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Chemical Investigations on Lac and Its Derived Products

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CHEMICAL INVESTIGATIONS ON LAC AND ITS DERIVED PRODUCTS

THESIS SUBMITTED TO THE RAJSHAHI UNIVERSITY
FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY
IN FACULTY OF SCIENCE (CHEMISTRY)

By
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RAJSHAHI UNIVERSITY
AUGUST, 1999.

DECLARATION

I hereby declare that the work entitled "CHEMICAL INVESTIGATIONS ON LAC AND ITS DERIVED PRODUCTS" has been carried out under the supervision of (i) Dr. M. Umar Ali, Professor, Department of Chemistry, Rajshahi University, Rajshahi and (ii) Dr. M. Omar Faruq, Director (Retd.), BCSIR Laboratories, Rajshahi. It has not been submitted earlier to any University or Institution for award of any diploma or degree.

Muhammad Zahurul Haque

Muhammad Zahurul Haque

Rajshahi

Dated : 19·8·99.

CERTIFICATE

This is to certify that Muhammad Zahurul Haque, has carried out his research work on the topic "CHEMICAL INVESTIGATIONS ON LAC AND ITS DERIVED PRODUCTS" during the period from January 1995 to July 1999 under our supervision, in the Department of Chemistry, Rajshahi University, Rajshahi. The work presented in this thesis is the own work of the candidate.

19.8.99

Dr. M. Umar Ali
Supervisor

Dr. M. Omar Faruq
Co-Supervisor

Rajshahi
Dated : 19.8.99

PREFACE

Allah, the Almighty has created each and everything in this universe. There are creatures, most negligible in shape and size that has tremendous importance. One of such a creature is lac insect, *Kerria lacca*. Its size is 0.35 mm but its importance considering industrial value is of magnificent nature. Its resinous secretion obtained on the branches of some selected host plants is of vital industrial importance in many fields and is benefiting the human beings. This secretion from the glands of the lac insect is called lac. This is one of Allah's Qudrat that such a small insect (creature) can produce a widely applicable secretion, the lac. Hence a piece of research work in this field is undertaken in order to investigate the properties of different lac products and to study the chemistry of lac.

In the beginning of the thesis is given a General Introduction comprising of the origin and history of lac, lac production in Bangladesh etc. For convenience of presentation, the experimental work has been divided into four small chapters. Each chapter is complete within itself and has been written in the conventional form of a paper. Effort has been made for literature coverage upto date.

The thesis is appended with a list of paper and also reprint of publications.

I express my sincere gratitude and indebtedness to my respected teachers, Dr. M. Umar Ali, Professor, Department of Chemistry, Rajshahi University, Rajshahi and Dr. M. Omar Faruq, Director (Retd), Bangladesh Council of Scientific and Industrial Research (BCSIR) Laboratories, Rajshahi for their keen interests and valuable inspiring and indespensable guidance throughout the course of these studies and preparation of this thesis.

I am very much grateful to Dr. M. Yusuff Ali, Ex-Vice Chancellor, Rajshahi University, Professor, Department of Chemistry, Rajshahi University, Rajshahi for his inspiration and encouragement during the study period.

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I wish to express my thankfulness to the authority, BCSIR, Dhaka and Ministry of Sceince & Technology, Government of Bangladesh for the award of scholarship under Human Resource Development Programme (HRDP) and also for granting me study leave with full pay for Ph.D. Programme.

I am thankful to Mr. Akram Hossain, Department of Chemistry, Dhaka University, Dhaka for recording IR spectra of my research samples.

I have no hesitation to express my gratefulness to my friends, M. Maksud Ali, M. Siddiqur Rahman, M. Abdul Hye and M. Rafiquzzaman for their occasional help during this work at the Laboratories.

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I express my heartiest gratitude to my parents who brought me up and opened my eyes of knowledge.

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- Muhammad Zahurul Haque

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SYNOPSIS OF THE PRESENT WORK

The thesis is divided into five chapters. The chapter-wise summary is as follows :

Chapter 1 : Chapter 1 is a general introduction involving the history and background of the investigation on chemistry of lac.

Chapter 2 : This chapter describes the production of different varieties of lac. The products are -

Stick lac : Stick lac is obtained by scrapping encrustation of lac from the twigs of lac host.

Seed lac : Seed lac is the product obtained by crushing and washing of stick lac.

Shellac : Seed lac when subjected to hot filtration through cloth bag followed by hand-stretching to thin sheets and then crumbling to small pieces gives shellac.

Dewaxed shellac : Shellac contains wax (6.0%) which when removed gives dewaxed shellac. A new method is employed for the production of dewaxed shellac.

Bleached lac : Seed lac is orange in colour. This colour is removed by the sodium hypochorite bleaching and bleached lac is obtained.

This chapter is also a record of composition of varieties of lac. The quality of Bangladeshi lac and lac products conform with the standard literature value for those of Indian products. In addition to the above products isolation of two important by-products namely lac wax and kiri has also been reported.

Chapter 3 : This chapter gives new information on solubility behaviour of different varieties of the polymerized lac. Freshly prepared seed lac, shellac, bleached lac and dewaxed shellac are found to be highly soluble in ethanol both in cold and hot condition. The solubility of the said varieties of lac decreases on ageing when stored at room temperature. After one year the solubility decreases markedly and ultimately after two years storage all the varieties of lac become almost insoluble both in cold and hot ethanol. The percentages of alcohol insolubilities are recorded.

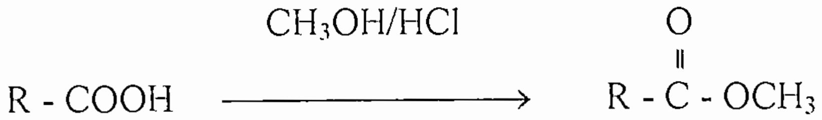
Behaviour of lac on thermal polymerization at temperature above their melting point has been studied. The reaction is attended with a gradual splitting off of water vapour along with the gradual rise in alcohol insolubilities of the products. The behaviour of polymerization of lac in terms of viscosity has also been studied and found that the relative viscosity increases with the progress of polymerization.

Various chemicals, viz. oxalic acid, tartaric acid, citric acid and urea have been found to play an important role in accelerating the thermal curing of shellac. The effect of these chemicals on life of shellac under heat at different temperatures were studied. The degree of polymerization of the accelerators at different temperatures were also determined.

Aleuritic acid has also been found to undergo polymerization by heat treatment. The behaviour of this polymerization has been studied from kinetic point of view. The over all reaction is found to be of the third order. Other properties of the polymer sample, such as acid value, suponification value and ester value have also been determined.

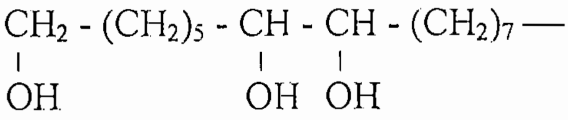
Chapter 4 : This chapter deals with the chemical modification of lac. Attempts have been made to improve or modify the properties of lac (shellac) and lac acids by combination with polyhydric alcohols like ethylene glycol in presence of catalyst. The prepared lac-glycol resin on further esterification with linseed oil lead to the formation of an oil soluble lac-glycol fatty acid compound. An improved varnish is prepared from this modified lac. The physico-chemical properties of the products are ascertained. Application of these modified products on jute fibre is studied to improve its serviceability. It is observed that the tensile strength, tenacity and moisture regain properties of the treated jute fibre decreases and percent elongation increases in comparison with the raw jute (control). The nature the shades developed on jute fibre by the application of various modified lac are also reported.

Chapter 5 : This chapter is an account of the synthesis of some new thiocarbamides. The reaction of aleurityl hydrazide and different isothiocyanates in boiling benzene medium afforded new thiocarbamides. The synthesis involved can be precisely represented through the following scheme :

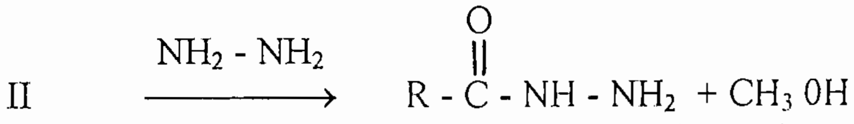


$$R - COOH \xrightarrow{CH_3OH/HCl} R - \overset{\overset{O}{\|}}{C} - OCH_3$$

Aleuritic acid (I) Methyl aleuritate (II)



Where, R = $\underset{\substack{| \\ OH}}{CH_2} - (CH_2)_5 - \underset{\substack{| \\ OH}}{CH} - \underset{\substack{| \\ OH}}{CH} - (CH_2)_7 —$

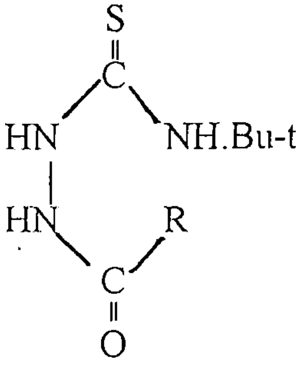


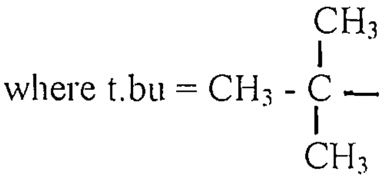
$$II \xrightarrow{NH_2 - NH_2} R - \overset{\overset{O}{\|}}{C} - NH - NH_2 + CH_3OH$$

Aleurityl hydrazide (III)

$$\text{III} + t\text{- Bu - N = C = S} \xrightarrow[\text{reflux}]{\text{Benzene}}$$

tert.butyl isothiocyanate



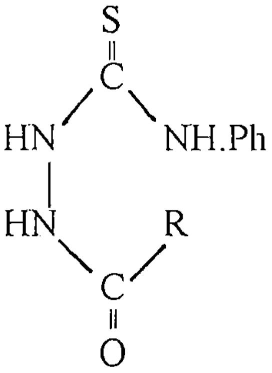


$$\text{where t.bu} = CH_3 - \overset{\overset{\large CH_3}{|}}{\underset{\underset{\large CH_3}{|}}{C}} -$$

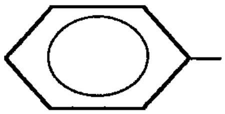
1-t-Butyl-3-N-aleuritamido thiocarbamide (IV)

$$\text{III} + \text{Ph - N = C = S} \xrightarrow[\text{reflux}]{\text{Benzene}}$$

Phenylisothiocyanate



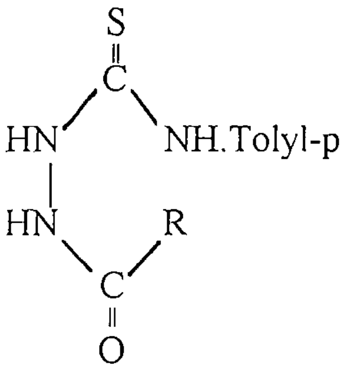
Where, Ph =



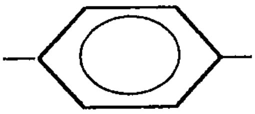
1-Phenyl-3-N-aleuritamido thiocarbamide (V)

$$\text{III} + \text{p - Tolyl - N=C=S} \xrightarrow[\text{reflux}]{\text{Benzene}}$$

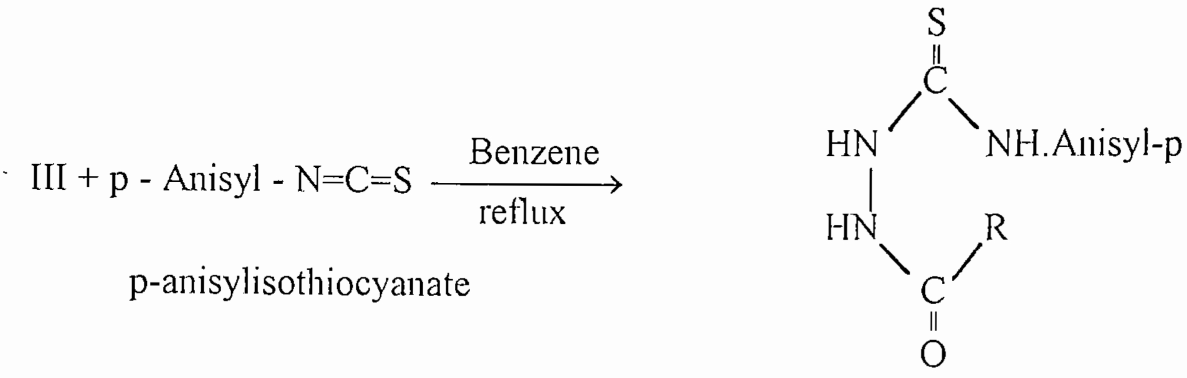
p-tolylisothiocyanate



Where, p-tolyl = CH_3 —

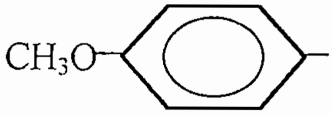


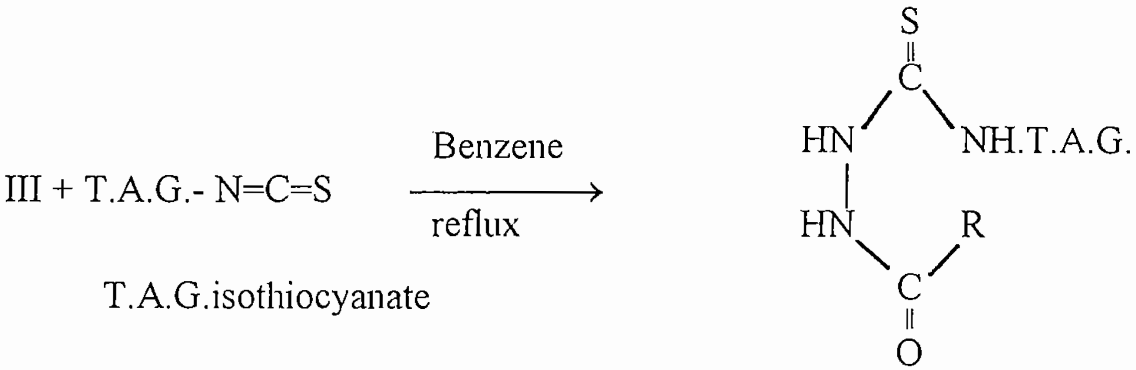
1-p-Tolyl-3-N-aleuritamido thiocarbamide(VI)



1-p-Anisyl-3-N-aleuritamido thiocarbamide (VII)

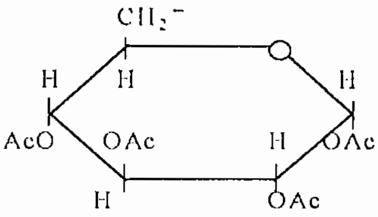
Where, p-anisyl =





1-tetra-acetyl-glucosyl-3-N-aleuritamido thiocarbamide (VIII)

Where, T.A.G. =



Structures of all the above thiocarbamides have been established on the basis of their elemental analysis and spectral evidences. This chapter also deals with the antibacterial studies of the synthesised products. The antibacterial properties of the above sulphur and nitrogen containing organic compounds have been studied *in vitro* against 16 pathogenic bacteria. Most of them were found to be highly active.

CHAPTER 1

GENERAL INTRODUCTION

GENERAL INTRODUCTION

1.1. The origin and history of lac

Lac is a resinous substance, secreted by some insect, *Kerria lacca.* Lac is known in Indo-Pak-Bangladesh from ancient time as Raksha, Laksha (Lukshma), Racta, Alakta, Jatu, Rumiha, Khadirika, Laa, Laha, Lakh and Gala. The term lac or lakh is a numerical Lakh (Lac) meaning one hundred thousand and is indicative of the large number of insects producing lac of commerce.

It is stated in the literature "Periplus" published in the year 80 A.D. that lac dye was an export item from India. In 250 A.D. Aelianus[1] gives some description of the lac insect in his sixteen-volume work on natural history.

Lac is known to China from the 4th century[2]. History mentions the use of lac in Japan and Thailand from the 8th century[2]. It is known as shiko in Japan and tju-kong in China. In old days lac were cultivated on Palas (*Butea frondosa*) and that is why this plant is usually known as lac-tree. In 1590 during the reign of the Moghal emperor the lac and lac dye[3] are reported to be used respectively in polishing doors and windows and for dyeing wool.

The present lac growing areas of the Nawabganj district was a part of Maldaha district in Undivided Bengal. Santals coming from different parts of south India started there lac cultivation for the first time. It is also reported that the aboriginals of Assam also used to grow lac in its jungle.

The Arabian merchants used to export lac to Western Europe from this sub-continent from ancient time. Since then Europe was familiar with lac. Urissa and Bengal had a monopoly in lac business during the reign of *Aurangzeb.* The

Dutchmen used to export lac to Persia. Lac was exported to Europe for the first time in 1907 by the East India Company.

1.2. Lac growing countries

India, Pakistan, Bangladesh, Burma, Nepal, Bhutan, Yemen, Thailand, Indo-China, Japan, Formosa, Amman, Cambodia, USA, Mexico, South-East Africa and Egypt are the countries producing lac[2]. India occupies the first place in lac cultivation. Sind of Pakistan[4,5] and East Punjab, Madhya Pradesh, Bombay, Madras, Bihar, Urissa, West Bengal and Assam of India are the centres of lac cultivation. Shibganj, Nawabganj, Gomastapur, Bholahat, Nachol and Godagari upa-zillas of greater Rajshahi area are the main places of lac cultivation in Bangladesh. A few places of Dinajpur are also reported as lac producing areas.

