic core with shellac coated papers. The surfacing material on the paper is usually similar to the solid record composition except that the flock is omitted.

The process for making coated paper discs is not a difficult one. The finely ground shellac composition is dropped from a sieve in a dust free chamber, through which the paper discs are passing on a belt conveyor. The coated discs, with their loose coating of powder then travel through a heated tunnel-oven and are finally passed under a cold roller, where the slightly plastic powder is made to coalesce together and adhere to the paper disc.

In another process the paper discs are first coated with a heavy shellac-spirit varnish before dusting them with composition powder. The discs are then dried in a travelling oven and pressed between hot rolls to compact the material.<sup>13</sup> The coated discs can be handled without risk of damaging them and are easily stored until required for use in the press shop.

The core may consist of coal-tar pitch, natural resins and sometimes a little linseed oil, in addition to cheap mineral fillers and usually some mica-powder to increase its strength.<sup>14</sup> The core material is mixed and sheeted into slabs, known as "stock" of approximately the correct weight. Both the "stock" and the coated paper discs used are preheated on a steam-table before use.

The pressing is carried out by placing a hot coated paper disc on the bottom stamper with the shellaced side facing the matrix. The softened "stock" rolled into a ball is placed on the centre of the paper disc and having laid another heated coated paper disc (shellaced side facing upwards) on the top of the stock, the press head is closed and the pressure turned on. As the mould closes, the stock spreads outwards from the centre, the coated paper discs are closely pressed against the surfaces of the matrices and when all the surplus of the stock has overflowed into the sprue-ring, the mould completely closes, forming the coated paper and core into one solid piece, which is removed after rapidly cooling by passing cold water through the mould. A special press has also been developed in which the two dies open like the covers of a book for easy access.



The successful production of laminated records was considered as the highest peak of technical achievement of its time, since the records of this type did not require a plastic material of high lateral flow for pressing. In addition to the price advantage ensuing from the use of a cheap core, the laminating process eliminates air-locks, folded surfaces, burns, etc. These laminated records were manufactured until 1932 in England when the process was abandoned for non-technical reasons.

During the World War I, the price of shellac became prohibitive and it was replaced to some extent by synthetic resins.<sup>15</sup> The performance of these records was, however, very poor and shellac recaptured almost all of the lost ground when its price became normal again. In recent years, however, numerous attempts have been made to use various synthetic plastic materials. It is difficult to realise the amount of ingenuity which has been spent on trying to find plastics for replacing shellac in the manufacture of gramophone records, until a search is made in the patent literature. Only a partial success has so far been achieved with phenolic resins, resorcinol resins, cellulose nitrate, acetate, and xanthate.<sup>16-18</sup> The main drawback with these records is their inferior scratch-resistance; it is estimated<sup>15</sup> that the pressure exerted by the point of a needle on a revolving record is of the order of 50,000-80,000 lbs. per sq. inch. Shellac is therefore almost exclusively employed in the manufacture of the more expensive records.

However, records made from vinyl resin have met with some success, particularly for radio broadcasting work. They are lighter, stronger and less brittle than shellac records. Addition of flock is thus unnecessary and the omission of which results in improved resistance to atmospheric humidity. Owing to the higher fusing point of the vinyl resins, the moulding cycle of these records is longer than that of shellac records.

### SHELLAC MOULDINGS

In addition to its use in gramophone records, shellac has also some outlet in other mouldings, particularly for such small items as dials, discs, knobs, dominoes, draughtsmen, dental plates, etc. Electrical insulators of various designs are also made from shellac moulding powders. Some properties of the filler-free shellac mouldings are recorded<sup>19</sup> in Table XIV.



TABLE XIV  
PROPERTIES OF MOULDED SHELLAC SPECIMENS (FILLER-FREE)

	Baisakhi Seed Lac	Kusmi Seed Lac	Pure Shellac	London T.N. Shellac (3% rosin)	Dewaxed Shellac	Partially Heat-cured Pure Shellac (6 hrs. @ 110° C.)	Lac Wax
Specific Gravity at 155° C. ..	1.156	1.150	1.154	1.151	—	1.150	—
Hardness by Shores Sclero- scope .. ..	60	59	60	61	—	52	—
Hardness by Brinell Test ..	18.5	18.3	18.5	18.1	—	15.9	—
Hardness by Vickers D.P. Test .. ..	16.6	16.3	16.7	16.7	—	18.2	—
Tensile strength by Michaelis's machine (average stress, lbs./sq. in.) ..	486	292	394	275	—	—	—
Electric strength by rapidly applied voltage method at 20° C. volts/mil. ..	423	399	429	420	416	405	356
Electric strength by Step Test method (at 20° C.) volts/mil. ..	—	—	—	277	—	—	340
Power factor at 20° C. (Schering Bridge method) ..	0.0112	0.0139	0.0046	0.0043	0.0072	0.0047	0.058
Dielectric constant at 20° C. ..	3.94	4.05	3.74	3.68	4.01	3.44	1.79
Loss factor at 20° C. ..	0.0379	0.057	0.0169	0.0158	0.028	0.0162	0.104

## Moulding Powders

In the making of shellac-moulding powders, the usual fillers like clay, talc, woodflour, silica, powdered mica, asbestos, cotton flock, jute waste, etc., and diluents like rosin and wax are generally compounded by any of the methods common to the manufacture of moulding powders. A typical composition would consist of 25–30 per cent. shellac and 75–50 per cent. fillers. The moulding powder is usually softened on a steam table at 105–110° C. before compression-moulding it at 120–135° C. under a pressure of 1,000–3,500 lbs. per sq. inch. Before releasing the pressure, the mould must be chilled to 30–40° C.

Very large shellac mouldings have been made by the extrusion process, wherein the heated plastic composition is slowly forced into a closed mould. This process is naturally slow and the moulding cycle may consist of several hours, but the resulting moulding has better mechanical and electrical properties than the ordinary compression shellac moulding, due presumably to curing of the resin during the process.

Shellac has not, however, found any extended use in the modern moulding industry on account of its low heat-resistance, thermo-plasticity and relatively inferior strength. It is true that shellac can be heat-polymerised but the process is so slow that the heat curing of the moulding is not practicable under modern moulding techniques. Thus, shellac is usually treated as a thermoplastic material and shellac mouldings must be cooled before ejection from the mould. It is not surprising, therefore, that a search is continually being made to reduce the curing time and improve the heat-distortion of shellac mouldings. Incorporation of various hard resins such as copals,<sup>20</sup> alkyds,<sup>21, 22</sup> and phenolics<sup>23</sup> is said to improve the heat resistance of shellac mouldings. Fusion point of lac can be increased by addition of phenol,<sup>24</sup> aniline,<sup>25</sup> nitro-naphthol,  $\beta$ -naphthol, nitro-benzol,<sup>26</sup> and *p*-phenylene diamine.<sup>21</sup> Daniels and Snell<sup>28</sup> have suggested the use of 1 per cent. on the weight of lac of various other chemicals for the same purpose.

For reducing the heat-curing time Ranganathan and Aldis<sup>29</sup> have suggested urea, hexamine, oxalic, citric and tartaric acids. The mechanism by which these chemicals accelerate the rate of heat-polymerisation of lac has already been discussed in a previous chapter. Rapid heat-curing of the shellac mouldings can also be obtained by pre-curing of the moulding





compositions to B stage before moulding.<sup>30</sup> Improved shellac-moulding powders are obtained by incorporating small quantities of polyreactive materials such as dicyandiamide, amino sulphonic acids, biguanides, phthalic acid and its anhydride or succinic acid in the powder and pre-curing it to B stage by baking.<sup>31-33</sup> Depending upon the degree of precure, these improved powders can be moulded at 135-170° C. under a pressure of 2,500-3,800 lbs. per sq. inch. Gardner<sup>33</sup> has reported the following properties for these improved mouldings.

TABLE XV  
PROPERTIES OF MOULDED SHELLAC COMPOSITIONS

	<i>New compositions</i>	<i>Previously reported</i>
Compressive strength ..	10,000-16,700 lb./sq. in.	10,000
Tensile strength ..	1,900-3,500 lb./sq. in.	900-2,000
Shock resistance (Izod) ..	2.6-2.9	—
Modulus of elasticity ..	540-640 lb./sq. in.	—
Temperature limit ..	215-280° F.	150-190° F. 175°
Accuracy ..	0.001 in.	0.002 in.
Machining ..	Excellent	Poor; brittle.
Burning rate ..	Slow	High; will not support flame.*
Water absorption, 48 hrs.	1.5-6.00% †	—
Dielectric strength (break-down voltage) ..	470-530 volts per mil.	100-400
Bulking value ..	2-3	—
Moulding temperature °F.	280-330°	240
Moulding pressure ..	2,500-3,500 lb./sq. in.	1,000-1,200
Specific gravity ..	1.20-1.4	1.1-2.7
Effect of light (ultra-violet)	Extremely slight	—
Effect of water ..	Very slight	Very slight
Effect of weak acids ..	Decomposes	Decomposes
Effect of strong acids ..	Decomposes	Decomposes
Effect of alkalis ..	Decomposes	Decomposes
Effect of alcohol 1/1 ..	Very slight	—
Effect of permanganate solution, 3% ..	Decomposes	—

\* True for asbestos composition.

† Asbestos composition, 0.2%.

Contrary to the general belief, shellac mouldings can be produced in all colours, except whites and pale pastel shades. Mottled and other decorative effects are obtained in the usual manner by admixing different coloured powders.

Recent work at the Indian Lac Research Institute has



shown that although addition of 3-6 per cent. urea on the weight of lac in the powder brings about an improvement in the moulding, the powder has poor flow and is difficult to fuse.<sup>34</sup> On the other hand, good moulding powders are obtained by first combining shellac with formaldehyde into a shellac-formal followed by reaction of urea on the latter compound and incorporation of suitable fillers.<sup>35, 36</sup> This type of a powder can be compression moulded at 130-140° C. under a pressure of 4,500-5,500 lbs. per sq. inch and the mouldings can be ejected while still hot. These mouldings have shown heat-resistance of 87° C. by Marten's method, an impact strength of 6 Kg. cm./cm.<sup>2</sup> and 1.0 per cent. water absorption in 24 hours.

A moulding powder containing lac and casein has been described by Venugopalan and Sen.<sup>37</sup> Ammoniacal solution of casein and lac are mixed together and fillers, pigments and mould lubricants incorporated. The mixture after well-kneading is dried, ground and sifted. The powder can be moulded at 135-140° C. using a pressure of 3,250-4,000 lbs. per sq. inch and the mouldings removed while still hot. The mouldings have an impact strength of 3.5 Kg. cm./cm.<sup>2</sup> and heat resistance of 93° C. which can be raised to 110° C. by post-baking.

By modifying lac with melamine and formaldehyde, thermosetting resins are produced.<sup>38</sup> The reaction is carried out in alcoholic solution by refluxing. With appropriate fillers, a moulding powder is obtained that can be moulded at 140-145° C. and 1-1½ tons per sq. inch.<sup>39</sup> The mouldings which are ejected at the same temperature without distortion are both water and heat resistant. Their average impact strength is 6.5-7 Kg. cm./cm.<sup>2</sup>, heat resistance (Martens) 72-74° C. and water absorption of about 1 per cent. in 24 hours.

Mention might also be made of shellac-formaldehyde-coal tar powders<sup>40</sup>, which are mouldable at 140-145° C. under 1-1½ tons per sq. inch. The moulded articles develop considerable hardness, heat and water resistance when baked at 120° C.

### Shellac Injection Mouldings

It has already been mentioned that large mouldings from shellac are made by the extrusion process which is rather slow and therefore necessarily expensive. Research work has, therefore, been directed to developing new shellac compositions



which could be moulded by the injection process. A fairly successful injection powder<sup>41</sup> consists of 60 parts shellac, 40 woodflour, 2 urea, and 1 calcium stearate. Pigments or dyes may be incorporated as desired. This powder can be moulded at 110° C., the time cycle for mouldings being 1-2 minutes depending upon size.

The strength of these mouldings is said to be adequate for ordinary purposes but can be further increased by replacing woodflour with a fibrous filler such as jute waste. Only dry mixing of the ingredients is possible as in the presence of urea, the wet process leads to polymerisation of lac affecting the flow of the powder.<sup>42</sup> However, the main defect of this powder is that because of its poor heat-resistance, it becomes unsuitable for continuous working since the temperature developed in the mould after a few impressions is sufficient to prevent hardening of the moulding.

This difficulty is overcome by the use of alkaline accelerators in place of urea. Five per cent. of either guinidine carbonate or gaunyl urea or 3 per cent. of 0.888 ammonia have given very promising results. The composition of the best powder made so far is :

<i>Parts by Weight</i>			
Ground shellac (30 mesh)	..	100	
Ground jute (12-18 mesh)		66.6	
Kaolin	.. ..	33.3	
or			
Barytes	.. ..	100	
Pigments	.. ..	5	
Calcium stearate	.. ..	3	
0.888 Ammonia	.. ..	3 in 166.6 parts water.	

All the ingredients except ammonia are first dry mixed and then well-kneaded with the aqueous solution of ammonia. After air-drying, the dough is run through steam-heated hot rollers to thoroughly homogenise the powder. The resulting thin sheets are cooled, course crushed (5-10 mesh) and precured in a tray oven at 85-90° C. for 90 minutes. This powder can be moulded in an injection press at 135-150° C. using a pressure of 440 lbs. per sq. inch and may be used for continuous operations for any length of time with efficient water cooled dies. The mouldings are glossy, have an impact strength of 4.2-4.4 Kg. cm./cm.<sup>2</sup> and heat resistance of 68-70° C. (Martens).



The water absorption in 24 hours, however, is 3.5-4 per cent. which admittedly is rather high but it can be brought down to 1.5-2 per cent. by first treating shellac in alcoholic solution with formaldehyde and then with the base. However, for general purposes, it has been suggested that formaldehyde may be dispensed with and the mouldings sprayed with a weather-resisting lacquer.

#### SHELLAC IN RUBBER MOULDINGS

Shellac, even in large quantities, is easily incorporated into rubber by the normal process of mixing on a roll mill. No heating is necessary as the heat of milling is sufficient to soften the shellac and disperse it homogeneously in the mix. Shellac does not assist "breakdown" of the rubber, nor increase the elastic recovery of the mixing, but it accentuates "calender grain" which however disappears during vulcanisation.<sup>43</sup> In mixings containing large proportion of fillers or reinforcing agents, e.g. carbon black or china clay, addition of a small proportion of shellac greatly increases the hardness of the vulcanisate. Shellac has an anti-scorching effect on the rubber-mix and can be used with both raw and alkali reclaimed rubber.

Broadly speaking, incorporation of shellac in rubber results in a mixture which while hot is more fluid, smooth and easily worked and which when cold gives a strong, tough but less elastic product. Shellac also reduces the amount of shrinkage of a tubed or calendered stock making it easier to produce accurate gauges. Under heat, shellac acts as a lubricant, increasing the flow of the rubber mix and thus permitting the production of accurate mouldings with smooth surface, even in intricate designs. This indicates the direction of its usefulness and the various applications where shellac may be incorporated with benefit.

#### Porosity Reduction

Shellac improves the ageing characteristics of rubber. It also reduces the porosity of rubber, for example, addition of 5 per cent. shellac helps to hold the gas longer in balloons.<sup>44</sup> But contrary to the general belief, shellac does not improve resistance of rubber to hydrocarbon solvents.<sup>45</sup>

Rubber mixes containing small percentages of shellac have



been advantageously employed in the manufacture of soles, heels, floorings, mats, tiles, toys and moulded goods, rubber cloth (made by calendering a thin rubber-shellac sheet on to the base cloth) and extruded goods such as tubing, rubber covered cables, etc.

Rubber mixes containing larger proportions of shellac are thermoplastic and may be used with or without fillers, rubber vulcanisers and shellac polymerising agents, as moulding compositions, adhesives, etc. For example, a rubber mix containing not less than 40 per cent. shellac has been suggested as an adhesive for plywood-manufacture.<sup>45</sup> On the other hand, addition of small quantities of rubber to shellac mouldings reduces their brittleness.<sup>46</sup>

#### GRINDING WHEELS

Shellac-bonded abrasive wheels are greatly appreciated in certain industries and are indispensable for such precision work as the grinding and polishing of lenses, razor blades, etc. The slight softening of shellac by heat generated during high speed grinding, gives to the wheel elasticity and power to resist fracture and in this respect has an advantage over phenolic resins.