1.3. Lac insect and its life cycle

Lac is the resinous secretion of an insect, *laccifer lacca* which is a member of the Order Hemiptera (Rhyncota) and of the super family coccidae[6].

Tachard published an account of the lac insect in 1709. Kerr[7] described the lac insect as *Coccus lacca*. This name was supported latter on by Ratzeburg[8] and Carter[9]. However the same was designated as *Tachardia lacca* by a series of workers[10-11]. Chamberlin[12] recorded species from different parts of the globe e.g. South-Western United States, Mexico, Jamaica, British Guiana, Brazil, Argentina, Australia, Formosa, Burma, Philippines, India, Nepal, Java, Ceylon and Africa. From these collection he reported six genera namely *Tachardina*, *Laccifer*, *Metatachardia*, *Tachardiella*, *Austrotachardia* and *Afrotachardia*. Amongst these only the genus Laccifer has been proved worthy to produce commercial lac substantially. Mahdihassan[13, 14] classified lac insect into a number of species, which he called physiological classification. His system was on the basis of nature of lac secreted and secretionary activity. He assigned to these species, the generic name Lakshadia. Among them are *Lakshadia nagoliensis*, *Lakshadia indica*, *Lakshadia chinensis*, *Lakshadia mysorensis* and *Lakshadia conumunis*[16] all of them secret lac of different physical and chemical properties.

There seems to be little doubt that in the major lac growing areas, the lac insect is actually one species, *Laccifer lacca* and that there are two main strains, the *Kusmi* and the *Rangeeni* with minor morphological differences and producing slightly different types of resin. It may also seem probable that a number of sub-strains may occur with preference for certain host plants. These may or may not bear any morphological differences. It also seems probable that if some of these sub-strains are transferred from one host to another host many of the characters which might be of use in identifying the sub-strains may be progressively changed.

Mahdihassan[15] described *Lakshadia nagoliensis* on *Schleichera trijuga* (kusum) as the most desirable insect for lac. According to him *Lakshadia chinensis* on *Cajanus indicus* (Arhar) has the greatest dye content. Misra, Awadh Behari[17] collected lac insects from Northern India and classified them as follows:

> *Laccifer longispinia* on *Cajanus indicus; Lacciferkydia* on *Kydia calicyna; Laccifer pusuna* on *Zizyphus jujuba* and dak *(Butea fromdosa); Laccifer ambigua* on jheolia; *Laccifer jhasiensis* on *Zizyphus jijuba* and *Laccifer indica* on the host *Zizyphus jujuba.*

The other lac insects as reported in the literature[18-26] are *Lakshadia albizziae*, *Lakshadia ficii*, *Lakshadia sindica*, *Tachardia blanch*, *Laccifer siamensis*, *Laccifer lacca*, *Tachardiella larrea*, *Gascardia*, *Lecanium*, *Tachardina theae*, *Tachardina afflnens*, *T. africana*, *T. diolipterae*, *T. digitala*, *T. protrudens* and *sclerosa*.

Varshney[27] proposed that the generic name of the lac insect to be called 'Kerria'. He followed this kind of nomenclature from Tozzette. This name has been approved by the International Commission of Zoological Nomenclature. Thus at present lac insects are known as *Kerria lacca.*

The lac insect starts its life as a minute red coloured larvae. At certain times of the year the larvae emerge from the cells of the female lac insects. They emerge in large number and this emergence is known as swarming. The larvae prefer tender and succulent shoots of trees (Lac-hosts). They can easily feed on their sap-juices. They choose the lower portion of the shoots. They do not, generally, settle on old and hard shoots, because they are unable to collect food from such shoots. Therefore trees to be used as lac-hosts should be prunned before infection in order to get tender shoots. Trees can also be used without pruning but in that case no good lac crop is expected.

The larvae of the lac insects are introduced to their new hosts by a process known as 'infection'. This consists in cutting branches bearing matured lac from which the larvae are about to emerge out, into pieces of length generally one feet and tying up these sticks to the new branches (resulted from pruning) of the lac hosts. In this condition lac is called brood lac as it contains the young swarms. Gradually the larvae emerge from the brood lac, crawl on to the new shoots and settle there. They begin to live on sap-juice of the shoots by forcing their mouth part through the bark into the phloem and zylem tissues. A resinous secretion from their dermal glands (gland cells)[28,29] cover them up gradually. The larvae settle on the shoots so closely that secretion from the body of one insect meets that of another and thus forms a continuous covering of lac.

Among the larvae there are males and females. Both males and females make lac-cells of their own having difference in size. Cells made by the females are globular and those made by males are elliptical. The males are lesser in number than the females. On the cells made by both males and females there are openings or slits for respiration and passing out stools. Through these slits comes out a white wax in the form of thin hair from time to time. Sometimes this type of substance comes out in such a rate that the whole of lac encrustation seems to be covered with white wool. This white substance on the cells proves the presence of the lac insects, inside the cells, to be in living condition. However, the absence of this white substance (wax) does not prove them to be dead or ill. Sometimes due to the blowing of air it may disappear. Within 40-50 days, counting from the date of infection, males come out of their cells and walk over the lac encrustation to fertilize the females within their cells. The males die after performing the function of fertilization. They do not secrete lac. Only the females secrete the lac of commerce.

The females once settled down never move again. They go on-secreting lac continuously and cover up the branches. This covering is known as lac in general. On each and every cell there is a slit through which comes out a honey-taste substance. This attracts ants very much. That is why large number of ants are found on the lac-hosts. These ants are rather useful to the growth of females and thereby to the secretion of lac. The ants use to eat up the honey-taste substance and prevents the closing of the slit and thus help the females to survive against suffocation.

The females begin to grow inside their cells and ultimately eggs are developed within their system. At proper time they lay eggs within the cells and finally the eggs are hatched into larvae which emerge out from their mother cells. The period of growth from the egg to the matured female giving rise to production of eggs again is known as life cycle. Life cycle of lac insects occur twice a year. Two types of insects *Rangeeni* and *Kusmi* are found in India. The former is the only type available in Bangladesh. In a year each of these two types give rise to two crops. For rangeeni type of insects, the crops are *katki* and *baisakhi* and for *kusmi* the crops are *aghani* and *jethui*. The crops are named as per names of the months in which they are harvested. Kusmi strains thrive on *kusum* trees only while rangeeni on so many hosts like *palas*, *her*, *dumur*, *khair*, *leechi* etc. Each rangeeni insect produces 0.029 gm of lac while each kusmi insect gives 0.069 gm.[30]

1.4. Lac cultivation

Lac insects are introduced to their new hosts in the month of june-july. Male insects come out by the month july-september. Larvae emerge from their mother cells in the month of september-november (kartik). This crop is called *katki* or *kartica*. This crop is mainly used as brood lac and hosts are infected by this brood lac in september-november. Males come out of the cells in the month february-march and the larvae (after maturity of the crop) come out from their mother cells in june-july. This crop is termed as *baisakhi* as because major part of this crop is harvested for commercial purpose in the month of april-may (baisakh) keeping a part of it as brood lac to be harvested in june-july. Brood lac from this crop, matured in june-july is used for the next crop *katki*. In every lac growing area *baisakhi* is the main crop (commercial crop) and *katki* crop is used as brood lac.

The above two crops relate to rangeeni strains of lac insect. Kusmi strains thrive on *kusum* trees. The lac thus produced in the host is scrapped from its twigs. Such lac in the scrapped condition is termed as stick lac or simply raw lac.

Raw lac is of two kinds, *ari* and *phunki*. When lac is harvested before swarming of larvae and the mother insects remain alive within the cells, it is called ari. If lac is cut after swarming or before swarming but the larvae are allowed to emerge out before selling we get phunki lac which contains the dead bodies of the insects. Brood lac after being used as seed can be scrapped and used.

When raw lac is crushed and washed a deep-crimson coloured dye is obtained. This is known as lac-dye. This dye is due to the presence of colouring matter of the bodies of lac insects.

1.5. Lac Host

The trees, shrubs and bushes where the lac insects thrive upon are known as lac hosts. The insects take food from the sap-juice of the host. There are so many trees, shrubs and bushes which can be used as the host-plants (food plants) of lac insects. Nonis, Dorothy, H.T. Bates and M. Rangaswami[31,32] described *acacia catechu* as an excellent alternative host instead of *schleichera trijuga* (kusum) for the cultivation of lac.

R.D. Richmon,[33] considered *Atylosia albicans* as an excellent host for lac insect. According to T. Hedley Barry[34] and P.M. Glover[35] butea frondosa (palas), *schleichera trijuga* (kusum), *zizyphus jujuba* (ber), *z. xylopyra* (ghont), *ficus relegiora* (pipal), *acacia arabica* (babla) and *cajanus indicus*) (arhar) are reported as important hosts for lac insects in India. Sharapov, Dzhasti and Prokopenko[36] stated that there are about 150 species of woody shrubs as hosts plants for lac insect in USSR.

Krishnaswami, Purakyastha and Chanhan[37] described *moghamia macropylla*, as a new host for Kusmi strain. *Moghania chappar*[38] has been reported to be suitable both for kusmi and rangeeni strains of lac insects. *Dyospyros tomentosa* Roxb. No. Ebanaceae[39] *Guazuma tomeutosa*[40] are also reported as a host. The following is a list of plants which are reported as hosts of lac insects.[41]

Botanical Name	Family	Vernacular Names
Acacia arabica[42,45]	Leguminosae	Babul, Kikar (Punjab), Babla (Bengali)
Acacia canescens	"	Karugai (Madras)
Acacia catechu	"	Khair (Bengali), Sa (Burma)
Acacia concima	"	-
Acacia farnesiana	"	Bilati Babul, Gul Babla (Bengali)
Acacia latronum	"	-
Acacia leucophloea	"	-
Acacia moniliformis	"	-
Acacia pennata	"	-
Acacia suma	"	Mankata (Bengali)
Albizzia lebbek	"	Siris (")
Albizzia lucida	"	Silkarai (")
Albizzia stipulata	"	Amlaki (")
Albizzia odoratissima	"	Siris (")
Atylosia albicaans	"	-
Atylosia mollis	"	-
Annona squamosa	Anonaceae	Ata (Bengali)
Annona squamosa	Anonaceae	Awja (Burma)
Bursera serrata	Burceraceae	Chitrika (Bengali) Thadi (Burma)
Berrya ammonilla	Tiliaceae	Pank-nwe (Burma)
Butea frondosa	Leguminosae	Palas (Bengali)
Butea superba	"	Lata Palas (Bengali)
Caesalpinia coriaria	"	Angrezi emli (cp) Lib Dibi Sumuk (Telegu)
Cajanus indicus	"	Arhar (Bengali), Nandu (Assam)
Croton oblongifolius	Euphorbiaceae	-

Botanical Name	Family	Vernacular Names
Dalbergia cultrata	Leguminosae	Yindaik (Burma)
Dalbergia lanceolaria	"	-
Dalbergia latifolia	"	Shitshal (Beng)
Dalbergia oliveri	"	Jamalam (Beng)
Dalbergia Paniculata	"	Dhoben (Hindi)
Dichrostachys cinerea	"	-
Dohlicos falcatus	"	-
Entada scandens	"	-
Engeltiardtia spicata	Juglandaceae	Wakgru (Assam)
Ficus altissima	Moraceae	-
Ficus benghalensis	"	Bot (Beng)
Ficus carica	"	Fig, Dumur (Beng.)
Ficus cunia	"	Jugdumur (Beng.)
Ficus glabella	"	Patkel (Beng.)
Ficus glomerata	"	Gular (Beng.)
Ficus hispida	"	Kanch Dumur, Kag dumur (Beng.)
Ficus indica	"	Bot (Beng.)
Ficus infectoria	"	Pakur (Beng.)
Ficus nervosa	"	Nyaeng-Peinul (Burma)
Ficus obtusifolia	"	Nyaeng-gya (Burma)
Ficus religiosa[44]	"	Pifal, Aswatha (Beng.)
Ficus roxburghii	"	Juinla, Dumur (Beng.)
Ficus rumphii	"	Jui, Aswatha (Beng.)
Ficus tsiela	"	-
Flemingia congesta	Leguminosae	Bara salpan (Beng)
Grewia laerigote	Tiliaceae	-
Grewia multiflora	"	Panisara (Beng.)
Kydia calycina	Malvaceae	-
Leea crispa	Ampelidaceae	-

Botanical Name	**Family**	**Vernacular Names**
Leea robusta	"	Gangma (Assam)
Nephelium lichi	Sapindaceae	Lichi, Lichu (Beng.)
Schleichra trijuga	"	Kusum (Hindi), Gyo (Burma)
Ougeinia	Leguminosae	Tinis (Beng)
Pentacene suavis	Dipterocarpaceae	Ingyin (Burma)
Polyathia subsosa	Annonaceae	-
Shorea obtusa	Diptrocarpaceae	Shal
Shorea talura	"	Talura (Tamil)
Zizyphys jujuba	Rhamnaceae	Ber, Kul (Beng.)
Zizyphus xylopyra	"	Ghont, Malhar (Punjab)

The following lac hosts are of special importance:

Kusum *Schelichera trijuga* (Sapindaceae)

Palas *Butea frondosa* (Leguminsae)

Plum (Ber) *Zizyphus jujuba* (Rhumnaceae)

Khair *Acacia catechu* (Leguminosae)

Raintree *Pithecolobium saman* (")

Moghania moghania macrophylla (")

Kusum

Kusum is the most valuable lac host producing the best quality of lac. It is found in the hilly places and jungles. It grows to a considerable size (a big tree). It is a tree of general economic value.

Palash

It is also a good lac host but not found everywhere. It is a semi-jungle and waste land tree. It grows abundantly in some region otherwise it is rearely found. It grows automatically. Its wood is very hard but of little value. It is rarely found in Bangladesh. This plant has been grown in BCSIR Labs., Rajshahi and is under trial.

Plum (ber.)

Plum (ber) tree, although, is not so good a lac host as kusum, yet as largely found, it is the only lac host producing the bulk of the lac of commerce in Bangladesh. It is a fairly rapid growing tree. It is useful as lac host at the age of 3 - 4 yrs. Its wood is of little value while its fruit the plum is favoured very much.

Khair

It is also a tree well worth planting as lac host. Khair is, in addition, a valuable tree in itself, catechu (kutch) and kath both being obtained by boiling the chips of its heart wood. The wood can also be used in making very much useful accessories like wheel etc. It also gives fuel and charcoal. Khair trees are largely found in Rajshahi districts. So, both lac and catechu cultivation may be simultaneously practiced upon them. From the experiments of Katki crop, 1962, in Silk and Lac Research-cum-Training Institute, Rajshahi, khair was found to be a good lac host for katki crop. Experiments in BCSIR Laboratories.[45], Rajshahi, also proved it suitable for lac cultivation.

Raintree

It is a large grown tree and found everywhere in Bangladesh. Unfortunately, this tree is not yet in use as lac host in the lac growing areas of Bangladesh. The reason is that it is not found largely in the present lac producing areas of our country. Moreover it is a tree generally found in the urban areas. Its wood is very soft and of little importance. Recent investigations in Silk and Lac Research-cum-Training Institute, Rajshahi proved it to be a good lac host. Experiments is BCSIR Laboratories, Rajshahi also proved it suitable for lac host.[46] Rain tree is one of the best lac host in Thailand.

Moghania Macrophylla (Syn. Flemingia congesta)

It is a bushy lac host growing to a height of about 5-6 feet. It is one of the suitable lac hosts in Thailand. In 1963, experiments in Silk and Lac Research-cum-Training Institute, Rajshahi, showed that it is a good lac host, specially for katki crop.

1.6. Pruning of Lac Host

Trees should be prunned in order to get better crop. If the old branches are prunned properly, new branches grow and the lac insect can find the tender and new shoots to settle on. They go upto the extreme end of the soft point of the branches and settle there. Growth of trees also depends on proper pruning. In some cases or sometimes the trees are subject to automatic pruning i.e. by harvesting, the trees get prunned. Actually, both pruning and harvesting are the same in case of trees which are already under lac cultivation. But after harvesting of katki crop the trees are again prunned in the march-april to make them again fit for infection in june-july.

Because the shoots resulting from pruning or harvesting in the month of october-november become old and hard by june-july so, they require to be prunned again in march-april.

Generally branches in between 1″ and 2″ in diameter should be prunned. Branches below 1″ in diameter, if needed to be cut off, should be prunned at the point from where they result. Waste and dry shoots should be cut off carefully. Some of the new branches which have been pruned once should be left at the time of pruning again.

1.7. Infection (Inoculation)

The process by which the larvae are introduced to their new hosts is known as infection or inoculation. The timings for infection are june-july, october-november and january-february. In june-july hosts other than kusum are infected by baisakhi or jethui brood. In october-november trees other than kusum are infected by katki brood lac for baisakhi crop. Agrhani brood lac is used in the month of january-february for jethui crop.