In the manufacture of shellac-grinding wheels, powder of an abrasive such as carborundum is heated at 170–180° C. until all the moisture is driven out and then mixed with ground shellac in a kneading machine. The quantity of shellac used varies between 5–20 per cent. of the total weight of the wheel depending upon the type of abrasive and whether a soft or a hard wheel is required.

The toffee-like mixture from the kneading machine after cooling is crushed and sifted. The powdered material is then packed into a steel mould and heated either in a hot press or an oven at about 175° C. until the composition has become sufficiently plastic. The mould is then placed in a hydraulic press and subjected to a pressure of 1–3 tons per sq. inch. After thoroughly cooling, the wheel is removed from the mould, conditioned for a few days at room temperature, embedded in sand and gradually heated to 175° C. over a period of 2–3 days. The baking of the wheel at this temperature is continued for 10–12 hours more and after cooling, the wheel is finally milled to size.



#### Cold Mixing

Some manufacturers favour cold mixing of the abrasive with powdered shellac using water-cooled ball mills for fine grit abrasive and rotating mixing pans for coarse grit powder respectively. A small quantity of a drying oil is usually incorporated in the latter case to prevent separation of the shellac from the abrasive. The resulting mixture is then moulded as described previously.

#### SHELLAC IN THE ELECTRICAL INDUSTRY

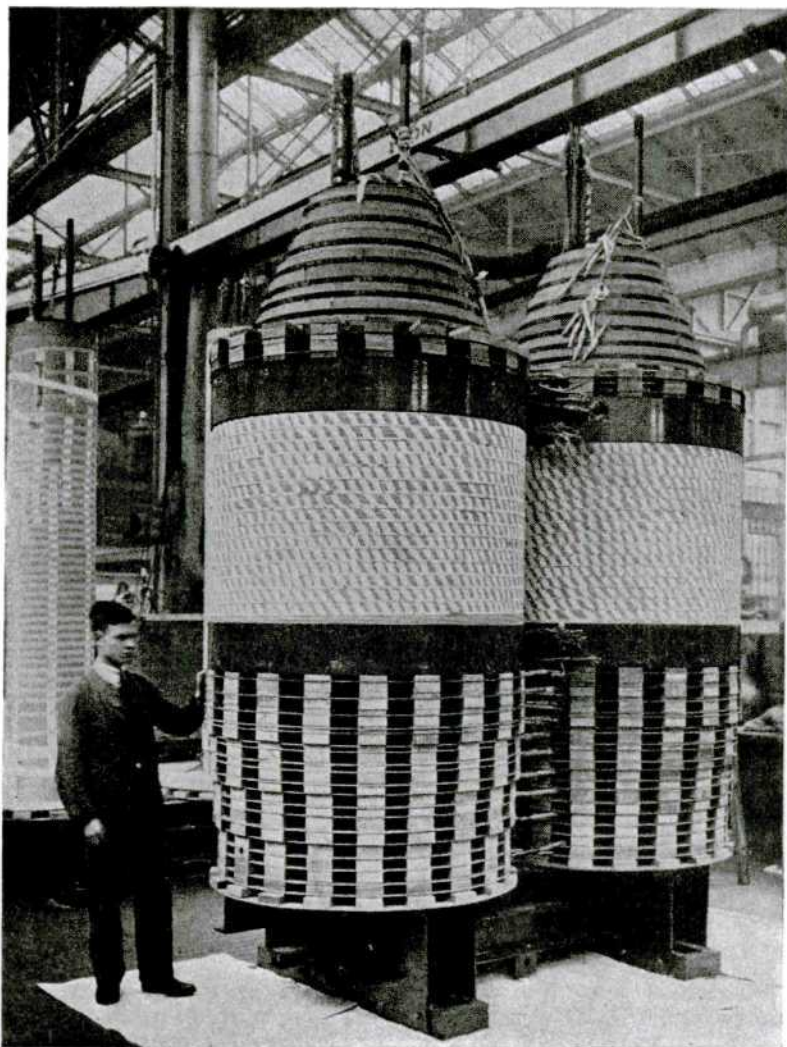
Shellac has always occupied a high place among dielectric materials and appreciable quantities are consumed annually in the electrical industry for insulating varnishes, adhesives and moulded insulators. The early use of shellac in the electrical industry was for replacing hard rubber insulators when this material became too expensive in the early years of the present century.<sup>47</sup> The moulding processes at the beginning were naturally similar to those of the gramophone record industry, but as the use of shellac expanded, the two fields gradually became increasingly divergent.<sup>48</sup> Its unique property of having both thermoplastic and thermosetting characteristics was turned to advantage by post-curing the moulded articles to obtain the required degree of heat-resistance.

The great advantage of shellac insulators is their freedom from surface carbonisation due to high-voltage silent discharges, and non-conductance and non-extension of carbon tracks formed by sparking discharges. Shellac insulators are therefore used in most high voltage installation as the danger of short circuit which would result from the use of phenolic-resin insulators is minimised. Moreover, shellac insulators are not as brittle and fragile as porcelain and will not readily shatter when struck. For instance, if a porcelain insulator on a transmission line is struck with a stray bullet, it will be completely shattered and the service may be impaired for a considerable time, whereas with a small shellac insulator, the bullet will pass through it without destroying its insulating properties.

In the electrical industry, shellac is generally used in the manufacture of the following :

- (1) Moulded insulators such as knobs, discs, handles, arc shields, etc.





(Metropolitan Vickers Electrical Co. Ltd.)

FIG. 14. GENERAL ASSEMBLY OF COILS AND SHELLAC INSULATIONS FOR 500,000 VOLTS TESTING TRANSFORMER

- (2) Laminated and moulded mica products.
- (3) Laminated paper boards and tubes.
- (4) Coated or impregnated paper, cloth and silk.
- (5) Insulating and finishing varnishes for small coils.
- (6) Insulating cements.

### Moulded Insulators

Electrical insulators of various sizes and designs are moulded from shellac-moulding powders by either the compression or injection process. The preparation of the moulding powders has been described previously; the fillers usually employed are asbestos and powdered mica.

During the past few years, synthetic resins particularly the thermosetting types have gradually replaced shellac moulded products mainly on account of their (a) rapid rate of moulding (b) better heat-resistance and (c) superior strength.

However, recent research leading to the development of shellac powders for the injection process whereby a high rate of production can be maintained, is expected to rehabilitate shellac in this field, to some extent.

### Mica Products

Mica is one of the most important insulating materials, but in its natural laminated form cannot be easily and economically fabricated into various shapes and sizes required for insulation of electrical equipment. Any process of manufacture which destroys its laminated structure, also ruins its dielectric value.<sup>49</sup>

In earlier days of the electrical industry, block mica was extensively employed for the insulation of commutators, requiring only flat pieces of segments for bar-insulation and relatively simple shapes for commutator cones or V-rings.

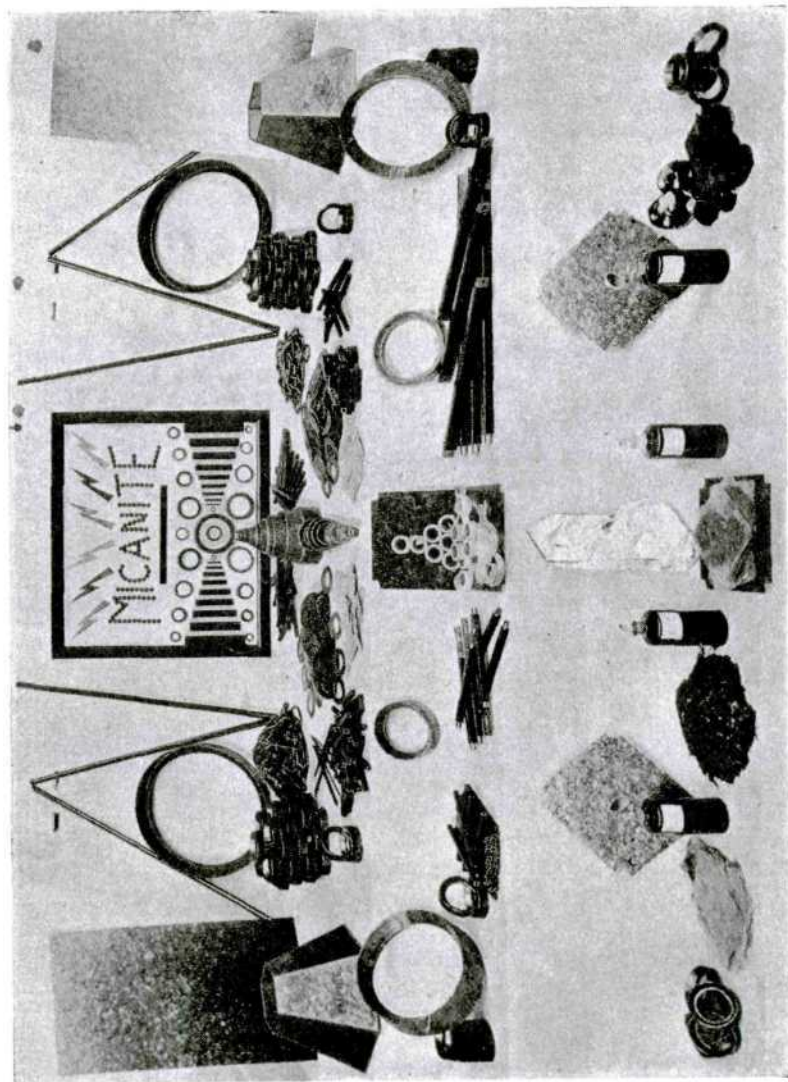
As the industry expanded, progressively larger commutators were produced in increasing quantities and the use of block mica cut from carefully selected sheets of considerable size became not only impracticable for economic reasons, but also involved considerable difficulties of fabrication because the natural plates of mica are easily broken when subjected to mechanical operations. Block mica, therefore, gave way to mica-splittings which were laminated together with a suitable bond. Block mica is now employed for only special applications.<sup>50</sup>