The brood lac to be used should first be examined whether is free from the attack of enemy insects (the parasite and predators). The damage done by the parasites chalchids is negligible (4.8%) while that by predators *Eublema amabli* and *Holcoera pulverea*[47-49] is heavy (30-40%)[47]. The larvae of the predators feed both on lac insect and the lac produced by it[48]. The brood lac affected by these insects should not be used.

1.8. Harvesting of Lac

The following are the harvesting seasons :

i. April-may : During this season, baisakhi crop is harvested for commercial purpose and a part of it is kept to be used as brood and to be harvested in june-july.

ii. October-november : During this season katki crop is harvested. This crop is totally used as brood lac for baishaki crop.

iii. June-july : a) A portion of the crop baisakhi, used as brood lac for katki crop is harvested during this period.

   b) Jethui crop is harvested during this time either for commercial or for brood purpose.

iv. November-december : Major portion of agrhani crop is harvested this time, leaving a part. as brood lac for jethui crop.

v. January-february : A portion of agrhani crop, left to be used as brood for jethui, is harvested this time.

Commercial crop, say, baisakhi or agrhani may be harvested a bit earlier or late than the above mentioned seasons. Brood lac crop, katki or jethui should be cut or harvested just at the time of swarming of the larvae (or emergence of larvae). The larvae emerged out in search for their settling on new shoots. Therefore, lac (brood lac) is harvested immediately after total infection of the hosts by it so that no larvae are spoiled. Generally larvae from brood lac, left from baisakhi crop emerge by last week of june and those from katki crop by first week of october.

From the following facts the approximate date of emergence can be determined :

a. On the encrustation of lac some crack marks are observed before 2-3 weeks of emergence.

b. The lac encrustation becomes dry and yellowish before 2-3 weeks of swarming.

c. If a lac cell is pressed by fingers and the mass inside is mixed with water, newly formed bodies of larvae are observed in water in a floating condition before 1-2 weeks of emergence.

1.9. Composition of Lac

The major constituent of raw lac is the resin (70-80%); other constituents present are; sugars, proteins, and soluble salts, 2-4%; colouring matter, 1-2%; wax, 4-6%; sand, woody matter, insect bodies and other extraneous matter, 8-12%; a volatile oil is present in traces[50].

Lac resin (mol. wt., 1,000; acid val., 59-75; hydroxyl val., 255-280; sap. val., 225-230) is composed of inter-esters of hydroxy fatty acid derivatives. Aleuritic acid (trihydroxypalmitic acid. $C_{16}H_{32}O_5$ m.p. 101°) is the major constituent; several isomers of aleuritic acid are also present. Shellolic acid ($C_{15}H_{20}O_6$), a dihydroxy hydroaromatic acid, occurs to the extent of 10%; two isomeric shellolic acids (m.p. 206° and 238°), two isomers of dihydroshellolic acid (m.p. 226° and 245°) and two isomers of the next higher homologue of dihydroshellolic acid (m.p. 166° and 226°) have been reported to be isolated. Other acid constituents present in lac are kerrolic acid ($C_{16}H_{32}O_6$, m.p., 32°) and butolic acid ($C_{13}H_{30}O_3$, m.p. 54-55°) : the former is a tetrahydroxy hexadecanoic acid, while butolic acid is a monohydroxy pentadecanoic acid.

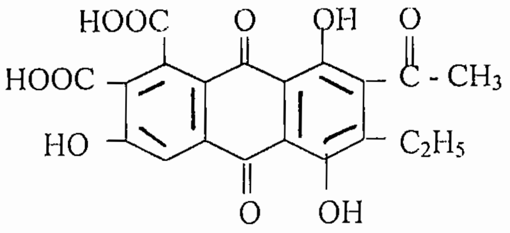
The resin can be fractionated into soft and hard components by exhaustive extraction with ether; the former constitutes 30% of the original resin and is brown in colour. Both soft and hard resins can be further fractionated by successive extraction with organic solvents. One fraction of soft resin contains free acids and neutral materials including the yellow dye, erythrolaccin. The second fraction possibly comprises inter-esters of equivalent amounts of aleuritic acid, an isomer of aleuritic acid and lacollic lactone. Mono and dihydroxy-palmitic acids, butolic acid, a liquid lactonic acid and two solid acids (m.p. 149° and 225°) have been reported to be identified in the resin. The largest fraction (50%) of the hard resin consists of a monobasic inter-ester ($C_{32}H_{54}O_9$) which on saponification yields equimolar proportions of aleuritic acid and lacollic lactone; the latter is a mixture of several constituents but has the properties of a single hydroxy acid lactone of the composition $C_{16}H_{24}O_5$. The second largest fraction (25%) is composed of inter-ester lactones of equivalent amounts of aleuritic acid, lacollic lactone and kerrolic acid.

Wax : The wax present in stick lac is usually obtained as a by-product in the manufacture of dewaxed shellac; it is known in the trade as shellac wax. The analytical constants of the wax fall within the following ranges; m.p. 72-82°; Sp.gr., 0.971-0.982; acid val. 12.0-24.3; sap. val. 79-126; ester val. 45.5-104.0; and iod. val. 6.8-8.8; It contains : esters (ceryl lignocerate, ceryl cerotate, lacceryl lacceroate, ceryl aleuritate) 80-82%; acids (lacceroic, cerotic), 10-14%; alcohols (Neoceryl, lacceryl) 1%; hydrocarbons (pentacosane, heptacosane) 2-6%; and resins, 2-4%. It resembles carnauba wax and although it is useful in formulations where a natural wax of the hard type is desired, its principal use is in the electrical industry.

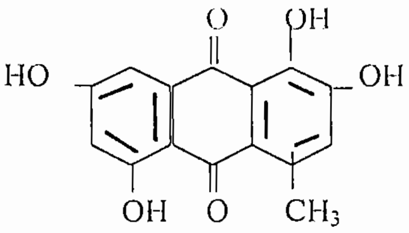
Colouring matter : Stick lac contains a water soluble dye, laccaic acid ($C_{20}H_{14}O_{10}$) and a water insoluble dye, erythrolaccin ($C_{15}H_{10}O_6$). Lac dye is an extremely ancient dye stuff (loc.cit). Dimroth and Gold Schmidt[3] concluded that laccaic acid has the formula $C_{20}H_{14}O_{10}$ and not $C_{16}H_{12}O_8$ as suggested by Schmidt.

It is well known that before the emergence of synthetic dyes lac dye was largely used for dyeing wool and silk.

The erythrolaccin is a dye insoluble in water but soluble in almost all the solvents of lac resin. It is a tetrahydroxy-methyl-anthraquinone. The position of methyl and hydroxyl groups are controversial. Recent studies have established that erythrolaccin is 1, 2, 5, 7-tetrahydroxy-4-methyl anthraquinone.



Laccaic acid according to
Mayer on the basis of Dimorth's



Erythrolaccin (1,2,5,7-tetra-hydroxy-
4- methyl anthraquinone)

Refining : Crude lac, as obtained by scrapping the resinous encrustations from harvested twigs, is known in commerce as stick lac. It is seldom used without refining.

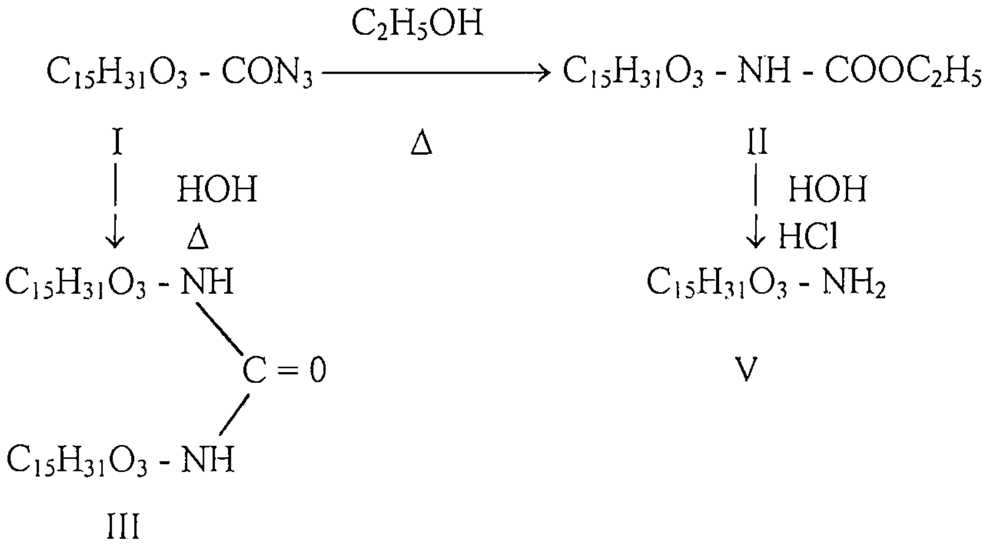
Stick lac is crushed by hand or power operated roll mills and washed with water repeatedly. It is then dried on cemented floors away from the direct rays of the sun and finally winnowed. The water soluble colouring mater is removed during washing. Washed lac or seed lac, thus obtained is in the form of grains (10 mesh/in. or less), yellow or reddish brown in colour. Adhering impurities amount to 3-10%.

The impurities are eliminated from seed lac by further treatment - hot filtration of molten material or by dissolution in a suitable solvent.

1.10 Nature and Constitution of Shellac

Aliphatic polyhydroxylamines have many interesting properties. They are valuable intermediates in the synthesis of several new compounds which would be useful in the paint and other fields. Such hydroxylamines might be prepared from polyhydroxy acids which have been obtained from shellac. The hydroxyl groups of such acids, however, have a tendency to react intermolecularly when subjected to elevated temperatures of 100° or more. Naegel[51] and others carried out several synthetic approaches starting from one of the important constituents of lac, like aleuritic acid. These series of reactions can be expressed as follows wherein the group $C_{15}H_{31}O_3$ may be represented as, CH_2OH- $(CH_2)_5$-CHOH-CHOH-$(CH_2)_7$–

CURTIUS SERIES OF REACTIONS



NAEGELI MODIFICATION

$$\underset{\text{I}}{C_{15}H_{31}O_3 - CON_3} \xrightarrow[\Delta]{C_6H_6} \underset{\text{IV}}{C_{15}H_{31}O_3 - NCO} \xrightarrow[\text{Alkali}]{HOH} \underset{\text{V}}{C_{15}H_{31}O_3 - NH_2}$$

In an attempt to prepare an amine (V) corresponding to aleuritic acid (9,10,16-trihydroxypalmitic acid) with the aid of the Curtius series of degradation reactions, the acid was esterified directly with anhydrous methyl alcoholic hydrogen chloride. The product, methyl aleuritate, was converted to the acid hydrazide, by the action of hydrazine hydrate on an alcoholic solution of the ester. This conversion was practically quantitative when highly purified samples of the ester were used. Nitrosation, at temperatures approaching 0°, converted the hydrazide into aleurityl azide I, as unstable, hygroscopic solid. When I was heated in water for three hours, N, N'-bis-8, 9, 15 -trihydroxypentadecylurea III was formed, while when I was refluxed with anhydrous ethyl alcohol for one and half hours, 8, 9, 15-trihydroxypentadecylurethan II was the resulting product. When I was decomposed by heating in anhydrous benzene for one hour, the corresponding isocyanate was formed.

Hydrolysis of the isocyanate IV with hot aqueous alkali produced 8, 9, 15-trihydorxypentadecyl-amine (V), melting at 146-147°. The picrate of the amine was a yellow powder melting at 118-119°.

1.11. Shellac Substitute

There is no better substitute for lac resin, as is known, amongst natural resin.[52] According to Metcalf and Flint[53] no modern superior substitute has been found. Lac in its purified form "shellac" as is known in commerce, is unequalled by any synthetic product because of its unique combination of mechanical, thermal and electrical properties. Although modern science has developed many synthetic resins in recent years; but no substitute has yet been produced which has all the characteristic of the shellac. Some substitutes are on phenol- formaldehyde basis.

Shellac substitute is derived from linseed oil fatty acids[54]. Harries and Nagel have recorded experiments on the synthesis of shellac[55]. A shellac substitute is claimed by adding sodium carbonate in quantity just less than that necessary to neutralize free acidity of pontianac gum, dissolved in a solvent comprising equal parts of rosin and accroides[56, 57]. Dammar soluble in hydrocarbon and Manila copal soluble in alcohol are very good substitutes for shellac[58]. Vinyl butyral resins could be added to Manila to produce shellac substitute products obtained from natural sources can hardly compete with their suitable synthetic substitutes[59].

1.12. Uses of different Lac Products

1.12.a. Seed lac : It is used in the manufacture of shellac, button lac, bleached lac, sandstone (for sharpening razors and scissors), hard lac resin, dewaxed shellac flakes, adhesive, wood varnish etc.

1.12.b. Shellac : It is largely used in varnish and polish making. Both spirit and aqueous types of varnish can be prepared from shellac. It is used in the manufacture of sealing wax, gramophone records, paper and leather finishing, in hat industries, grinding wheels, electrical insulation, mirror backing paints, lacquer for playing cards, shoe-dressing, water proof inks, vehicle for toys, varnish for water proofing for cartridges, shell cases, retarding agents in gun powder mixtures, for cigarette tips, lacquer and gold print, manufacture of laminated parts of electrical industries and in moulding powders.[60-62] Shellac is also used in hair spray, edible pharmaceutical inks and for coating tablets.[63-65] Lac (shellac) is also used in the preparation of Brihat Chandanadi Toil to cure fever and cough.[66]

1.12.c. Button lac : Button lac is used in jewellery as filler in ornaments, in quality polish and for bonding mica splittings into micanite[67] etc. and in the manufacture of sealing waxes[68] and also in varnish for railway bogies and wagons.

1.12.d. Garnet lac : As blended with other lacs it is used in the manufacture of electrical insulators, grinding wheels, leather finishes and polishes where colour is not an important factor[67].

1.12.e. Dewaxed shellac : It is used in glossy calf finish, shoe-dressing, repairs base solution, electrical industries, preparation of aleuritic and shellolic acids, baking varnish, oil insulating varnish, glossy and water resistance varnish[68] and in Ordnance factories for sealing and varnishing detonating caps etc., lead-tin foil sheets/discs for sealing cap components of various types, cartoons for exploder and ammunition components. The paper components are made water proof with dewaxed shellac and its adhesive property is utilized in sealing the cap detonators. Dewaxed shellac is also used in the preparation of varnish for coating fabrics, in cements for fixing backelite mouldings to metals.

1.12.f. Bleached lac : Bleached lac is largely used in the manufacture of pale-varnish and nitrocellulose lacquers as plasticizer[68], in floor polishes, in water-varnish for fur-felt-hat and in preparation of edge ink and black ink etc.

1.12.g. Hard lac Resin : It is used in varnish and electrical industries. It has got improved properties over shellac, specially with regard to heat and water resistance, better adhesion and elasticity etc. It is also used in the preparation of aleuritic acid[69-70] etc.

1.12.h. Lac wax : It can be used in shoe polishes in place of carnauba wax. It can also be used in carbon paper, lipstick and tailors chalk[72].

1.12.i. Lac dye : Lac dye can be used in dyeing silk, wool and jute[71] and umbrella sticks and boxes. It had an extensive field of uses as reported earlier, and food colouring material.[72]

1.12.j. Aleuritic acid : Aleuritic acid, the main constituent of shellac is used in the preparation of adhesives, plasticizers and in protective coating for electrical insulators. It is also used in perfume industry for the synthetic preparation of costly compounds such as civetone, dihydrocevetone and related lactones.[72]

1.13. Lac Productions in Bangladesh

The five upa-zillas such as Nawabganj, Shibganj, Bholahat, Gomastapur and Nachol under Nawabganj district and a few places of Dinajpur district are the present lac growing areas of Bangladesh. The lac host used in this areas is Ber (Zizyphus jujuba) only.

Late Mr. Idrish Ahmed EX-MLA of Dadanchak, formerly a member of Indian Lac Cess Committee believed that the present Bangladeshi portion of lac growing area produced one lac maunds of raw lac annually. However, the production figures of lac was fixed at 300 maunds[1]. Immediately after Partition (1947) the industry got disrupted. The production figures from 1952-1966 were as follows :

1952-54	4000 mds
1954-55	6000 mds
1955-56	8000 mds
1956-57	7000 mds
1957-58	8000 mds
1960-61	5000 mds

1962-63	8554 mds
1963-64	4550 mds
1964-65	3058 mds
1965-66	4573 mds

Upto date data for lac production is not available. However, as per opinion of the owners of some lac factories it may come upto 30000 mds. annually. Lac cultivation entirely depends upon weather of the region. Both draught and heavy rainfall are the adverse factors for lac cultivation. The places where there is no extreme heat in summer or extreme cold in winter and the extent of rainfall is between 30" and 35" are most suitable for the production of lac. In fact humid climate is able to supply lac seeds with nutrition.[73]

1.14. Area under lac cultivation

There is no systematic plantation of lac hosts in the present lac growing areas. The available number of (lac growing trees) lac hosts are about 40-50 thousands. There are about 34 lac factories at different places of Shibganj, Nawabganj and Rajshahi (town areas).

1.15. Yield of lac

A standard size of ber tree can produce about 28-37 kg of stick lac (raw lac). On an average the yield per tree (ber) can be estimated at 9 kg per tree.

1.16. Lac Development Projects in Bangladesh

As stated before lac production depends upon weather factors. Sometimes the growers fail to procure lac seed (brood lac) from their own crops due to adverse atmospheric conditions. A brood lac multiplication farm was established at Nawabganj district town for supplying healthy and disease free brood lac to growers. Agriculture Department set up small units attached to the seed multiplication farms for extension of lac cultivation.

1.17. Lac Research in Bangladesh

One research institute namely, "Silk and Lac Research-cum-Training Institute", was set up at Rajshahi for carrying out research on silk and lac. This Institute started functioning in 1961. Presently the lac research division of the BCSIR Laboratories, Rajshahi is deeply engazed in the related research work.

Lac research division of BCSIR laboratories took up projects aiming at the diversification of the uses of lac and for crop studies for finding better cross-strains of lac insects and other host plants suitable for lac cultivation other than the traditional host plant, ber.

After several years of experimental cultivation it has been reported that khair, babla, rain trees etc. are also suitable as host plants for lac cultivation along with conventional ber trees. Research also conducted to check the lac crop from destruction by flies and birds. In the processing side the contribution of this division are worth mentionable. They are described as follows[74] :

(i) Sealing wax from lac

A lac based sealing wax formulation was derived by this division. This is a selected and specially used item of commerce. The developed process has already been leased out.

(ii) Kiri varnish

Kiri is a lac waste and also a by-product of the indigenous shellac manufacturing industry. It is used as a good wood varnish, french polish, sealing wax etc. Lac Research Division has been prepared a cheaper varnish from this waste product. The developed process has already been leased out.

(iii) Capping cement

Lac-based water and heat resistant cement for cementing glass to metals are rare and valuable products of commerce. It is produced by admixing shellac resin, synthetic resin and fillers. On heating, it attains adhesive properties. The prepared sample was tested in Bangladesh Lamps Ltd., Dhaka for its suitability to metal to glass joint.

(iv) Printing ink from lac

Printing ink has a good demand in Bangladesh. An extensive research programme was undertaken with a view to developing a process for the production of printing ink. The project is now under pilot plant studies at Pilot Plant and Process Development Centre (PP & PDC), Dhaka.

(v) Glass clear cement

Lac based adhesive to join glass to glass and glass to metal cement have been evolved. These product has great demand in this country but none are produced locally. A research project is undertaken in this field to produce quality glass clear cement.

(vi) Ready made varnish from lac

Methylated spirit based lac varnish is used in our country for wood varnishing which is costly. An extensive research programme was undertaken for developing a process for the production of ready-made varnish.

1.18. Concluding remarks

It is evident from the foregoing section that lac is a valuable cash crop and it has wide use in industrial as well as other commercial fields. It can play a vital role in earning foreign exchange too. It has already been possible to convert raw lac into various kinds of finished products with the help of scientific research for their necessary use at home and abroad. It is hoped that if the results of the research together with Government support are applied in a wider scale, they would definitely give impetus to the growers and processors for increasing the volume of production of raw lac and various kinds of lac products. This, in turn, will lead to the rapid development of lac production and convert it into an export oriented important industrial sector of Bangladesh.

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CHAPTER 2

REFINING OF LAC, ITS CONSTITUENTS AND SPECIFICATION

1. REFINING OF LAC, ITS CONSTITUENTS AND SPECIFICATION

The lac used for the present investigation was collected from the experimental garden of BCSIR Laboratories, Rajshahi. In the field area of these Laboratories a project has been initiated for the cultivation of lac.

EXPERIMENTAL

1.1 Production of Stick lac

Stick lac is the crude product that is just collected from the lac bearing twigs. Lac crop was collected by cutting the lac bearing twigs (50 sticks) of hosts (ber.). Lac encrustations were separated from the twigs by a knife. Lac thus gathered in this form is known as raw lac or stick lac. Yield 10 kg.

1.2 Production of Seed lac

Seed lac is the starting material for the preparation of shellac, the refined product of lac. Seed lac is obtained by crushing, washing and drying of stick lac following the procedure given below :

(i) **Crushing of stick lac :** A moisture free dried portion (10 kg) of stick lac was crushed well in a grinding mill and the powdered mass was then sifted out from the relatively coarser wooden particles through a strainer. The dried powdered product weighed 9.5 kg.

(ii) **Washing of crushed lac** : The vessel used in washing was a cement vat having the shape of corner cup of a thermo-flask and about 2 ft. in height. The inner surface of the vat was rough. 5.0 kg of well crushed lac was taken in this vat and water (5 litre) was poured in. It was then rubbed against the bottom. Continuous rubbing thus crushes the lac cells and washed out the dye. This dye, laccaic acid ($C_{20}H_{14}O_{10}$), is of crimson colour and is due to the colouring matter of the bodies of lac insects. After rubbing for half an hour the fibrous matter, the coccus bodies, the wood chips etc. were removed. The water was then decanted off. This process was continued until the dye was separated. Finally it was washed with 1.6% sodium carbonate solution. After washing the collected lac was dried on cement floor in diffused sunlight. When dried, the resulting material is called seed lac (lac dana), Yield 3.5 kg (70%) calculated on the basis of weight of stick lac taken.

1.3 Preparation of Shellac

Seed lac, which is only a semi refined product, still contains some (3 to 7%) impurities including sand, wood-chips etc. It is further refined by hot filtration, i.e. by heating the material and straining the fused mass through cloth to free it from infusible impurities.

In this process seed lac (3.0 kg) was packed in a coarse cloth bag usually about 10 m long and 7.5 cm in diameter. It was heated in a special type of furnace. Twisting pressure was applied on the seed bag and the molten mass came out through the porous surface of the bag, which was then worked up with an iron spatula and transferred to the horizontal surface of a glazed porcelain hot water cylinder. This cylinder was about 75 cm long and of 25 cm in diameter. The molten mass was spread quickly with the help of a spatula. The sheet thus formed was broken into small pieces and the resulting product was the shellac of commercial importance. Yield 2.7 kg (90%), calculated on the basis of weight of seed lac taken.

During the entire process of shellac preparation the following by-products were obtained.

1.3.1. Molamma- During the process of washing, a finely ground dust like material was obtained which was called molamma. This can be used in sealing wax and garnet lac.

1.3.2. Kiri - The impurities that continuously accumulate inside the bag still contain an appreciable amount of lac (Ca. 11-12%). This by-product is known as kiri or kiri lac. It can be used in the manufacture of wood varnish, sealing wax production, french polish preparation etc.

1.4 Preparation of Dewaxed shellac

Lac contains 5-6% of wax. When wax is removed it is called dewaxed shellac. Dewaxed shellac was prepared by the following method.

1.0 kg of semi-powdered seed lac was taken in a 6 litre flat bottom flask and to it 4 litre rectified spirit was added. It was then kept over night at room temperature with occasional shaking. The lac solution thus obtained was filtered through nylon cloth. Most of the wax was removed by the filtration. The filtrate was distilled on a water bath to recover the solvent. The residue was transferred to a porcelain basin and was heated on a hot plate at 110°C so as to remove the residual solvent. The molten mass was cooled at 50°C and made into flakes. The yield obtained was 900 gm (90%), calculated on the basis of weight of seed lac used.

1.5 Production of Bleached lac

Seed lac is orange in colour. This colour is removed by the bleaching treatment and bleached lac is obtained. Seed lac is bleached for converting it into a white base. The pale yellow to orange red seed lac was decolourised by the following method :

500 gm of seed lac was taken in a stainless steel beaker (10 litre) and was dissolved in 5 litre 1.6% aqueous sodium carbonate solution and heated and stirred at 70-80°C, until seed lac goes into solution. The dissolved lac solution was filtered through a coarse cotton cloth to remove undissolved and suspended impurities. The filtrate was cooled down to 30-35°C. To the above filtrate 510-620 cm^3 of sodium hypochlorite solution was slowly added with stirring with the help of a mechanical stirrer at room temperature. On acidification with 1% H_2SO_4 solution (150 cm^3) the decolourised lac (bleached lac) was precipitated out. The precipitated bleached lac was filtered through a coarse cotton cloth and washed well with water until freed completely from acid. Residual chlorine was removed by washing with 2% $Na_2S_2O_3$ solution and was dried at room temperature (25-30°C). The yield of bleached lac obtained, was 375 gm (75%), calculated on the basis of weight of seed lac taken.

2. Constituents of Bangladeshi lac

2.1. Composition of Bangladeshi stick lac, seed lac, shellac, dewaxed shellac and bleached lac

Abstract

Bangladeshi stick lac, seed lac, shellac, dewaxed shellac and bleached lac were analysed. The analytical data showed that all the varieties of lac contain resin, dye and wax as major components. The percentage composition of the constituents were also determined.

H.W. Chatfield[1], Hatchatt[2], Schaefer[3] and Hans Wolff[4] described the composition of stick lac produced in India. The composition and specification of lac vary with the nature of lac producing insects, nature of the host plants and climatic features. Hence attempts were made to find out the composition of different varieties of lac, e.g. stick lac, seed lac, shellac, dewaxed shellac and bleached lac obtained from Baisakhi crop produced in BCSIR Laboratories, Rajshahi by the Ranginee type of insects on the host ber tree (*Zizyphus jujuba*). The percentage composition of the said varieties of lac were determined and the results are summarized in Table 1.

EXPERIMENTAL

Stick lac, seed lac, shellac, dewaxed shellac and bleached lac samples were crushed and mixed thoroughly and stored in desiccators. Samples were taken for the following individual test..

(i) Determination of moisture content

The moisture content of the different varieties of lac was determined by heating about 3 gm of each of the individual samples at 110±2°C for an hour and then keeping it in a desiccator over concentrated sulphuric acid for 18 hours. The percentage of moisture content was determined from the difference of weight of the various samples used in the experiment. The result is summarized in Table 1.

(ii) Determination of ash content

3-5 gm of each of the individual sample was weighed in a porcelain crucible of constant weight and burnt in a muffle furnace at 650-700°C for 4 hours. The percentage of ash content was determined from the difference of weight of various samples used in the experiment. The results are given in Table 1.

(iii) Determination of foreign bodies

About 200 gm of each of the sample was washed 5 times with 500 cm^3 of 5% aqueous sodium carbonate solution. The washings with floating matters were collected together and filtered. The residue was dried and weighed. The result is summarized in Table 1.

(iv) Determination of dye

The above filtrate was acidified with dilute hydrochloric acid and allowed to stand overnight. It was filtered, dried and weighed. The result is summarized in Table 1.

(v) Determination of wax

100 gm of the individual sample was extracted with chloroform in a soxhlet apparatus. The solvent was removed completely from the extract. The residue is the wax which was dried in vacuum and weighed. The result is summarized in Table 1.

(vi) Determination of resin

The above dewaxed powdered sample was then extracted with rectified spirit in a soxhlet apparatus. The solvent was completely removed from the extract. The residue is the resin. It was dried and weighed. The result is summarized in Table 1.

(vii) Determination of insolubles in hot alcohol

After separating wax and resin from the individual sample of lac the residue was dried and weighed. The result is summarized in Table 1.

Table 1 : Composition of Bangladeshi stick lac, seed lac, shellac, dewaxed shellac and bleached lac.

Composition of lac (%)	Stick lac	Seed lac	Shellac	Dewaxed shellac	Bleached lac
Resin	70.87	82.25	87.60	91.95	88.95
Dye	10.00	2.50	1.50	1.12	Nil
Wax	8.54	6.00	5.50	0.10	3.55
Foreign bodies	4.00	1.75	Nil	Nil	Nil
Insolubles in hot alcohol	2.50	1.80	1.50	0.10	1.10
Moisture	2.01	2.00	1.90	1.52	1.75
Ash	1.37	1.55	0.90	0.15	0.44

3. Specification of Lac

3.1 Specification of Bangladeshi shellac

Abstract

Shellac was prepared by usual process and analysed. The specification (physical and chemical constants) were determined and found : volatile matter, 2.0-2.5%; matter insoluble in hot alcohol, 1.5-2.0%; ash, 0.5-0.9%; wax, 5.5-6.0%; iodine value, 14.0-15.0; acid value, 65-75; saponification value, 220-230; softening point, 75-80°C; orpiment, nil; lead, nil and rosin nil.

Shellac is the product obtained by refining seed lac by heat treatment or solvent treatment following usual procedure. Shellac produced by country process is the hand-made shellac and that produced by mechanical process is the machine-made one. Composition of lac may vary from locality to locality for change of race of lac insects and the hosts they thrive upon. For a particular place a particular race of insect is suitable[5].

Lac is more complex in nature than any other natural resin, such as rosin, copal etc., or rubber and cellulose which are all vegetable product[6]. Foreign matter in shellac, added as adulterants, or to facilitate processing or to obtain certain properties, are rosin, copals and orpiment etc., upto certain limits.

The shellac produced here by heat (country process) and is called hand-made shellac. Lac has great demand in foreign countries. For its marketing facility in foreign countries studies of its specification is a must. So that purchasers by going through the specification can easily ascertain the quality of the shellac produced in Bangladesh. It was therefore, thought necessary to find out the specification of shellac produced in Bangladesh.

EXPERIMENTAL

Shellac samples from different batches were collected and stored in desiccators. A small portion of each of the sample was taken for individual test. All the experiments were carried out following standard procedure[7-11]. The outlines of the different experiments are given below.

(i) Determination of volatile matter

The volatile matter content was determined by heating 2.0 gm of shellac sample at 40±1°C for four hours and keeping it in a desiccator over concentrated sulphuric acid for 18 hours. The result is summarized in Table 2.

(ii) Determination of matter insoluble in hot ethanol

5.0 gm of shellac sample was taken in a filter paper and folded and extracted with 95% hot ethanol in a soxhlet apparatus for 4 hours and the insolubles were determined by weighing the residue in the folded filter paper after drying. The result is summarized in Table 2.

(iii) Determination of ash

5.0 gm of shellac sample was weighed in a porcelain crucible of constant weight and burnt in a muffle furnace at 650-700°C for 4 hours[12]. The percentage of ash content was determined from the difference of weight of sample. The result is summarized in Table 2.

(iv) Determination of wax

In a 250 cm^3 beaker 10.0 gm of shellac sample was dissolved in 100 cm^3 hot aqueous solution of sodium carbonate (1.6%) by stirring. It was then covered with a watch glass and cooled. It was filtered in a buchner funnel, the filter paper being covered with filter paper pulp dispersed in water. The wax was extracted from the filter paper with chloroform and the chloroform was evaporated and dried[13]. The result is summarized in Table 2.

(v) Determination of iodine value

In a 250 cm^3 iodine flask 0.6 gm of shellac sample was dissolved in 10 cm^3 of ethanol with gentle heat. To this 20 cm^3 of hanus solution was added and kept in the dark for 45 minutes. It was then added 10 cm^3 of 10% potassium iodide solution and then titrated with standardized sodium thiosulphate solution using starch as indicator. Exactly similarly a blank experiment with 10 cm^3 of ethanol and 20 cm^3 of hanus solution were carried out. Both the mixtures were then titrated with the standardized sodium thiosulphate solution. The result is summarized in Table 2.

(vi) Determination of acid value

Accurately weighed 2 gm of shellac sample was dissolved in 50 cm^3 ethanol with slightly warming and then titrated with 0.5 N alcoholic potassium hydroxide solution using thymol blue as indicator. The result is summarized in Table 2.

(vii) Determination of saponification value

Accurately weighed 5.0 gm of shellac sample was dissolved in 50 cm^3 of 0.5N alcoholic potassium hydroxide and refluxed for 2 hours. The excess of alkali was titrated with 0.5 N hydrochloric acid using phenolphthalein as indicator. The result is summarized in Table 2.

(viii) Determination of softening point

A small amount of the shellac sample was taken in a special glass tube and heated gently upto 25°C and then about 5 gm of mercury was poured in it and resumed heating gently on a glycerine bath, the temperature at which the mercury was broken through the gradually softening and liquefying sample was observed. The result is summarized in Table 2.

(ix) Determination of orpiment (Arsenic sulphide)

The orpiment was detected by allowing an alcoholic solution of shellac sample to stand when the orpiment was settled in a layer at the bottom, it was separated out and was determined by digesting the sample with nitric acid and sulphuric acid and arsenic compound, obtained by distillation after treating the solution with the chloride hydrazine-bromide mixture and titrating with standard potassium bromate solution. The result is summarized in Table 2.

(x) Determination of lead

Shellac sample was digested with nitric acid and sulphuric acid and tested for the presence of lead compound after removing the arsenic compound as above. The result is summarized in Table 2.

(xi) Determination of rosin

Iodine value of shellac samples were determined and from this presence of rosin was found to be nil.

Standard specification of shellac is shown in Table 3.