### Laminating Process

The process of laminating mica consists of building up thin mica splittings from which dirt, magnetic and other impurities have been previously removed, upon a foundation plate, coated with a thin film of a cement and covered with







(Micamite and Insulator Co. Ltd.)

FIG. 15. A GROUP OF MICA PRODUCTS

another layer of mica-splittings. The process is repeated until the desired thickness has been built up. The laminated sheet is then dried, generally in a vacuum oven at about  $100^{\circ}\text{C}$ . for approximately two hours and then pressed for an hour in a heavy hydraulic press at  $150\text{--}160^{\circ}\text{C}$ . and 1,000 lbs. per sq. inch. Sheets are cooled to  $40\text{--}50^{\circ}\text{C}$ . before releasing the pressure.

The cement recommended in Dyer's process<sup>51</sup> for bonding mica was a "varnish, shellac, or similar insulating material." Shellac, however, became the accepted and preferred bonder and until recently was used exclusively. During the last twenty years, shellac has had to face competition from many synthetic materials but particularly from alkyd resins<sup>52</sup> which have been employed in increasing quantities for both rigid and flexible mica sheet insulation, particularly for high temperature work. In more recent years, silicones<sup>53</sup> and some newer synthetic resins such as the G.E.C. new 7,000 resin<sup>49</sup> have been claimed to give better results. By far the largest quantity of mica products, however, are still bonded with shellac.

The building of mica laminates is usually carried out by hand labour which although somewhat laborious, is believed to give a better product than the machine-built one.<sup>50</sup>

One of the preferred machine-methods of building mica boards consists of dropping clean mica flakes from a "snow-storm machine" which may be briefly described as a tower with a mica distributing arrangement at the top.<sup>54</sup> The mica falls, (in a fairly uniform layer) to the bottom of the tower on a perforated and corrugated metal plate resting on a tray. The tray is then withdrawn and passed under varnish sprinklers, which apply to the upper surface of mica layer a thin film of the varnish. The whole process is then repeated until the desired thickness of the mica board has been built up. The board is then dried and pressed as described previously.

Instead of a shellac varnish, Sills<sup>55</sup> preferred to use powdered shellac which he dropped together with mica flakes from the top of the tower, blowing air to disperse the materials. This process has the advantage that the use and removal of solvent is dispensed with, and as soon as the requisite thickness has been built up, the board can straight away be consolidated under heat and pressure.

The first mention of the dry bond process appears to be by Tinnerholm and Peterson<sup>56</sup> in 1894, when they dusted powdered





shellac on mica sheets. Various modifications and improvements<sup>57-60</sup> on this and Sill's process have been patented from time to time and the mica-tower process is extensively employed both in this country and in the U.S.A.

Another mechanical method of building laminated mica boards is that of Lewis<sup>61</sup> wherein each layer of mica splitting is deposited by letting it drop an inch or so from a wire-mesh bottom of a suction box against which it has been drawn and held by reduced pressure. On breaking the vacuum, the splittings fall, forming a fairly uniform surface. The adhesive is then applied and another layer of mica deposited and so on until the desired thickness has been obtained.

Laminated mica products may be classified as under :

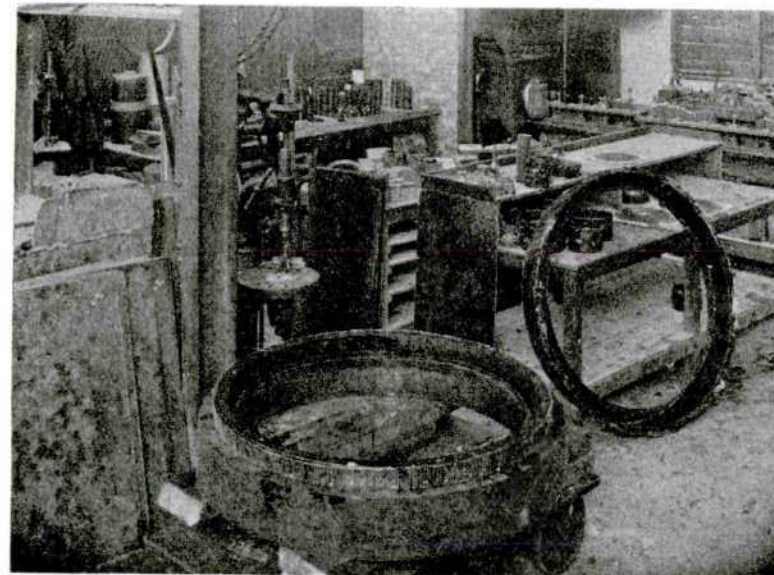
(1) *Hard or Segment Micanite* used for commutator work. A high grade shellac varnish is usually employed for bonding, taking care to use the minimum possible quantity. A well-made commutator segment micanite plate usually contains not more than 3 per cent. shellac by weight, while the general purposes hard micanite may contain as much as 5 per cent. Segment micanite is invariably milled and sanded to obtain uniform thickness within the prescribed fine limits ( $\pm 0.001$  inch) for commutator insulation. This type of micanite also finds outlet for coil and field spool insulation, insulation barriers, etc.

(2) *Hot Moulding Micanite* differs from hard micanite in that it is usually made of somewhat larger splittings and a considerably larger quantity of the bond (10-25 per cent. by weight) is employed, so that although hard and inflexible when cold, it can easily be softened and made plastic by warming on a hot-plate at 100-120° C. for moulding into various shapes. This type of micanite is used for commutator cones and large V-rings for which it is cut into suitable segments, built in staggered layers and hot moulded. It also finds extensive use in slot liners, transformer rings, troughs, tubes, switch bar insulation, etc.

(3) *Flexible or Cold Moulding Micanite*. This type, unlike the hot moulding micanite, is flexible at ordinary temperatures, and can be bent and formed to shape without the application of heat. This is due to the special permanently flexible bond used in its manufacture. The bond, constitut-



ing 7-10 per cent. by weight of micanite, usually consists of a mixture of shellac with other natural resins and gums and a non-drying oil such as castor oil. Recently, however, oil modified alkyds have been employed with considerable success. A shellac derivative<sup>62</sup> obtained by reacting lac with ethylene glycol has also proved useful for this purpose. Flexible micanite sheets are used for inter-coil insulation, slot lining, special wraps and as paper- or silk-backed tape for insulating strip windings for extra high tension transformers, etc.



(Micanite and Insulator Co. Ltd.)

FIG. 16. BUILDING A COMMUTATOR AND RING—THE RING PRESSED IN THE MOULD

(4) *Micafolium* is a wrapping material consisting of a thin layer of mica splittings bonded with a special shellac varnish on a continuous length of strong kraft paper backing. Up to three layers of mica are employed, although with three layers difficulties may be experienced in using the product on the Haefely wrapping machine. The bond content of a good micafolium varies between 7 to 10 per cent. Micafolium is extensively employed in the insulation of large



electrical machines, to conductors, coils, shafts, etc., and is always applied by a hot ironing process.