Table 2 : Specification of shellac (Bangladeshi)

Sample Nos.	1	2	3	4	5	6	7	8	9	10
Volatile matter (%)	2.0	2.1	2.4	2.2	2.5	2.0	2.1	2.5	2.2	2.3
Matter insoluble in hot alcohol (%)	1.5	1.8	2.0	2.0	1.9	1.6	1.95	1.6	1.9	2.0
Ash (%)	0.9	0.7	0.8	0.6	0.7	0.5	0.66	0.9	0.8	0.55
Wax (%)	5.5	5.2	5.1	5.4	5.9	6.0	5.58	5.80	6.0	5.75
Iodine value	14.2	14.9	15.0	14.4	14.6	14.95	14.5	15.0	14.66	14.8
Acid value	75	72	71	65	66	69	74	68	70	70
Sap. value	230	225	222	228	226	225	230	227	220	226
Softening point (°C)	75-80	75-80	75-80	75-80	75-80	75-80	75-80	75-80	75-80	75-80
Orpiment (%)	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil
Lead (%)	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil
Rosin (%)	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil

Table 3 : Standard specification of shellac[14]

	Constants	%
1.	Volatile matter (moisture)	2.0
2.	Matter insoluble in hot alcohol	0.5 - 1.0
3.	Ash	0.25
4.	Wax	2.5-5.0
5.	Iodine value	18-20
6.	Acid value	As agreed between the purchaser and the vendor
7.	Orpiment	0.25
8.	Lead	0.03
9.	Rosin	Nil
10.	Matter soluble in water	0.5
11.	Dewaxed shellac	As agreed between the purchaser and the vendor

The physical and chemical constants of all the individual samples vary within a small limit and conforms with the standard specification of shellac (Table 3).

3.2 Specification of Dewaxed shellac

Abstract

Dewaxed shellac flakes were prepared from seed lac. The specifications (physical and chemical constants) were determined and found : volatile matter, 2%; lead content, nil; rosin, nil; arsenic, nil; ash content, 0.1 to 0.15%; matter insoluble in hot alcohol, 0.1%; wax content, 0.02 to 0.05%; iodine value, 18-18.9; acid value 70-80; saponification value, 231-233 and softening point, 75-80°C.

Dewaxed shellac is an important and useful product of lac, specially for its utility in ordnance factories for sealing and varnishing ammunition, electrical industries, preparation of adhesive etc.

Seed lac contains 5-6% of wax which when removed gives dewaxed shellac. This is an exportable item. To explore the marketing possibility abroad its specification must be of international standard. Therefore, it was thought necessary to find out the specifications of dewaxed shellac flakes produced in these laboratories.

EXPERIMENTAL

Dewaxed shellac flakes were prepared by a method as described in section 1.4 (p.p. 40). Specification of dewaxed shellac were determined as described in section 3.1 (p.p. 45). The results are given in Table 4 below :

Table 4 : Specification of dewaxed shellac (Bangladeshi)

Sample Nos.	1	2	3	4	5	6	7	8	9	10
Volatile matter (%)	1.95	2.0	2.05	2.10	1.90	2.0	2.0	1.90	2.0	2.0
Matter insoluble in hot alcohol (%)	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10
Ash (%)	0.10	0.12	0.15	0.13	0.15	0.11	0.14	0.10	0.10	0.14
Wax (%)	0.03	0.02	0.04	0.04	0.03	0.02	0.02	0.04	0.02	0.03
Iodine value	18.0	18.5	18.3	18.6	18.0	18.7	18.3	18.0	18.9	18.0
Acid value	70.0	71.0	73.0	72.0	74.0	76.0	75.0	78.0	79.0	80.0
Sap. value	233	233	232	233	233	234	232	232	231	233
Softening point (°C)	75-80	75-80	75-80	75-80	75-80	75-80	75-80	75-80	75-80	75-80
Orpiment (%)	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil
Lead (%)	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil
Rosin (%)	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil

Results and Discussion

Dewaxing of shellac, that is, elimination of the wax from shellac and using this wax-free shellac for the varnish result in a film which is more glossy and somewhat more water-resistant than the ordinary shellac film. But complete water-resistance cannot be attained and the film lacks adhesion, elasticity and hardness[15].

From Table 4 it is observed that dewaxed shellac flakes samples produced in these laboratories is of the same specification as for shellac (Table 2). Lead salt, rosin and arsenic salts are not used in the production of dewaxed shellac flakes in these laboratories. From Table 4, it is found that the physical and chemical constants of all the individual sample vary within a small limit. Shellac should not contain wax in excess of 5.5%. Shellac and dewaxed shellac should not contain any rosin. Dewaxed shellac should not leave, on incineration, ash in excess of half the value found for matter insoluble in hot alcohol but in no case, should the ash exceed 1.0%

3.3 Specification of Bleached lac

Abstract

Seed lac was bleached for converting it into a white base, considering its huge demand for manufacture of nitro-cellulose lacquers, light coloured quick drying varnishes etc. The spirit soluble dye erythrolaccin, present in seed lac, was removed by bleaching the seed lac with sodium hypochlorite. Specifications of bleached lac obtained were also determined.

One of the most important commercial commodity is the bleached lac generally used in the manufacture of nitro-cellulose lacquers, light coloured quick drying varnishes, floor polishes, water varnish for furfelt hat, preparation of edgeink. Huge quantity of bleached lac are prepared in countries like USA, UK and Germany. Seed lac obtained by crushing, washing and drying of raw lac is finding favour for its use as raw material for the manufacture of bleached lac. Various methods are employed for bleaching of lac, but the best and widely used one is the bleaching with sodium hypochlorite.[16-22]

EXPERIMENTAL

The required bleached lac was prepared by the method as described in section 1.5 (p.p. 40). Specification of bleached lac were determined as described in section 3.1 (p.p. 45). The results are given in Table 5. Specification of standard bleached lac is also shown in Table 5 for comparison.

Table 5 : Specification of Bangladeshi bleached lac and standard specification of bleached lac.

Constants	Bangladeshi bleached lac	Standard bleached lac[23]
Volatile matter (%)	5.5	6.0
Matter insoluble in hot alcohol (%)	1.1	1.0
Wax (%)	3.55	5.5
Ash (%)	0.44	1.0
Moisture (%)	1.75	1.0
Iodine value	8.0	10.0-11.0
Saponification value	250-256	176-276
Acid value	65-67	73-118

The physical and chemical constants of Bangladeshi bleached lac conforms with the standard bleached lac (Table 5).

3.4 Specification of Kiri (lac waste)

Abstract

Kiri is a lac waste and also a by-product of the indigenous shellac manufacturing industry. Kiri was analysed and the percentage of moisture content, ash content, matters insoluble in hot alcohol, resin and wax are worked out. The other specifications of kiri, like, iodine value, acid value and saponification value were also determined.

Lac encrustations[24] are separated from the twigs manually. Seed lac is the product obtained by crushing and washing of stick lac. In the country process seed lac is filled in a long cloth bag usually about 10 meter long and 5.0 to 7.5 cm in diameter. The filled bag, which looks like a long sausage, is then heated, portion-wise, from one end, over a semi-circular oven containing wood charcoal fire[25]. The bag is held at the end near the oven by a melter while the other end is continuously twisted by means of a windlass by his assistant. Lac resin and associated wax melt due to the radiated heat from the embers and are squeezed out by the twisting pressure through the cloth which acts as filter. The impurities that continuously accumulate inside the bag still retain an appreciable amount of lac. When sufficient quantity of this material has been accumulated, the bag is slit with a knife and the semi-molten mass poured out on the floor and made into circular slabs of about 10-15 cm in diameter and 2.5 cm thick. This by-product, which is known as Kiri or Kiri-lac, finds its application to some of the users for the production of cheaper commodities. In order to ascertain the quality of Bangladeshi Kiri, its analytical data was needed. Hence, an attempt was made for chemical analysis of kiri obtained from baisakhi crops.

EXPERIMENT

Kiri was collected from the local shellac manufacturing factory (New Lac Industry, Baliapukur, Rajshahi). Kiri was washed with water and dried in diffused sun light. The dried kiri was powdered in a grinding machine. It was then sieved through 200 mesh sieve. This fine powder was used for the present analysis. Specification of kiri were determined as described in section 3.1 (p.p. 45). and the results are summarized in Table 6. Specification of seed lac, shellac and bleached lac are also given in Table 6 for comparison.

Table- 6 : A Comparative Study of Bangladeshi Kiri, Seed lac, Shellac and Bleached Lac.

Composition (%)	Kiri	Seed lac	Shellac	Bleached lac
Moisture	4.00	2.00	1.90	1.75
Ash	7.24	1.55	0.90	0.44
Matters insoluble in hot alcohol	44.50	1.80	2.0	1.10
Resin	38.50	82.25	87.60	89.00
Wax	3.25	6.00	5.50	3.55
Iodine value	21.0	16.0	14.0	8.0
Acid value	65-67	70-75	65-75	66-67
Saponification value	170-175	279-285	220-230	250-256

Results and Discussion

Since kiri, a waste product, contains a sizable amount of resinous compounds, it would be interesting to investigate other physical and chemical constants such as moisture content, ash content, matters insoluble in hot alcohol, resin and wax content in kiri. For the determination of the specification standard methods were used. For accurate analysis, kiri sample was washed with water and dried at low temperature. Drying at higher temperature was avoided to minimize decomposition of any heat sensitive substance. The analytical data of kiri in comparison to seed lac, shellac and bleached lac are shown in Table 6.

From Table 6, it is observed that the moisture content, ash content, matters insoluble in hot alcohol of kiri are always higher than those of seed lac, shellac and bleached lac. But resin and wax values of kiri are lower than those of seed lac, shellac and bleached lac. From Table 6, it is observed that iodine value of kiri is higher than that of seed lac, shellac and bleached lac but acid value are almost identical. Saponification value is lower than that of others. The plausible explanation of the above variations may be due to the heat absorbed from the semi-circular oven containing wood charcoal fire. In this heating process some minor chemical changes might have been taken place within the various products.

It is observed that kiri produced in different shellac factories have almost same specifications. The physical and chemical constants of kiri vary within a reasonable limit.

Kiri is used in India for manufacture of garnet lac. The economic utilization of kiri is also reported in the manufacture of french polish[26]. Besides, it can also be used in the manufacture of wood varnish, sealing wax etc.[27]

3.5. Specification of Bangladeshi lac wax

Abstract

Lac wax was isolated (6.0%) during the course of production of dewaxed shellac flakes. The physical and chemical constants of lac wax were determined and found melting point, 76-77°C, ash content, 0.14%, acid value, 7.0-7.5, saponification value, 58.0-60.0, Iodine value, 6.0-6.5, boiling alcohol-soluble fraction, 75.0% and boiling alcohol-insoluble fraction, 25.0%.

The lac insect secretes the wax in the form of thin white filaments along with lac resin. These filaments get embedded in the resin and thus form an essential, minor constituent associated with lac[28]. The amount separated from the resin can vary from 4 to 8% depending on the source of lac. Lac (shellac) wax is essentially a mixture of esters (about 60%) and free alcohol (35%)[29]. It is an ester of an alcohol $C_{32}H_{66}O$ (Laccerols) and an acid, lacceroic acid ($C_{32}H_{64}O_2$). It also contains a hydrocarbon of high molecular weight[30]. It resembles carnauba wax in its hardness and general physical properties. It can be used in shoe polishes and other polishes in place of carnauba wax. It can also be used in carbon paper, lipsticks and tailors chalk[31]. Lac wax is in great demand due to the shortage of carnauba and other waxes for making boot polishes, floor and furniture finishes etc[32]. Lac wax acts as a natural plasticizer and a necessity is often felt in the varnish industry to add synthetic or natural substances to the varnish to give greater flexibility and durability to the film than what the natural wax can impart[33]. Wax may, therefore, be considered to be a desirable and even an essential constituent and this view is also supported by Bhattacharya[34]. The available information on lac wax is also contradictory. It has become, therefore, imperative in recent times to estimate the amount of wax contents in Bangladeshi lac. But no data is available for the same.

Hence the present work deals with the isolation, utilization and analysis of Bangladeshi lac (shellac) wax.

EXPERIMENTAL

3.5.a Isolation of lac wax from Seed lac

1st treatment : Kerosene was deodorised by treating several times with conc. sulphuric acid. The deodorised kerosene was neutralized with dilute NaOH solution and finally washed repeatedly with distilled water. The residual water was freed by treatment with anhydrous $CaCl_2$ chips. This deodorised kerosene is called white spirit.

1 kg. of seed lac was taken in a saucepan and 2 liters of the above treated kerosene (white spirit) and 330 cm^3 of water were added to it. Then it was heated on a heater for 2 hrs. It was kept over night and ppt. of wax thus freed with white spirit was decanted off and kept in a conical flask. The lac in pan was washed 4 times with 75 cm^3 of white spirit.

2nd treatment : The lac left in the pan was again treated with a fresh quantity of 2 liters of white spirit and 300 cm^3. of water and heated for 2 hrs. After half an hour it was decanted off and the freed wax was kept in a conical flask. Repeated washing was done as before, 4 times with 75 cm^3 of white spirit. The lac remains in the pan was used for the production of dewaxed shellac flakes and for spirit varnishes.

The total quantity of lac wax separated from seed lac (fr. I and fr. II) was treated in the following way to make it kerosene free.

It was filtered through a bunchner funnel (under water pump). The wax was dissolved in rectified spirit on heating and filtered. The hot isolated wax was again treated with chloroform when the impurities (insolubles) were separated out by filtration (hot). The filtrate, the wax-chloroform solution was then distilled to reduce its volume. The concentrated wax solution was then kept in the refrigerator so that it became solidified and was separated out from the solvent. The same process was repeated several times and the wax thus obtained was kept in a desiccator for drying, using phosphorous pentoxide (P_2O_5) as desiccant. The resultant wax freed from seed lac weighed 60 gm; yield 6.0%.

Physical and Chemical Properties of the isolated wax (shellac wax)

(i) **Determination of melting point :** Melting point of lac (shellac) wax was recorded on an electro-thermal melting point apparatus (Gallenkamp) and was found to be 76-77°C.

(ii) **Determination of specific gravity :** The sp. gr. was determined following the standard method[35] and was found to be 0.975-0.977 at 15°C.

(iii) **Determination of ash content :** The ash content of lac wax was determined following the procedure as described in Section 2.1 (p.p. 43). Ash percentage was found to be 0.14.

(iv) **Determination of acid value[36] :** Acid value of lac wax was determined as described in Section 3.1 (p. p. 47). The acid value of lac wax was calculated and was found to be 7.0-7.5.

(v) **Determination of iodine value[36] :** Iodine value of lac wax was determined as described in Section 3.1 (p.p. 47). Iodine value of lac wax was calculated and was found to be 6.0-6.5.

(vi) **Determination of saponification value**[37] : Saponification value of lac wax was determined following the usual procedure as described in Section 3.1 (p.p. 47). Saponification value of lac wax was calculated and was found to be 58-60.

(vii) **Determination of ester value :** 5.0 gm. of wax sample was weighed accurately and was placed in a 50 cm^3 flask. To it 25 cm^3 of acetic anhydride was added and refluxed for 2 hours on a glycerine bath. It was then dissolved in 25 cm^3 of ether, shaken with water, neutralized with N/2 alcoholic potassium hydroxide and saponified. Ester value was calculated (Sap. value minus acid value) and it was found to be 51.2.

(viii) **Determination of alcohol solubility :** Wax is made up of two fractions (1) fraction soluble in boiling alcohol and (2) fraction insoluble in boiling alcohol. Their percentages were calculated and found soluble portion, 75.0 and insoluble portion 25.0.

(ix) **Determination of unsaponifiable matters :** The matters unsaponifiable in lac wax was determined following standard method[35] and was found to be 45-50%.

Results and Discussion

The wax in stick lac, seed lac and shellac can readily be detected and isolated. Standard method has been used to isolate wax from seed lac. The yield of lac wax found from our experiment is 6.0%. This satisfactory yield may be due to good quality of Bangladeshi seed lac. The physical and chemical constants studied on lac wax are shown in Table 7.

Observation on the results given in Table 7, clearly indicates that the properties of Bangladeshi lac wax are closely comparable to that of the Indian variety[39].

We know that the most important wax in polish industry is carnauba wax. On account of high price of this wax, attempts have been made to substitute this wax by a cheaper one e.g. lac wax. The chemical and physical properties of carnauba wax[38] are also shown in Table 7 for comparison.

Table 7 : Physical and Chemical Constants of lac wax

Physical and Chemical Constants	Bangladeshi lac wax	Indian lac wax[39]	Carnauba wax[38]
Melting point	76-77°C	72-82°C	35-84°C
Sp. gravity, at 15°C	0.975-0.977	0.971-0.982	0.990-0.999
Acid value	7.0-7.5	12.0-24.3	4.0-9.0
Sap. value	58.0-60.0	79.13	78.0-87.0
Ester number	51.2	45.5-104	52.0-55.0%
Iodine value	6.0-6.5	6.0-8.8	13.1-13.5
Ash percent	3.14	0.08	-

From this data, it is apparent that lac wax can be a good substitute for carnauba wax, both having excellent gloss producing qualities and being equally hard. Hence attempts were made to replace carnauba wax partially by lac wax in various polish compositions and thereby good quality shoe polishes were resulted. This fact is very far-reaching in its implications because it may expand the commercial application of lac wax. However, lac wax cannot replace carnauba wax entirely from a polish composition. A polish prepared from lac wax as the chief constituent and containing no carnauba wax has been found to be "hard" in texture and consequently unsuitable. The hardness of lac wax, however, can be decreased by incorporating a considerable amount of paraffin wax in the polish composition. But in that case the polishing quality of the resulting wax becomes very poor.