(5) *Mica Cambric, Mica Silk, Mica Tape, etc.* Laminated mica products backed with fibrous materials such as cambric, silk, and paper are used for a variety of insulation work in the form of tapes. For instance, mica silk is employed for insulation of large turbo-alternators. A special bonding varnish containing a large percentage of shellac is employed which permits the tapes to remain flexible for considerable time.

(6) *Composite Mica Boards, etc.* These composite boards are used for linings and covers for special boxes, barriers, inter-coil spacers, etc., The boards are prepared by bonding and consolidating alternate layers of fibrous sheet material such as paper, press-board, or asbestos with layers of mica splittings, using shellac varnish as a bond. The products are usually hand-built, lightly pressed and baked to produce mechanical strength.

#### LAMINATED PAPER PRODUCTS

Large quantities of shellac bonded paper products in the form of tubes, cylinders, and boards are also employed for insulation work. These products are extensively used for transformers insulation, high tension terminals, bushings, circuit-breakers, etc.

They cannot, however, be employed for applications where temperatures higher than  $60^{\circ}\text{C}$ . are met, unless they have been carefully cured and hardened when their heat resistance is increased to about  $120^{\circ}\text{C}$ .<sup>63</sup> Although slightly inferior mechanically, their electrical properties are superior to the synthetic resin bonded paper goods and they also show better resistance to surface carbonisation. Due to the latter property, they are widely used for compound filled switchgear and high-voltage air-cooled transformers.

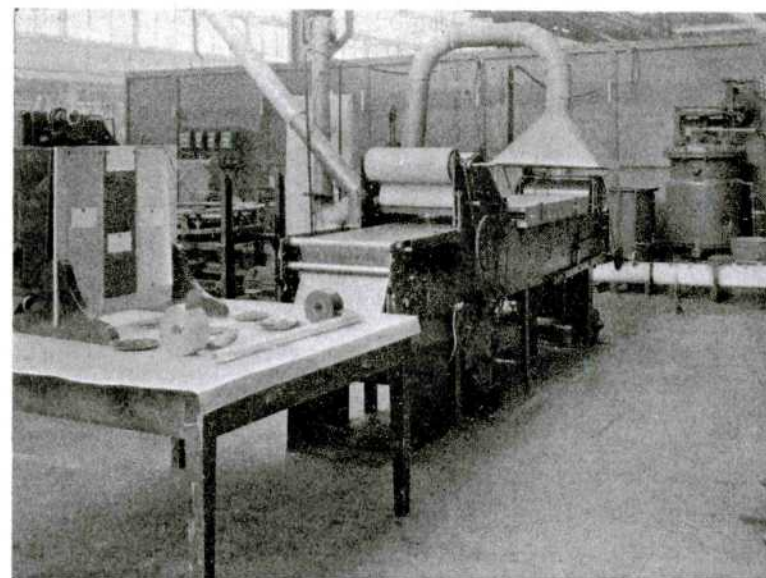
#### Manufacture

The manufacture of shellac-laminated paper products is carried out by both the wet as well as the dry process. In the wet process, the sheet material is either impregnated or coated with a shellac varnish and carefully dried to remove all the



solvent. For making tubes, the coated paper is tightly wound round a hot mandrel at such a temperature that the lac is softened sufficiently to provide a satisfactory bond. When the desired thickness has been built up, the tube is subjected to a carefully graded baking process.

Alternatively the paper may be coated with molten shellac<sup>64</sup> without the use of solvents, or powdered shellac may be sprinkled on the paper as it passes over a heated table and roll. A new method recently developed consists of spraying powdered shellac through a flame gun<sup>65</sup> and a special machine has been



(Micanite and Insulator Co. Ltd.)

FIG. 17. VIEW OF EXPERIMENTED SHELLAC BOND PAPER TREATING MACHINE

designed for automatically spraying continuous sheet material.<sup>66</sup> Following advantages are claimed for the hot spraying:

(a) There is no loss of solvent and attendant hazards of fire, etc.

(b) The resin does not penetrate into the base material, thus permitting a pre-treatment of the base material with another dielectric to improve the electrical or the mechanical properties of the laminate. For instance, oil impregnated paper may be hot-sprayed with shellac and then laminated.



(c) Considering the compactness of the machine which occupies but a fraction of the space required for a similar capacity machine employing solvent method, a very high rate of coating can be obtained. On a paper of 40 inch width, a coating of 1.47 oz. shellac per sq. yard of paper can be deposited at the rate of 325 feet per hour when two guns are employed in one machine.

Superior electrical properties have also been claimed for such hot sprayed shellac coatings. Fillers such as mica, asbestos, lignin, woodflour or metallic powders may be mixed with powdered shellac before hot spraying and are stated<sup>67</sup> to toughen and to reduce the brittleness of the coating.

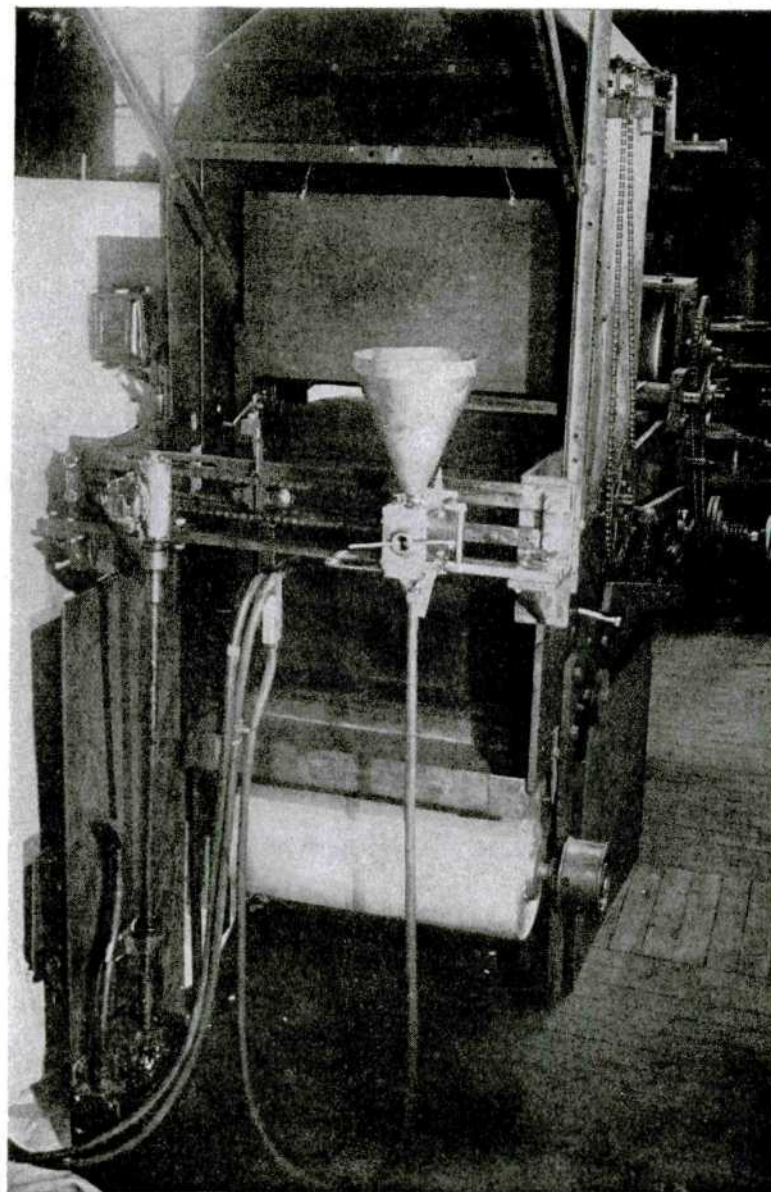
Mechanical properties of shellac products can be improved by incorporation of synthetic resins. Shellac may be dissolved in a warm syrup of phenolic resin or their alcoholic solutions may be mixed. The properties of laminated products prepared with such mixtures naturally depend upon the relative proportion of the two resins. Improved resistance to surface carbonisation can be imparted to phenolic resin insulators by surfacing them with a layer of shellac impregnated paper.<sup>68</sup>

Shellac has also been advantageously used for laminating most sheet materials. Recently hard boards, tubes, rods, etc., have been produced by laminating shellac coated jute fabric.<sup>69, 70</sup> Shellac bonded jute boards have proved particularly useful for packaging purposes, for instance as a replacement for plywood in the manufacture of tea-chests, and as a substitute for black iron plate for grease and oil containers.