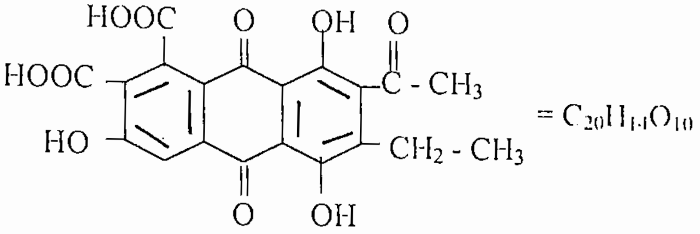
4. Investigation on Bangladeshi lac dye

Abstract

Lac dye (10%) was isolated from stick lac of Bangladesh origin. Chromatographic studies show that it contains three closely related components; however chromatographic separation led to the isolation of the major component, laccaic acid A_1 in pure state. The physico-chemical properties and spectral analysis of the component were also determined.

When stick lac is washed with water, a pinkish solution results. This is due to the presence of water soluble dye in the lac. The isolation of the dye has been reported by various investigators. Pearson and John[40] first extracted stick lac with alcohol and precipitated out the resin from the alcoholic solution by dilution with water. The aqueous layer was then evaporated and the dye extracted with ether. The dye, which they termed "stick lac acid", was purified through its lead salt. John[41] also, later on, described almost a similar process. He, incidentally, recognized the similarity of the dye with the colouring matter of cochineal. It was proposed that most probably this stick lac acid was identical with malic acid.

Hatchett[42] reported the percentages of this dye in different forms of lac. According to him, stick lac, seed lac and shellac contain the dye to the extent of 10.0, 2.5 and 0.5 percent respectively. Schmidt[43] obtained the pure dye to the extent of 10.4-13.2% from commercial dye cakes by treatment with mineral acids. He designated the product as "Laccaic acid", Tschirch and Farner[44] also isolated this dye and identified it by spectral analysis with Schmidt's laccaic acid. Dimroth and Goldschmidt's[45] method was slightly different. They isolated laccaic acid by extracting powdered stick lac with water. Chemical studies of Thomson[46] led Dimroth and Goldschmidt to a partial formulation of laccaic acid as a polysubstituted anthra-quinone. This was elaborated by Mayer[47] as shown in expression (I).



(I)

Helen Mitrea[48] has shown that lac dye is not a single entity but consists of at least two components which can be separated by fractional crystallization from ethyl acetate. α- laccain which forms about 80% of the dye and is obtained in the form of clusters of red needle-like crystals and β-laccain which is obtained in the form of yellow, plate-like crystals.

It is of interest to note that depending on the region, host tree, type of insect and harvesting season the relative proportions of the various ingredients vary widely. So, the purpose of this work is to report work carried out on laccaic acid, isolated in pure form from Bangladeshi stick lac.

EXPERIMENTAL

4.1 Isolation of laccaic acid

Laccaic acid was isolated following the Kamath and Potnis[45] method as described below :

Stick lac (1 kg) was coarsely ground by hand and freed from twigs and then powdered in a grinding mill. The powdered material was stirred with distilled water (5 litre). The suspension was allowed to settle for 1 hour. Decantation from the sludge, filtration through coarse cloth gave a clear wine red solution. This aqueous solution was then treated with a solution of calcium chloride as result of which the colouring matter was precipitated out as its calcium salt. The calcium salt was filtered, repeatedly washed with water to make it free from water soluble components and then treated with 3 N hydrochloric acid (100 cm^3). On standing, the dye was separated out in the form of needle shaped red crystals. These were separated by filtration, washed with small quantity of water and dried at 50°C. It was recrystallised by dissolving the dye in ethanol and pouring the alcoholic solution into aqueous hydrochloric acid. The yield of dye (laccaic acid) was 100 gm (10%), calculated on the basis of weight of stick lac taken. It was acidic in nature. The dye decomposed at 220°C and gradually got charred at higher temperature. It was fairly soluble in methyl alcohol, amyl alcohol, acetic acid and formic acid and sparingly soluble in ether, chloroform and benzene. It was dissolved in alkali and thereby a deep violet colour was developed.

On TLC plates developed in n-butanol : acetic acid : water (4:1:5) a major spot at R_f 0.75 for laccaic acid A_1 and a minor spot at R_f 0.85 for laccaic acid (B+C) were observed.

4.2 Column chromatographic separation of the component of the dye

Column chromatography of 1.0 gm of the isolated laccaic acid dissolved in 15 cm^3 of ethanol was carried out over silica gel 60 (70 -230 mesh ASTM, 50 gm) in ethanol. The flow rate of the elution was controlled at a rate of 2.0 cm^3/minute. Three different bands with three components were observed. One of the component was readily eluted by ethanol, while the second and third components were eluted by ethanol containing hydrochloric acid (90:10). Each fraction was evaporated under reduced pressure at room temperature and the residues were dried to constant weight. The results of a typical run are given in Table 8.

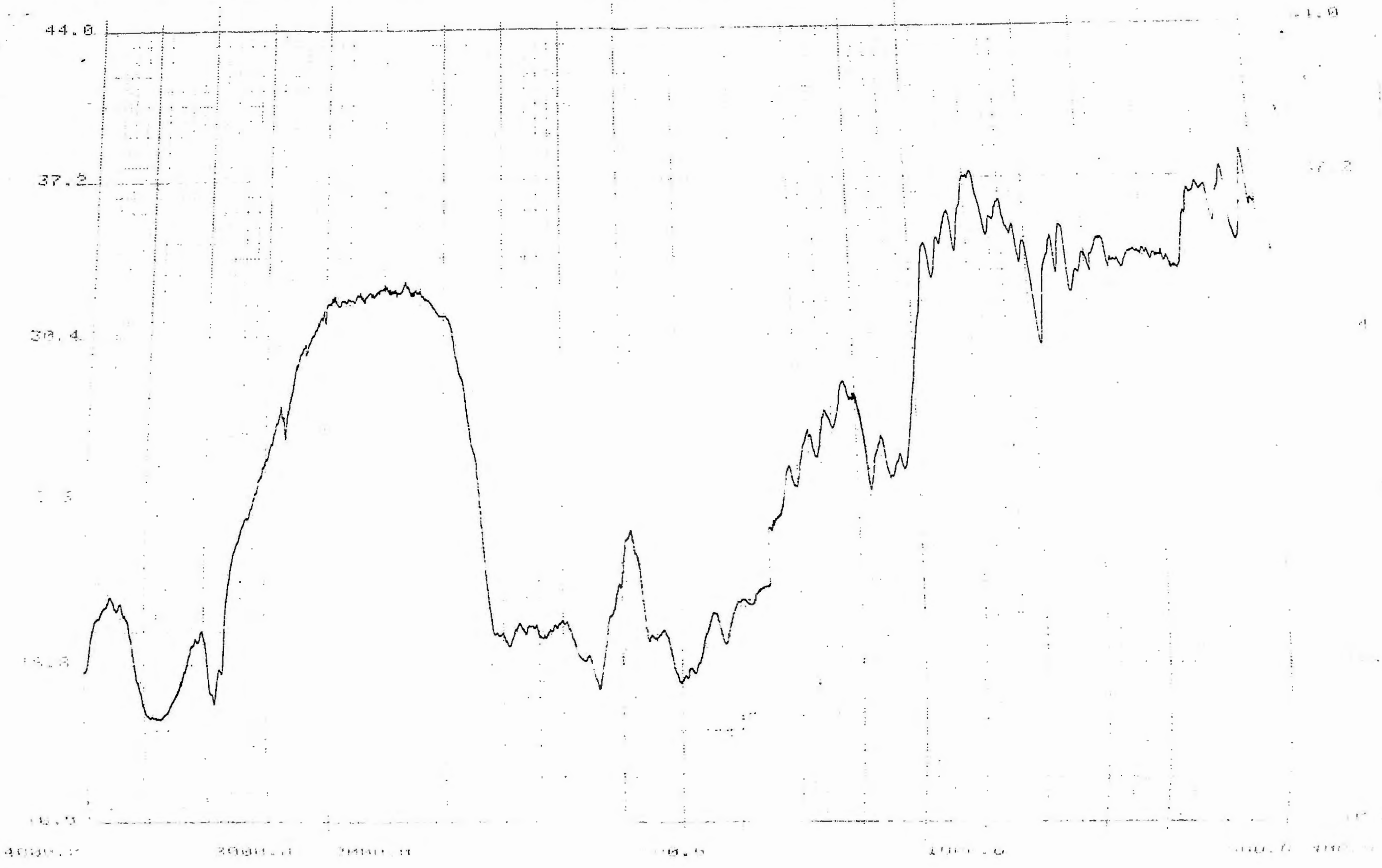


Fig. 1 : INFRARED SPECTRUM OF FIRST FRACTION

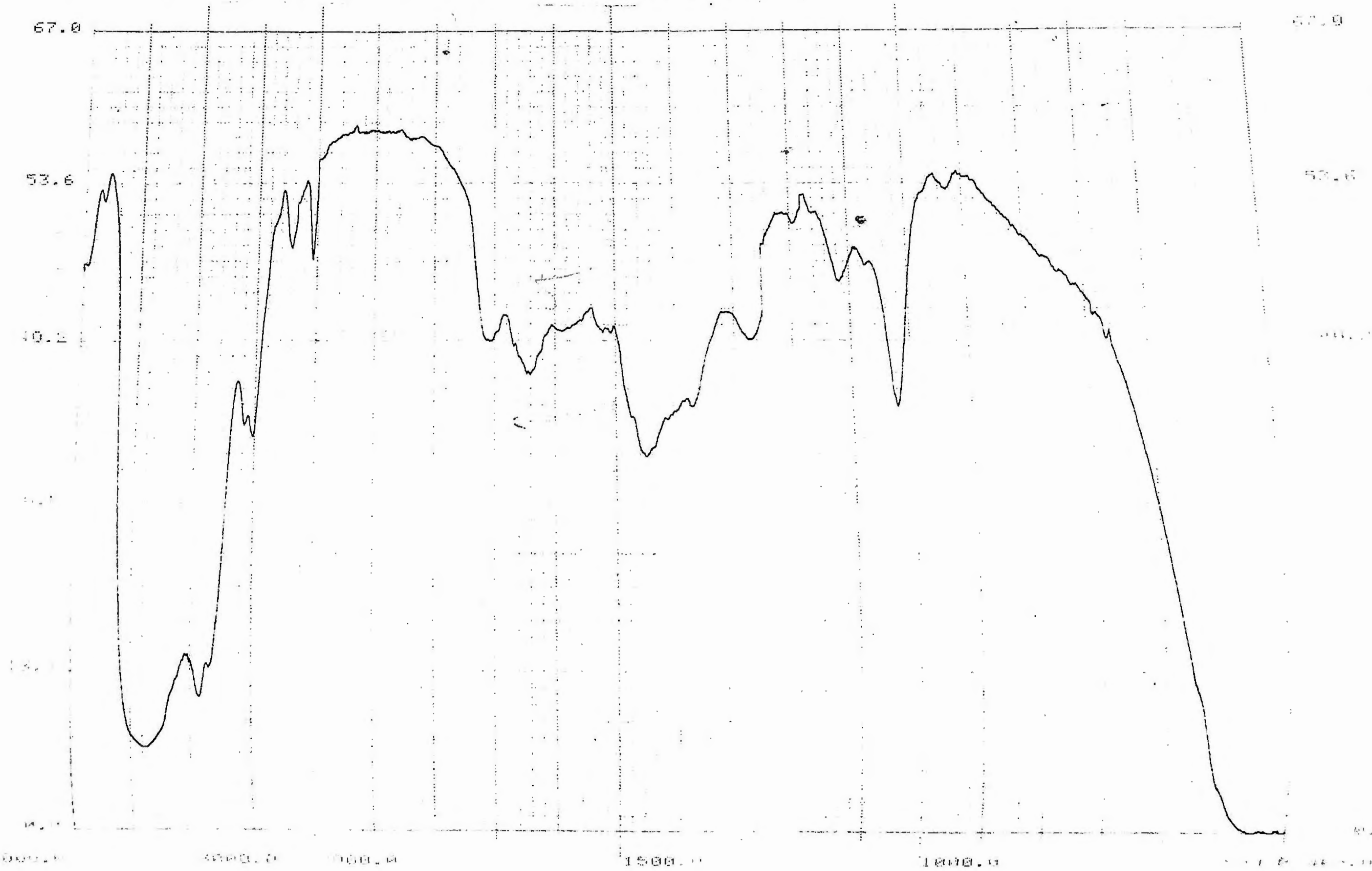


Fig. 2 : INFRARED SPECTRUM OF SECOND FRACTION

Fig. 3 : INFRARED SPECTRUM OF THIRD FRACTION

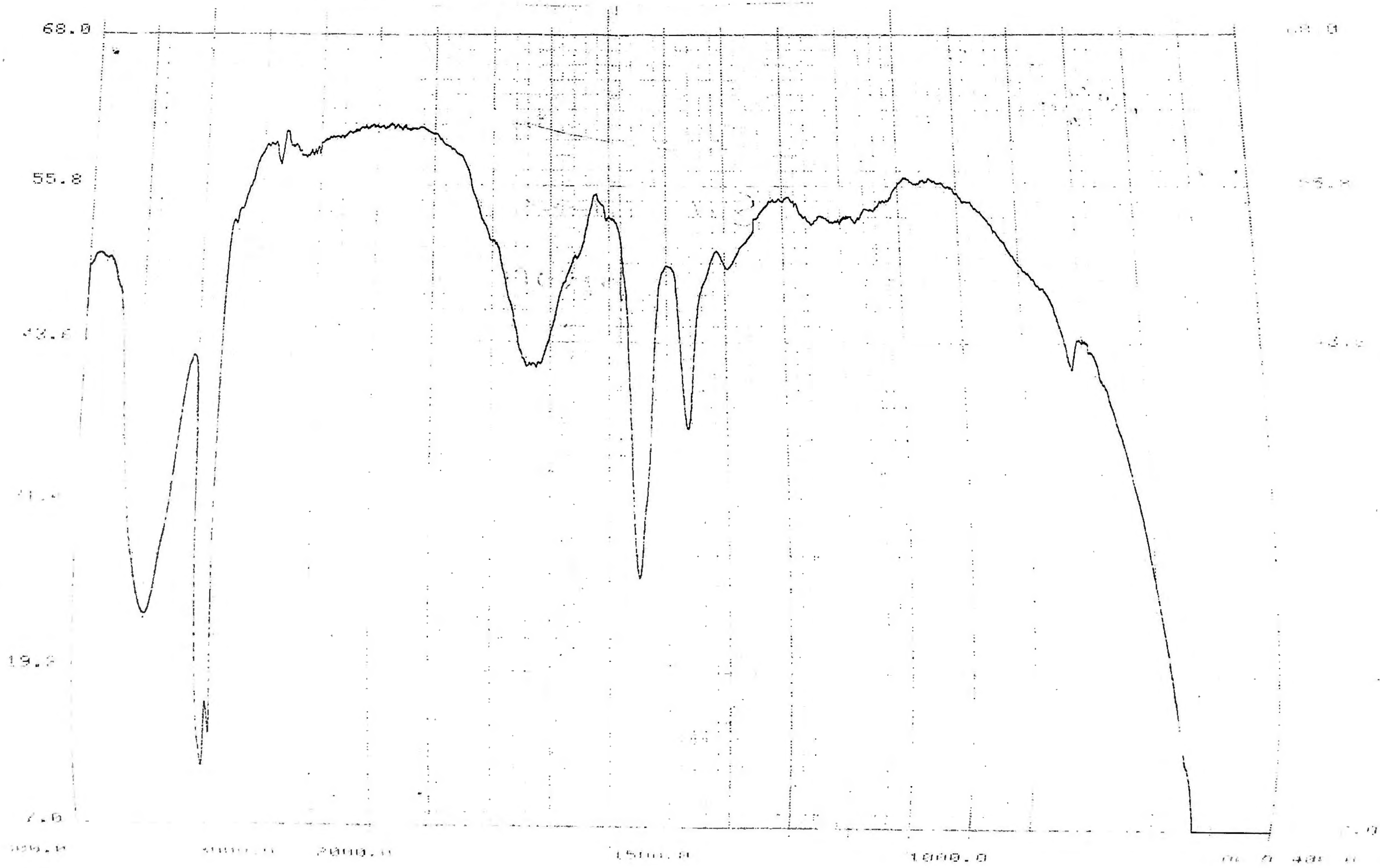


Table 8 : Chromatographic separation of crude lac dye

Fraction	Vol. of eluant (cm^3)	Fraction of dye (%)	Component	Eluant
1	100	15.0	Laccaic acid C	Ethanol
2	20	5.0	Laccaic acid B	Ethanol : HCl
3	150	80.0	Laccaic acid A_1	Ethanol : HCl

The purity of separated fraction was checked by TLC using n-butanol : acetic acid : water (4:1:5) solvent system and showed single spots at R_f values 0.85, 0.80 and 0.75 for fraction 1, 2 and 3 respectively. The third fraction was the major component (Laccaic acid A_1) and re-crystallised from 85% formic acid.

The infra-red spectrum of the three components showed the following absorption bands (Figure - 1, 2 and 3).

For first fraction (orange band), $\upsilon_{max.}$ 3400, 2900, 1540, 1400, 1080 and 780 cm^{-1} (KBr disc).