#### SHELLAC IN PAINTS AND VARNISHES

The use of shellac in the manufacture of various types of protective and decorative coatings for all kinds of surfaces has been known for centuries. For example, French polish which is valued for its high grade finish on wood is nothing else but a solution of shellac in alcohol. Shellac has been used as a wood filler, knotting varnish for stopping resinous exudations from wood, primary coat under a variety of other finishes, surface finish and polish reviver.

Shellac-spirit varnishes have been extensively used for furniture, toys, musical instruments, patterns for metal



(Metropolitan Vickers Electrical Co. Ltd.)

FIG. 18. EXPERIMENTAL MACHINE FOR AUTOMATIC HOT SPRAYING SHELLAC ON SHEET MATERIALS



castings and in the U.S.A. for floors, bowling alleys, stair treads, etc.

The other uses of alcohol solutions of shellac would include goldsize for metal joints, lacquers for metals especially for water and oil tanks, lacquers for tin and aluminium foils, suction-stopping lacquer for plaster, identification paints for metals, white line road paints, paints for bituminous battery boxes, anti-fouling ships' paints, anti-corrosive finishes, wall-paper finishes, glazes for art paper and playing cards, protective lacquers for food and medicinal products such as coffee beans, chocolates and pills, interior lacquers for artillery shells, fuses and detonators, leather finishes, lacquers for rubber goods, finishes for paper including manufacture of greaseproof paper, papers for dry-mounting photographs and printing inks.

Shellac-spirit varnishes, particularly those of bleached lac should not be stored for any length of time as gradual esterification of shellac with alcohol takes place.<sup>71, 72</sup> Old shellac varnishes are consequently slower to dry and their films are less resistant to water.<sup>73</sup> The loss of drying power and resistance to water can, however, be retarded by incorporation of non-esterifying diluents such as methyl ethyl ketone, isopropyl alcohol, etc.<sup>74</sup> Shellac varnishes when stored in metal containers have a tendency to darken due to interaction of shellac with the metal of the container.<sup>75</sup> The discolouration can be inhibited by addition of a small quantity of oxalic acid.<sup>76</sup>

For certain uses, shellac films require to be plasticised. Resistances to oils, extremely low temperatures, etc., can be improved by the addition of special plasticisers,<sup>77</sup> but for general purposes methyl cyclohexanol phthalate and dimethyl glycol phthalate are particularly suitable.<sup>78, 79</sup>

Shellac films show pronounced tendency to retain solvent; for example the presence of alcohol has been detected in 0.1 mm. thick air-dried films after a year.<sup>80</sup> Similarly Nagel and Baumann<sup>81</sup> have reported that 0.05–0.1 mm. thick shellac films showed 15 per cent. ethoxyl content after two days at 50–60° C.

When properly formulated, shellac-spirit varnishes may be applied by rubbing, brushing or spraying. The modern technique for wood finishing calls for rapid air-drying varnishes so that goods may be polished and packed the same day. It is not surprising that for furniture finishing, French polish has

gradually given way to cellulose lacquers which are usually based on dammar and cellulose nitrate. Recent research has shown that equally rapid drying lacquers are obtained by incorporating in the plasticised shellac varnish as little as 15 per cent. cellulose nitrate<sup>82</sup> or 7.5 per cent. ethyl cellulose<sup>83</sup> on the weight of lac. These lacquers show improved gloss and water resistance, have excellent adhesion, and may be used for outdoor work.<sup>74</sup>

### Shellac Aqueous Varnishes

Shellac is readily soluble in aqueous solutions of alkalis such as ammonia, caustic alkalis, carbonates, borates and organic amines. It may also be dissolved in solution of sodium silicate, sodium phosphate, sodium bisulphite and sulphurous acid.<sup>84</sup>

Shellac aqueous solutions are used for a number of applications amongst which are stiffening of felt and straw hats, paper coatings, leather finishes, photo-engraving, stiffening of crepe and other textiles, removing tack from oiled silks, coatings for crayons and writing chalks, media for white line road paints, oil bound distempers, floor polishes, wax preparations, protective coatings and glazes for food and fruit, etc. Shellac alkali compositions are also employed for optical gratitudes.

The films from aqueous solutions of shellac are usually more brittle and friable than those from spirit varnishes. Glycerine, glycols, sulphonated castor oil, acetins, triethanolamine and similar materials that are soluble in water have been used for plasticising these films. Disadvantages of such plasticisers are obvious but the main objections to their use is that they are easily leached out when the dried film comes in contact with water. Recent investigations have, however, shown that many of the ordinary water-insoluble plasticisers can be incorporated with ease in lac aqueous solutions, the best being "Reomol G" and dimethyl glycol phthalate.<sup>85</sup>

Aqueous solutions of shellac can be photosensitised by the addition of chromate or dichromate solutions.<sup>86–88</sup> Films are prepared on metals, glass or other required surface in the dark. Printing with a negative is carried out by exposure under a double arc lamp and the plates are developed in alcohol to which a dye is usually added to facilitate examination. The plates are then etched with acid.





## Shellac-Oil Varnishes

One of the old applications of shellac was its use in the manufacture of carriage- and coach-makers japans. These japans were prepared by cooking shellac in linseed oil at high temperatures in the presence of litharge. Recent investigations have shown that shellac can be incorporated at much lower temperatures when in place of the oil, glycerine and fatty acids or monoglycerides are employed.<sup>89-92</sup> Such varnishes have found many other uses besides as japans; for example as metal lacquers, stoving enamels, coil-impregnating varnishes, etc.

### OTHER USES OF SHELLAC

In addition to the use of shellac in sealing waxes, appreciable quantities of shellac are also consumed in the manufacture of adhesives and cements. Instances are cements for bonding metal or Bakelite caps to electric lamps and radio tubes; de Khotinsky's cement for fixing strain gauges and pick-ups to aircraft propellers, laboratory cements, gaskets and jointing compounds. Recent investigation in the field of shellac adhesives has led to the development of new compositions which are particularly useful for bonding metal to metal, metal to glass, glass to Bakelite, Bakelite to copper, aluminium to aluminium or to any other metal. These cements are unaffected by extreme changes in temperatures and humidities and can be recommended for K.110 specification. Some of these compositions are based on hydrolysed shellac while others are obtained by refluxing alcoholic solution of shellac with hydroxy acids such as tartaric acid.

The versatility of lac for industrial applications is clearly seen from the following list compiled by Yarsley and Gibson,<sup>93</sup> which also shows some alternative plastic materials that have been successfully employed for similar purposes.

### THE KNOWN USES OF LAC AND SOME ALTERNATIVE MATERIALS

COMPILED BY

DR. V. E. YARSLEY AND A. J. GIBSON

#### Shellac

##### A. SHELLAC VARNISHES

###### (a) Spirit and Alkali Varnishes

##### I. INSULATING VARNISHES AND IMPREGNATING COMPOUNDS:

#### Alternative material

Cellulose esters and ethers, vinyl compounds.

Cellulose acetate, benzyl cellulose, ethyl cellulose, vinyl compounds.



#### Shellac

1. To prevent copper wire "greening":  
Hard lac-alcohol  
Shellac-p-toluene sulphonamide.
2. To resist effect of lubricating oils and greases  
Shellac-alcohol  
Lac-glycol ether in solvents.
3. In micanite and micafolium:  
Shellac-alcohol (dry powdered lac)
4. (i) In building up paper and fabric tubes and impregnating tape and fabrics:  
Shellac-alcohol  
Shellac-glycol ether.  
Hard lac resin and alcohol.  
(Hot spraying of dry powdered lac).  
(ii) Grease-proof paper:  
Bleached lac-alcohol
5. To resist high temperature:  
Shellac-glycol ether and esters.
6. For brake linings:  
Asbestos fibre bonded with shellac in solvents.  
Hard lac resin in solvents.  
Shellac-tung oil varnish.

#### Alternative material

Cellulose ester (nitro-cellulose and cellulose acetate) lacquers  
Polyvinyl chloride.

Vinyl co-polymers, specially plasticised cellulose acetate.

Phenol-formaldehyde; urea-formaldehyde; alkyds.

Phenol/formaldehyde; urea/formaldehyde.

Melamine/formaldehyde.

Viscose coated with nitro-cellulose/wax or vinyl lacquers.

Methyl silicones.

Asbestos fibre with phenol/formaldehyde; cellulose acetate or methyl methacrylate as bonding agent.