For Second fraction (violet band), $\upsilon_{max.}$ 3400, 2900, 1650, 1450, 1275 and 1020 cm^{-1} (direct).

For third fraction (red band), $\upsilon_{max.}$ 3400, 2900, 1640, 1450, 1360 and 720 cm^{-1} (direct) .

4.3 Acetylation of laccaic acid A_1[49]

Laccaic acid A_1 (0.5 gm) was shaken with acetic anhydride (25 cm^3) and conc. sulphuric acid (10 drops). The red suspension quickly gave an orange solution which on standing (18 hours) became yellow. The liquid was poured on ice water (150 cm^3) and the yellow solution was extracted continuously with ethyl acetate. The solvent was removed and the residue was freed from traces of solvent by storage in a desiccator over NaOH. The yellow product was crystallised from acetic acid, giving the tetra-acetate as yellow prisms, yield 0.45 gm (90%), m.p. 175°C. R_f = 0.65 in n-butanol; acetic acid : water (4:1:5) solvent system.

4.4 Benzoylation of laccaic acid A_1[49]

Laccaic acid (0.5 gm) was dissolved in 0.5 N sodium hydroxide solution (25 cm^3). Benzoyl chloride (50 cm^3) was added to it with vigorous shaking for 30 minutes. Benzoyl derivative of laccaic acid A_1 was precipitated out, filtered and washed with distilled water, yield 0.32 gm (65%), m.p. 125°C. R_f = 0.60 in ether : benzene (1:3) solvent system.

Results and discussion

The methods employed by earlier investigators for the isolation of lac dye were very labourious and time consuming. The aqueous extract starts degenerating even if it is left over night. So, it is essential to have a rapid method for the isolation of the dye. In the present investigation we have isolated laccaic acid through its calcium salt formation from a water extract of stick lac. Excess of calcium chloride were avoided in order to prevent the precipitation of proteinous or other materials. For obtaining pure dye from the washings of stick lac optimum conditions were studied.

The dye appears to consists of at least three components on the basis of its absorption on activated silica gel column. The first fraction was orange band, yield 15% of the mixture. The second fraction was violet band, yield 5% of the mixture and the third fraction was the main red band, afforded laccaic acid A_1, yield 80% of the mixture.

The infra-red spectra of laccaic acid A_1 shows characteristic band for the carbonyl stretching at 1640 cm^{-1}. This is consistent with a 1,4 quinone in which both carboxyl groups are chelated by a total of two or three peri-hydroxyl groups.

On the basis of the foregoing physico-chemical investigations, spectral analyses etc., the isolated product conformed with the properties of laccaic acid A_1[47,49].

Different investigators have recorded different crystalline structures and colour characteristics for laccaic acid as shown in Table 9.

Table 9 : Different investigators with crystalline structures of laccaic acid

Investigators	Crystalline structure
John[41]	Different granular crystals of acid taste
Schmidt[43]	Brownish red crystallisable powder
Tschirch and Farner[44]	Red-brown coloured matter
Mitrea[48]	Amorphous or crystalline; brown red to bright-red or carmine red
Spoerri *et al.*[49]	Dark red rectangular crystals

The isolated laccaic acid was red crystalline solid. The variation in the observations might be due to the mode of crystallisation. The dye thus obtained on further investigation was attempted for utilisation as a dye for dyeing silk, wool, cotton and jute fibre and found fast colour with different shades[50]. A brief description of the method of dyeing silk, wool, cotton and jute fibre is given below:

4.5 Mordanting of silk with potassium dichromate

Mordanting bath was prepared with 0.5% potassium dichromate in a 250 cm^3 beaker. 1 gm of stock sample of silk was dipped into the mordanting bath in cold and heated to boiling for 30 minutes with occasional stirring. The bath was allowed to cool. The mordanted silk was taken out, squeezed and dried at room temperature (28±2°C). In the similar way, silk sample was mordanted with copper sulphate, ferrous sulphate, chromium sulphate and stannous chloride.

4.6 Dyeing of mordanted potassium dichromate-silk, copper sulphate-silk, ferrous sulphate-silk, chromium sulphate-silk and stannous-chloride silk

A dye bath (250 cm^3 beaker) was prepared by dissolving 5 gm of lac dye in 1 cm^3 formic acid and diluted by adding distilled water to make its volume 100 cm^3 Then the solution was heated for 30 minutes with occasional stirring. The bath was allowed to cool. Then it was filtered. Now the mordanted silk sample (1 gm) was dipped into the filtrate and again heated to boiling for 30 minutes. 1 gm of sodium chloride was added and heating continued for further 10 minutes. The dyeing bath was allowed to stand overnight. It was then washed well with water and subjected to be washed repeatedly with soap and allowed to dry. In the similar way, dyeing of mordanted copper sulphate-silk, ferrous sulphate-silk, chromium sulphate-silk and stannous chloride-silk were completed. The dying of unmordanted silk was carried out following the same procedure.

The dyeing of wool, jute and cotton both mordanted and unmordanted were carried out as described above. The shades produced on samples of silk, wool, jute and cotton fibre using different mordants is shown in Table 10.

4.6.a. Light fastness Test :

A sample of size 2″×1″ from all the dyed samples were cut off. Half of these samples were shaded with the help of hard board of size 1″×1″ and the rest half of the dyed samples were exposed to sunlight for 100 hours. Any change of shades were measured with the help of Grey scale. The results are shown in Table 10.

4.6.b. Wash fastness Test

All the dyed samples of silk, wool, jute and cotton fibres were separately washed with soap for several times, squeezed and allowed to dry at defused sunlight. The dried samples were compared with the controlled samples by means of Grey scale. The results are shown in Table 10.

Table 10 : Shades produced on silk, wool, jute and cotton fibre and fastness test data of laccaic acid.

Mordant used	Silk			Wool			Jute			Cotton		
	Shade	L.F.	W.F.	Shade	L.F.	W.F.	Shade	L.F.	W.F.	Shade	L.F.	W.F.
$K_2Cr_2O_7$	Maroon	4	4	Maroon	4	3	Light Maroon	4	4	Reddish yellow	2	3
$SnCl_2$	Reddish pink	4	4	Reddish pink	3	3	Light brown	3	4	Ash	2	2
$CrSO_4$	Light violet	4	4	Light violet	4	3	Steel gray	3	4	Light berry	3	3
$FeSO_4$	Steel grey	4	4	Ash	4	3	Violet black	3	3	Light pink	4	4
$CuSO_4$	Reddish orange	4	4	Reddish tinge	4	3	Reddish orange	4	4	Light brown	3	3
None	Deep violet	4	4	Light chocolate	3	3	Violet	3	4	Violet	3	3

L.F = Light fastness test grade; W.F = Wash fastness test grade

5. Isolation And Purification Of Aleuritic Acid And Its Esters From Bangladeshi Shellac (Lac)

Abstract

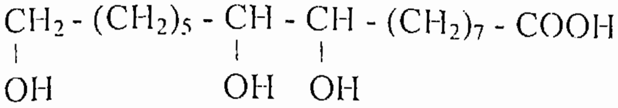
Shellac (lac) resin contains aleuritic acid combined with other ingredients. It was isolated to an extent of 30% and purified. Some derivatives of the isolated aleuritic acid were prepared. Thin layer chromatography of the acid and its derivatives revealed some notable information. Aleuritic acid may be used in making quality adhesive to join glass to glass properly.

Shellac (Lac) is known to comprise of hydroxy acid units. But inspite of work on the chemistry of lac for several decades, only about 65 percent of its constituent acids have been isolated in pure form. The isolation of the various acids has been carried out by a number of investigators using different methods with the consequence of divergent results.[51]

Aleuritic acid and its esters have great importance in industrial domain. Aleuritic acid has been found to be a valuable starting material for the preparation of transparent water-clear adhesive, plasticizers and resins in combination with other chemicals[52]. The esters of aleuritic acid may be incorporated in plastic composition containing cellulose derivatives and these compositions may be moulded, rolled or extended into any desired shape such as sheets, rods, tubes and the like. Filaments, yarns and other textile materials may be made from solutions containing organic derivatives of cellulose and an ester of aleuritic acid by extrusions through orifices into an evaporative atmosphere as in dry spinning or into a precipitating bath as in wet spinning[53].

In order to obtain further insight into the chemistry of lac, chemical investigation has been employed for the isolation and purification of the hydroxy acid (aleuritic acid) and its esters obtained from hydrolysed shellac (Bangladeshi). The result of this study are presented here :

According to Nagel the structural formula of aleuritic acid is:



$$\underset{OH}{CH_2} - (CH_2)_5 - \underset{OH}{CH} - \underset{OH}{CH} - (CH_2)_7 - COOH$$

EXPERIMENTAL

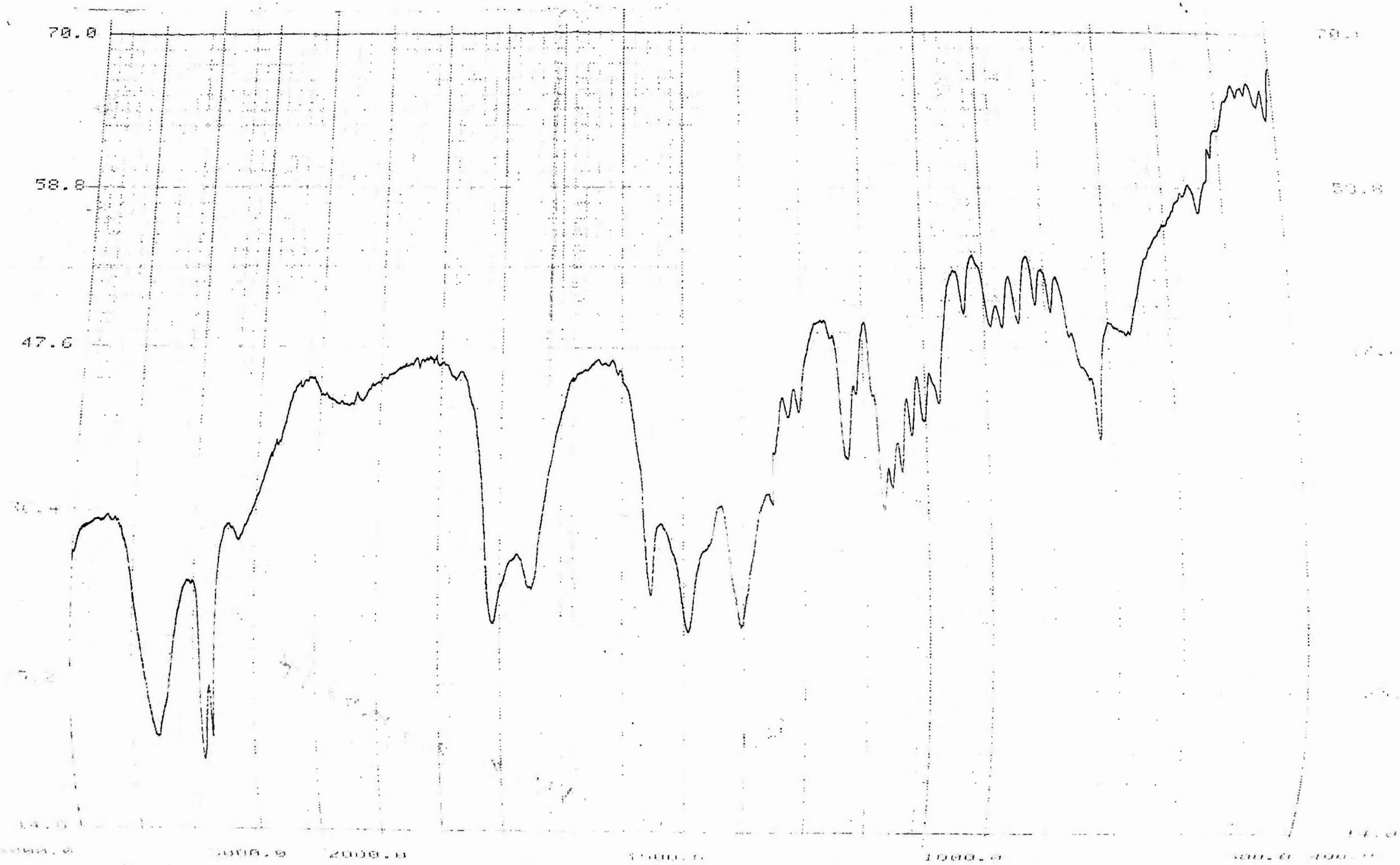
Melting points were determined on an elecrtro-thermal melting point apparatus. For thin layer chromatography, Kieselgel GF_{254} was used and spots were developed in an iodine chamber or viewed under UV light.

5.1. Collection of lac : Lac was collected from the experimental garden of BCSIR Laboratories, Rajshahi for the present investigation.

5.2. Preparation of dewaxed shellac : Dewaxed shellac was prepared following the method as described in section 1.4 (p.p. 40).

5.3. Isolation of aleuritic acid[5] : 100 gm of finely powdered dewaxed shellac was dissolved in 100 cm^3 of 20% sodium hydroxide solution by warming on a steam bath. After 14 days the mixture was diluted with 150 cm^3 of 20% sodium hydroxide solution and filtered through celite and the residue was washed with 20% sodium chloride solution (50 cm^3). The filtrate together with washing was concentrated to 75 cm^3 on the water bath and kept over night at room temperature until no further precipitation occurred. The sodium salt on the filter was dissolved in hot water (100 cm^3) and filtered. On acidification with 2N sulphuric acid, it yielded aleuritic acid along with other acids as a pasty mass. The pasty mass was repeatedly shaken up with ether. Aleuritic acid was left undissolved while other acids went into solution. It was then recrystallized from hot water and dried at 40°C, yield 30 gm (30%). Its melting point was found to be 100-1°C and the

Fig. 4 : INFRARED SPECTRUM OF ALEURITIC ACID



mixed m.p. with authentic sample was 100-100.5°C. It is soluble in hot water and in alcohol, acetone and ammonia in cold. It is insoluble in ether, petroleum ether and carbon disulphide. The infra-red spectra of the isolated aleuritic acid showed the absorption bands at υ_{max} 3300, 2900, 1710, 1650, 1460, 1395, 1310 cm^{-1} (KBr disc). (Fig. 4)

5.4. Preparation of ester of aleuritic acid : The following alkyl esters of aleuritic acid were prepared and purified. For this purpose standard methods were followed[54] :

5.4.a. Methyl aleuritate : A solution of 10 gm of the isolated aleuritic acid in 80 cm^3 of 5% hydrogen chloride in absolute methanol, was allowed to stand for 3 days, it was then neutralized with a solution of sodium hydroxide in absolute methanol, the precipitated sodium chloride filtered off and the filtrate poured into a large excess of cold (10°) water. The solid was filtered, washed with 10% aqueous sodium carbonate. It was recrystallized from ethanol. It was soluble in alcohol, acetone and insoluble in water, benzene and chloroform.

Ethyl aleuritate, butyl aleuritate and amyl aleuritate were prepared following exactly the same procedure by dissolving the prepared aleuritic acid in the desired alcohol (e. g. ethyl alcohol for ethyl aleuritate, butyl alcohol for butyl aleuritate and amyl alcohol for amyl aleuritate). Melting points of the esters were determined to be: methyl aleuritate, 72-73°C; ethyl aleuritate, 56-57°C; butyl aleuritate, 59-60°C; amyl aleuritate, 61-62°C.

The isolated aleuritic acid and its esters were applied on TLC plates and were run using different solvent systems amongst which ethanol: ammonia (20:1) solvent mixture was found to be most suitable. The products showed a single spot and the R_f values were 0.81, 0.68, 0.75, 0.72 and 0.73 for aleuritic acid, methyl aleuritate, ethyl aleuritate, butyl aleuritate and amyl aleuritate respectively. The authentic sample of aleuritic acid was also run on TLC plate in the same solvent system and showed single spot at R_f value. 0.81 which was identical to that of the isolated acid.

Results and Discussion

The composition and specification of lac vary with the nature of lac producing insects. nature of the host plants and climatic features. A survey of the available literature on the chemical nature of the shellac have shown that a different interpretation of the published data is possible. Various workers, have reported the isolation of aleuritic acid which is shown in Table 11.

Table 11 : Aleuritic acid contents of shellac resin

Investigator[55]	Year of Publication	Source of Shellac	% of aleuritic acid in shellac
Tschirch and Farner	1899	Indian lac	10.5
Harries and Nagel	1923	"	21.0
Gidvani	1944	"	43.0
Wright	1949	"	26.6
Sen Gupta	1956	"	23.0

The yield of aleuritic acid which has been isolated from Bangladeshi shellac during the present study (30%) is satisfactory and conforms with the chemical literature.

Aleuritic acid was first isolated by Tschirch and Farner from the hard resin portion of lac[55]. Harries and Nagel also isolated this acid from lac and observed that the acids from lac resin could be separated into ether soluble ones consisting of shellolic and other acids and ether insoluble consisting of aleuritic acid. In no case did he succeed in isolating aleuritic or any other acid directly from pure resin before hydrolysis. He, therefore, concluded like Tschirch and Farner, that aleuritic acid was present in shellac not in the free state but only in a combined form.