### II. SHOE TRADE.

1. Shellac stiffeners for toes and soles of shoes, etc.:  
in alcohol solutions.  
in ammonia solutions.
2. Shellac varnishes and finishes:  
in alcohol solutions;  
in ammonia solutions;  
in borax solutions.

Cellulose ester and ether compositions.

Nitrocellulose, vinyl and methyl methacrylate coating compositions.

### III. LEATHER TRADE.

Pigmented and unpigmented shellac finishes:  
in alcohol;  
in ammonia.  
Shellac-stearic acid compound.  
Shellac-metallic oxides and alcohol.

Plasticised methyl methacrylate; vinyl co-polymer lacquers.

### IV. HAT INDUSTRY.

Felt and fur hats, service hats and helmets:  
Shellac and bleached lac:  
in alcohol solutions;  
in borax solutions;  
in other alkaline solutions.

Nitrocellulose, cellulose acetate, phenol/formaldehyde for service helmets.



## Shellac

### V. PHOTOGRAPHIC INDUSTRY.

1. *Negative varnish* :  
Shellac-alcohol.
2. *Antihalation plate and film backing* :  
Soft lac resin in alkali solution.  
Hydrolysed lac in alkali solution.
3. *Dry mounting paper* :  
Tissue paper impregnated with :  
Bleached lac-alcohol solution.
4. *Preparing photographic gratings* :  
Shellac alkali solutions.
5. *Photosensitising processes* :  
*Cold tops in photo-engraving and etching.*  
Shellac-alcohol.  
Hard lac resin-alcohol.  
Shellac in aqueous ammonia and ammonium dichromate.
6. *For protecting sound tracks on "talkie" films* :  
Dewaxed shellac-nitrocellulose and solvents.

### VI. PROTECTIVE COATINGS FOR WOOD, PAPER, METAL AND FABRIC :

1. *French polish* :  
Shellac-alcohol.  
Hard lac resin—alcohol.  
Shellac—metallic oxides and alcohol.  
Bleached lac—alcohol.  
Shellac—urea and alcohol.  
Shellac—alcohol—ammonia.
2. *In medicine* :  
*For semi-rigid bandages* :  
*For coating pills* :  
Shellac in alcohol.
3. *In confectionery* :  
*Glazing candies and chocolates.*  
Shellac in alcohol.  
Bleached lac in alcohol.
4. *For burnishing coffee beans* :  
Dry powdered shellac.

### VII. POLISHES AND FINISHES GENERALLY :

- (a) 1. *Shellac esters.*  
Rosin—shellac ester in turpentine and white spirit.  
Shellac—stearic acid ester as above.
2. *Shellac-sodium bisulphite* ; *for distempers.*  
*For coatings resistant to petrol.*

## Alternative material

Cellulose acetobutyrate lacquer,  
vinyl acetal composition.

Methyl methacrylate or vinyl  
acetal resin compositions.

Phenol/formaldehyde impreg-  
nated tissue paper.

Casein, gelatine, or gum arabic  
with dichromates.

Gelatine or glue with chromates

Melamine/formaldehyde.

Nitrocellulose, miscellaneous  
glyptal and sulphonamide/  
formaldehyde resin composi-  
tions.

Methyl methacrylate ; cellu-  
loid ; cellulose acetate.

Nitrocellulose ; cellulose aceto  
butyrate.

Phenol/formaldehyde.

Urea/formaldehyde.

## Shellac

- (b) *Shellac varnishes ; other types.*  
For spraying :  
Cellulose nitrate—shellac and  
alcohol plus other solvents ;  
Ethyl cellulose as above ;  
Bleached lac as above ;  
Dewaxed lac as above.
- (c) *Shellac oil varnishes.*  
For general application :  
Shellac—drying oil fatty acids  
—glycerol.  
Shellac esters—mono and poly-  
glycerides—drying oils.
- (d) *In Inks.*  
*Waterproof ink* :  
*Coloured inks* :  
*Lithographic inks* :  
Shellac in alkali or alcohol solu-  
tions with other materials.
- (e) *In paints.*  
*Antifouling compositions* :  
*Road paints* :  
Solutions of shellac with other  
materials, poisons, pigments,  
etc.

### B. SHELLAC CEMENTS AND ADHESIVES.

1. *For glass to glass, glass to metal,  
metal to metal, etc.*

#### Cements :

- De Khotinsky cement :
- Shellac—pine tar.
- Pottman's cement :
- Shellac—Stockholm tar.

#### Laboratory cement :

- Shellac—Venice turpentine.

Shellac—lac glycol ester.

#### Adhesives.

- Shellac—tartaric acid and alcohol
- Shellac—rubber latex and am-  
monia.
- Shellac—rubber and solvents.
- Dewaxed lac—lac glycol ester.

2. *For abrasive wheels, emery paper,  
blackboard surfaces* :  
Shellac—alcohol.  
Hard lac resin—alcohol.  
Hard lac resin—urea and alcohol.

3. *Sealing wax* :

#### (i) As such :

- Shellac with fillers.
- Bleached lac with fillers.

#### (ii) In turnery and toys :

- Shellac and colouring media.
- Coloured dry lac, in sticks.

## Alternative material

Glyptal compositions.

Coumarone resins.  
Nitrocellulose, ethyl cellulose,  
glyptal compositions.  
Gilonite.

Phenol/formaldehyde ; mela-  
mine/formaldehyde.

Butyl methacrylate ; chlorin-  
ated diphenyl resins.

Organic polysulphides ; cellulose  
acetate ; nitrocellulose.

Rosin, ester gums, modified  
rosin.  
Phenol/formaldehyde deriva-  
tives.

Modified glyptals.

Vinyl chloride.  
Vinyl acetal.

Methyl methacrylate ; phenol/  
formaldehyde ; vinyl poly-  
mers.

Rosin, ester gums.



### Shellac

#### 4. Optical instruments :

Shellac in alcohol.  
Modified lacs.

#### 5. Semi-rigid and flexible cements:

To resist various solvents :  
Modified lacs.

Shellac—lac acids and glycol ester.

#### 6. For rubber manufactures :

(i) Rubber soles and heels :

(ii) Rubber sheet :

Modified lacs and shellac.

(iii) For rubber surface lacquers :

Lac glycol ether with nitro-cellulose in solvents.

### C. SHELLAC MOULDINGS.

For Gramophone Records :

Electrical uses : Dominoes:

Dental Plates:

Shellac in various forms:

(i) Open moulding :

(ii) Closed moulding :

(iii) Injection moulding :

Shellac, hard lac resin and modified lacs in combination with :

Stearic acid.

Fillers, micronised mica.

Phenol/formaldehyde.

Formaldehyde.

Urea.

Melamine.

Protein.

Cashew nut shell oil.

Jute.

### D. OTHER USES.

Bengal and signal lights and rockets ;

Pyrotechnics generally ;

In foundry work ;

Playing cards finish :

Stiffening crepe :

American cloth, waterproof silk and sou'wester finishes :

Sweets and cheese metal foil finishes :

Shellac and hard lac resin in alcohol.

Tank steamer coatings :

Shellac.

Hard lac resin.

Modified lacs.

### Alternative material

Butyl methacrylate ; vinyl chloride.

Vinyl acetal.

Ketone/phenol condensation products.

Polyvinyl chloride, highly plasticised cellulose esters and ethers.

Synthetic rubbers.

Phenol/formaldehyde, vinyl, cellulose (esters and ethers).

Phenol/formaldehyde.

Urea/formaldehyde.

Methyl methacrylate.

Cellulose esters and ethers.

Phenol/formaldehyde : urea/formaldehyde.

Cellulose acetate ; polystyrene ; vinyl plastics ; ethyl cellulose.

Methyl methacrylate.

Cellulose acetate sheet.

Cellulose acetate lacquer.

Nitrocellulose, benzyl cellulose.

Polyvinyl chloride.

Nitrocellulose lacquer.

Phenol/formaldehyde : urea/formaldehyde.

### Shellac

Lac products as starting materials for synthesis.

Cosmetics : Hair dyes : Setting

lotions : Finger nail polishes :

Shellac in solvents.

Hard lac resin in solvents.

### Alternative material

Nitrocellulose, vinyl lacquers.

### REFERENCES CITED

- (1) G. Watt, *The Agr. Ledger*, India, 1901, **9**, 181.
- (2) Gardner, U.S.P. 73,088/1868.
- (3) Merrick, U.S.P. 85,018/1868.
- (4) R. W. Rowell, "Technology of Plastics", 1936.
- (5) Hyatt, B.P. 16,413/1881.
- (6) A. N. Petit, U.S.P., 689,408/1901.
- (7) G. C. Marks, B.P. 7993/1905.
- (8) T. H. Macdonald, U.S.P. 862,407/1907 and U.S.P. 878,547/1908.
- (9) R. W. James, B.P. 12,035/1910.
- (10) H. R. Simonds and C. Ellis, "Handbook of Plastics", Chapman and Hall, London, 1943, p. 796.
- (11) W. H. Gardner, *British Plastics*, 1934-5, **6**, 459.
- (12) H. C. Bryson, "The Gramophone Record", Ernest Benn Ltd., London, 1935.
- (13) W. T. Forse, U.S.P. 1,702,564/1929.
- (14) C. Ellis, "The Chemistry of Synthetic Resins", p. 1338, Reinhold Publishing Corporation, New York, 1935.
- (15) W. H. Gardner, *Paint, Oil & Chem. Review*, 1937, **99**, 34.
- (16) H. C. Bryson, *British Plastics*, 1930-1, **3**, 104, 160, 223, 259.
- (17) H. C. Bryson, *Ibid.*, 1931-2, **4**, 48, 90, 160, 206.
- (18) H. C. Bryson, *J.S.C.I.*, 1933, **52**, 495.
- (19) A. Karim, "A Study of the Mechanical and Electrical Properties of Some Commercial Standard Lacs", *Ind. Lac Res. Inst.*, 1937.
- (20) E. de Stubner, U.S.P. 1,456,369/1923.
- (21) L. Weisberg, U.S.P. 1,443,936/1922.
- (22) Continental Diamond Fibre Co., U.S.P. 1,999,096 and 1,999,097/1935.
- (23) J. W. Aylsworth, U.S.P. 1,167,468/1916.
- (24) A. A. Knusdon, B.P. 5730/1890.
- (25) L. Berend, B.P. 4154/1909.
- (26) J. C. English, U.S.P. 948,314/1910.
- (27) T. A. Edison, U.S.P. 1,342,326/1920.
- (28) E. A. Daniels and H. S. Snell, U.S.P. 1,673,803-8/1928.





- (29) S. Ranganathan and R. W. Aldis, *Ind. Lac Res. Inst.*, Bull. No. 14, 1933.
- (30) W. H. Gardner, U.S.P. 1,994,071/1935.
- (31) W. H. Gardner, U.S.P. 2,010,224-7/1935.
- (32) W. H. Gardner, *British Plastics*, 1934-5, **6**, 524.
- (33) W. H. Gardner, *et al.*, *Ibid.*, 1934-5, **6**, 571.
- (34) S. Ranganathan, *Ind. Lac Res. Inst.*, Bull. No. 30, 1938.
- (35) H. K. Sen, *J. Ind. Chem. Soc.* (Indust. & News Ed.), 1939, **11**, 3.
- (36) M. Venugopalan and H. K. Sen, *British Plastics*, 1938-9, **10**, 626.
- (37) M. Venugopalan and H. K. Sen, *Ind. Lac Res. Inst.*, Res. Note No. 21, 1940.
- (38) Y. Sankaranarayanan and H. K. Sen, *Ind. Lac Res. Inst.*, Res. Note No. 22, 1940.
- (39) Y. Sankaranarayanan and H. K. Sen., *Ibid.*, Bull. No. 57, 1944.
- (40) M. Venugopalan and H. K. Sen, *Ibid.*, Res. Note No. 23, 1940.
- (41) S. Ranganathan and H. K. Sen, *Ibid.*, Res. Note No. 19, 1938.
- (42) Y. Sankaranarayanan and H. K. Sen, *J. & Proc. Inst. Chem.* (India), 1941, **13**, 145-160.
- (43) J. R. Scott, *J. Sci. Ind. Res.*, India, 1945, **3**, 345-353; 407-417.
- (44) Angelo Bros. (England) Ltd., "General Notes Concerning Shellac-Rubber Compound", 1935.
- (45) B. D. Porrit and J. R. Scott, B.P. 517,816/1940.
- (46) H. F. Albright, U.S.P. 1,659,936/1928.
- (47) E. Hemming, "Moulded Electrical Insulators and Plastics", Chemical Catalogue Co., New York, 1914.
- (48) *The Times*: Imperial and Foreign Trade and Eng. Suppl., London, 28th May, 1931.
- (49) L. E. Barringer and K. N. Mathes, *Gen. Elec. Rev.*, Oct. 1944, p. 15.
- (50) A. Monkhouse, "Electrical Insulating Materials", Sir Isaac Pitman & Sons, 1926, p. 177.
- (51) A. H. S. Dyer, U.S.P. 483,646/1892.
- (52) L. E. Barringer and C. F. Peterson, U.S.P. 1,589,094/1926.
- (53) S. L. Bass, *et al.*, *Modern Plastics*, 1944, **22**, 124.
- (54) M. Warren, "Electrical Insulating Materials", Ernest Benn Ltd., 1931, p. 40.
- (55) W. H. Sills, U.S.P. 1,133,325/1915.
- (56) A. F. Tinnerholm and C. F. Peterson, U.S.P. 522,242/1894.
- (57) W. J. Longmore, U.S.P. 1,138,676/1915.



- (58) J. R. Sanborn, U.S.P. 1,138,691/1915.
- (59) Westinghouse Elec. & Manuf., Co., U.S.P. 1,239,894/1917.
- (60) R. W. Aldis, "A Shellac Patent Index," *Ind. Lac Res. Inst.*, 1935, pp. 42-45.
- (61) B. G. Lewis, U.S.P. 833,401/1906.
- (62) B. S. Gidvani, *London Shellac Research Bureau*, Tech. Paper No. 17, 1939.
- (63) H. K. Sen and S. Ranganathan, "Uses of Lac", *Ind. Lac Res. Inst.*, 1939, p. 29.
- (64) R. M. Briggs, U.S.P. 1,311,491/1919.
- (65) *London Shellac Research Bureau*, Bull. No. 5, 1939 and Supplement, 1940.
- (66) N. N. Murty, *Plastics*, 1945, **9**, 288.
- (67) C. F. Lumb, B.P. 539,633/1941.
- (68) H. W. H. Warren and A. E. Smith, B.P. 299,906/1928.
- (69) Ind. Jute Mills Assoc. and Angelo Bros. Ind. P. 29370/1944.
- (70) Ind. Jute Mills Assoc. and Angelo Bros. Ind. P. 29628/1944.
- (71) Zoellner, *Drugs, Oils, Paints*, 1934, **49**, 51.
- (72) W. H. Gardner, chapter on shellac in "Protective and Decorative Coatings", Vol. 1, edited by J. J. Mattiello; John Wiley & Sons, New York, 1941, p. 272.
- (73) Zoellner, *Drugs, Oils, Paints*, 1934, **49**, 236.
- (74) P. Bruins, *Paint, Oil Chem. Rev.*, 1939, **101**, 9-12.
- (75) H. A. Gardner and Levy, *U.S. Paint Manuf. Assoc. Circ.* No. 304, 1927.
- (76) R. Bhattacharya and L. C. Verman, *London Shellac Research Bureau*, Tech. Paper No. 8, 1936.
- (77) N. R. Kamath, *Ibid.*, Bull. No. 6, 1944.
- (78) L. C. Verman and R. Bhattacharya, *Ibid.*, Tech. Paper No. 9, 1936.
- (79) G. D. Heath and B. S. Gidvani, *Ibid.*, Tech. Paper No. 20, 1941.
- (80) Lubke, *Farbe u Lack.*, 1937, 619.
- (81) W. Nagel and E. Baumann, *Angew. Chem.*, 1936, **49**, 309, 369.
- (82) B. S. Gidvani and R. Bhattacharya, *London Shellac Research Bureau*, Tech. Paper No. 19, 1940.
- (83) N. R. Kamath and B. S. Gidvani, *Ibid.*, Tech. Paper No. 27, 1945.
- (84) R. Bhattacharya and L. C. Verman, *Ibid.*, Tech. Paper No. 6, 1936.
- (85) B. S. Gidvani, *Ibid.*, Tech. Paper No. 24, 1944.
- (86) J. W. Smith, *et al.*, "Photoengraving in Relief", Sir Isaac Pitman & Sons, London, 1932.