Recently the use of aleuritic acid as such or its esters in various industries is gradually increasing for the production of quality transparent water clear adhesive to join glass to glass with hard binding and lacquer for coating metal. These products have great demand in our country but none are produced locally. The isolated acid and its esters are expected to facilitate better utilization for the production of these articles of commercial interest.

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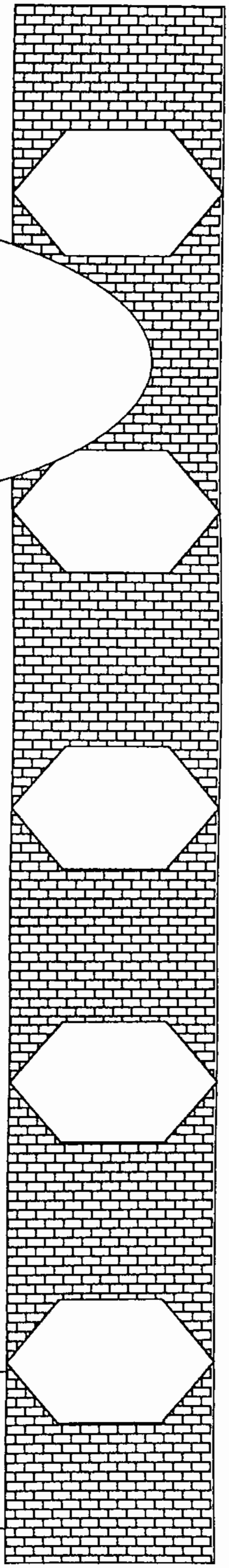
CHAPTER 3



POLYMERIZATION OF LAC

1. Polymerization of lac

Lac has been found to undergo polymerization when it is stored for a long time (on ageing and storage) and by heat treatment. The physico-chemical properties of the polymer samples were ascertained. The details of the work is given below :

1.1 Polymerization of Lac on ageing and storage

Abstract

Freshly prepared seed lac, shellac, bleached lac and dewaxed shellac are highly soluble in ethanol both in cold and hot condition. The solubility of the said varieties of lac decreases on ageing when stored at room temperature. After one year the rate of solubility decreases and ultimately after two years' storage all the varieties of lac become almost insoluble both in cold and hot ethanol. The percentage of insolubilities were ascertained.

It has been observed for a long time that lac product, like seed lac, shellac, bleached lac and dewaxed shellac loose its solubility in ethanol on storage. It is well known that lac, if not properly stored, deterorates in quality with gradual loss of solubility in ethanol, increase in melting point and rise in saponifiables[1]. In the case of seed lac the fragments of insect cells are present as hard tough particles, not readily soluble in solvents[2]. The present study was undertaken to see the effect of ageing on solubility behaviour of seed lac, shellac, bleached lac and dewaxed shellac in cold and hot ethanol and thereby determine the quality of the sample under investigation.

EXPERIMENTAL

All the verities of lac (seed lac, shellac, bleached lac and dewaxed shellac) were finely powdered and stored at room temperature in separate sample bottles. Each sample (10 gm) was taken out from the sample bottle and tested for its solubility in ethanol both in cold and hot condition. The following experiments were carried out and repeated after every 2 months interval of time for a period of 2 years.

1.1.a. Determination of matters insoluble in cold ethanol

Seed lac (10 gm) from the sample bottle was taken in a beaker (250 cm^3). To it was added 95% ethyl alcohol (100 cm^3) and stirred frequently for 2 hours to dissolve all the soluble matters and kept stand overnight. The solution was filtered and the insolubles from the beaker was washed with cold ethyl alcohol (50 cm^3). Dried the residues at 110±2°C for 2 hours. The percentage of cold alcohol insolubles was calculated. The percentage of insoluble matters of shellac, bleached lac and dewaxed shellac in cold ethanol was determined in the same manner as described for seed lac. The experiments for all the varieties of lac were repeated regularly after every 2 months interval of time for 2 years and the data were recorded (Table 1).

Table 1 : Insoluble matter of seed lac, shellac, bleached lac and dewaxed shellac in cold ethanol

Period of experiment (in month)	Matter insoluble in cold ethanol (%)			
	Seed lac	Shellac	Bleached lac	Dewaxed shellac
0	25.0	0.0	1.0	0.0
2	30.0	0.0	3.0	0.0
4	35.5	2.0	5.0	4.0
6	37.0	4.5	28.5	8.0
8	45.0	7.0	40.0	13.5
10	50.0	10.0	55.0	20.0
12	58.8	15.0	64.0	26.0
14	65.0	30.0	75.5	35.0
16	74.8	42.0	84.0	48.0
18	78.0	55.0	90.0	60.0
20	82.0	62.0	95.0	70.0
22	85.0	72.0	96.0	75.5
24	87.0	81.0	97.0	85.0

1.1.b. Determination of matters insoluble in hot ethanol

Seed lac (10 gm) from the sample bottle was taken in a weighed filter paper thimble and placed in a soxhlet apparatus (250 cm^3). It was then refluxed for 6 hours using ethyl alcohol (95%) as solvent. After the experiment the filter paper thimble was taken out and dried in an oven at 110±2°C for 2 hours. The dried thimble was then kept in a desiccator. At room temperature its weight was taken. The percentage of insoluble portion was determined. The insolubility of shellac, bleached lac and dewaxed shellac were also determined exactly in the same manner and the percentage of insolubilities were recorded. The above experiments for all the varieties of lac were repeated regularly after 2 months interval of time for 2 years and the results are shown in Table 2.

Table 2 : Insoluble matter of seed lac, shellac, bleached lac and dewaxed shellac in hot ethanol

Period of experiment (in month)	Matter insoluble in hot ethanol (%)			
	Seed lac	Shellac	Bleached lac	Dewaxed shellac
0	25.0	0.0	1.0	0.0
2	25.0	0.0	2.2	0.0
4	29.5	1.5	18.0	3.0
6	30.5	3.0	30.0	8.2
8	36.0	5.0	42.0	15.0
10	41.0	12.5	54.5	22.5
12	50.0	25.0	65.0	30.0
14	60.0	35.0	76.8	39.9
16	63.5	42.0	80.5	50.0
18	67.0	52.0	92.0	61.0
20	74.0	65.0	95.0	68.8
22	77.0	78.0	97.0	70.0
24	81.5	85.0	98.0	76.0

The solubility behaviour of seed lac, shellac, bleached lac and dewaxed shellac in cold and hot ethanol were graphically shown in Fig. 1 and 2.

Results and discussion

The determination of matter insoluble in cold ethanol is very useful test, giving the observer a better idea of the quality of the lac under observation than the impurities test for matter insoluble in hot ethanol. From Table 1 and 2, it is evident that in the case of seed lac the higher percentage of insolubilities in starting stage of storage is due to the fragments of insect cells which are present as hard, tough particles not soluble in solvent and practically insoluble in both cold and hot alcohol. On boiling, however, or if the material in finely powdered, it is peptized into a colloidal solution either by alcohol or by alkalis. The cold ethanol test is, therefore, specially useful in the case of seed lac for detecting the impurities. In the case of shellac, bleached lac and dewaxed shellac no appreciable quantity of undissolved lac was found at the initial stage of storage. Undissolved lac is a sign of old lac of poor quality. It is also observed that after 2 years of storage, about 15-20% of seed lac, shellac and dewaxed shellac always remain in solution but bleached lac becomes almost insoluble in ethanol. The complete insolubility of bleached lac is due to chloro-bleaching. Its solubility can be regained in solvent (95% ethanol) if it is treated with 10% diethyl ether[3].

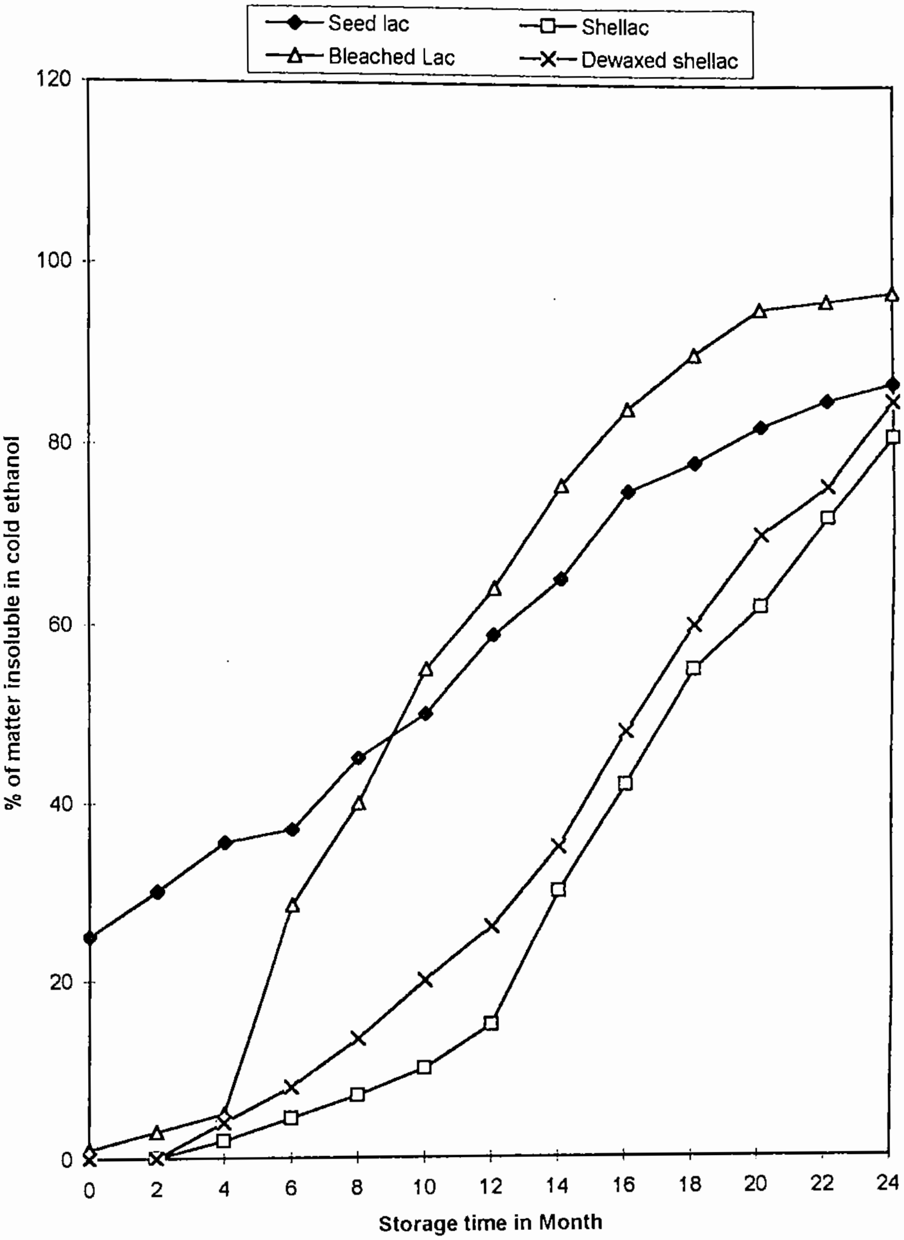


Fig. 1 : Effect of solubility behaviour of seed lac, shellac, bleached lac and dewaxed shellac in cold ethanol

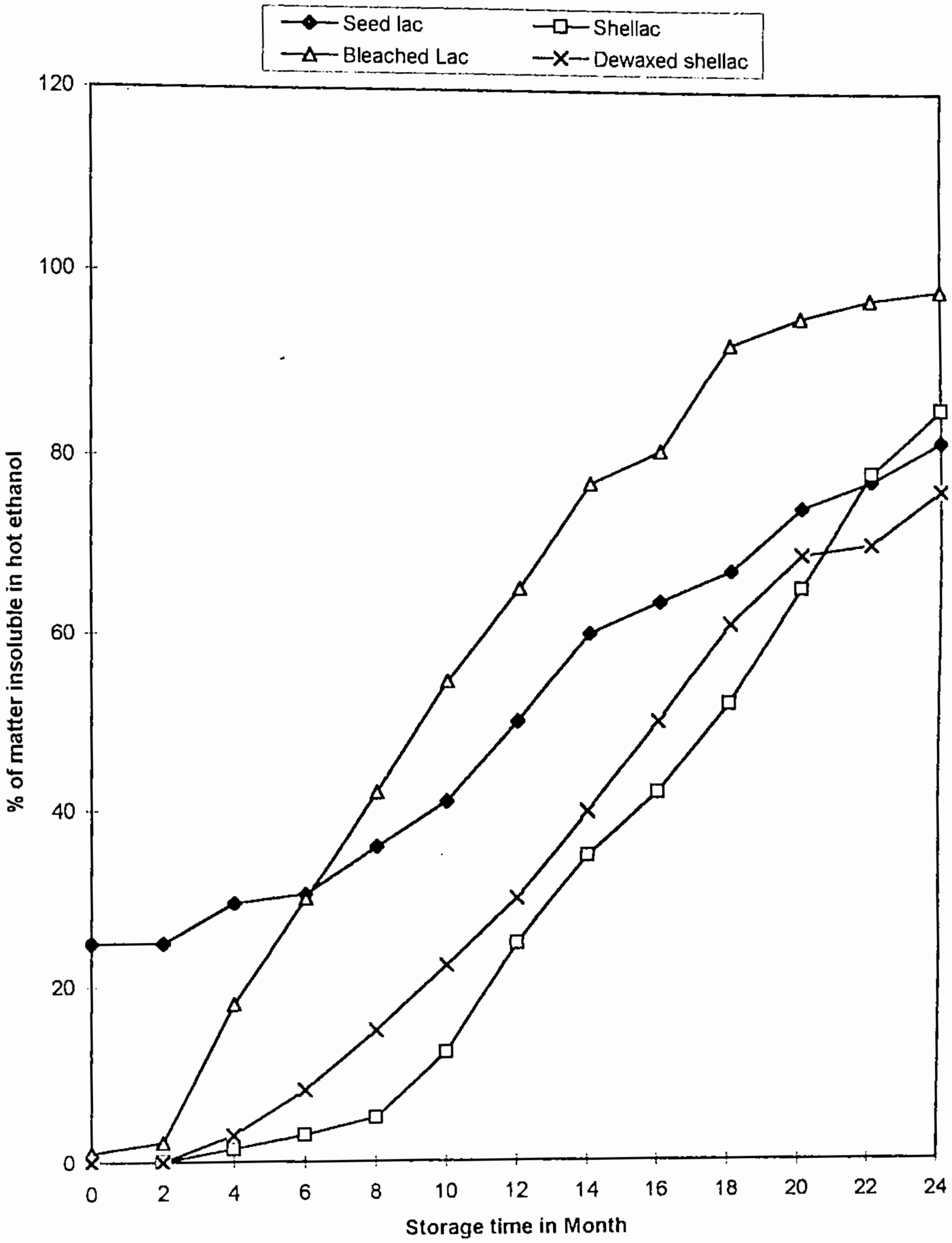


Fig. 2 : Effect of solubility behaviour of seed lac, shellac, bleached lac and dewaxed shellac in hot ethanol

1.2 Polymerization of lac under heat treatment

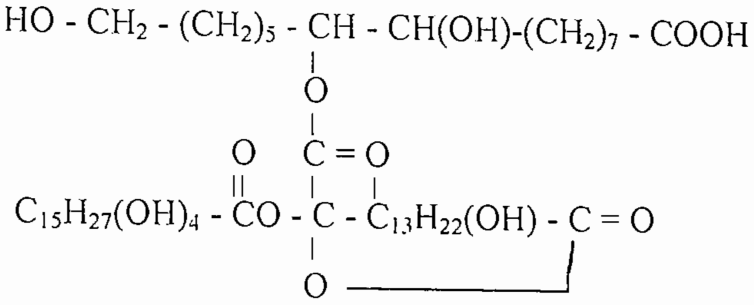
The chemistry of polymerized shellac (lac) under heat treatment has not much studied. Recently the use of lac as such or modified lac in various industries is gradually increasing for the production of many useful articles of commercial interest. Keeping this idea in mind, a piece of research work on this topic was undertaken. The results observed in the present investigation is expected to facilitate the utilization of various modified shellac obtained through controlled experiments for specific requirements in different industries. The details of the observation is given below :

1.2.a. Solubility behaviour of thermally polymerized seed lac, shellac and dewaxed shellac

Abstract

Freshly prepared seed lac, shellac and dewaxed shellac are highly soluble in ethanol. It is observed that when the said variety of lac is heated above its melting point, it undergoes a slow process of polymerization and ultimately becomes insoluble in ethanol. The percentage of alcohol insolubilities and the amount of water split off from seed lac, shellac and dewaxed shellac when heated at different temperatures are reported.

The solubility of shellac in spirit as well as in alkaline solution has been long known. Its partial solubility in ether was first recognized by Unverdorben[4] which property was later utilized for separating it into pure (or hard) and soft resins. Tschirch and Farner[5] noted its solubility in ethyl and methyl alcohols, acetic acid, caustic soda, sodium carbonate and borax solution. They also observed that its partial solubility in ether, ethyl acetate, chloroform, carbon disulphide and acetone and its insolubility in petroleum ether, benzene and toluene. Gardner and Whitemore[6] made an exhaustive study on the solubility behaviour of different varieties of lac. Reviewing these idea, the authors recognized that the best solvents for shellac are alcohols, organic acids and ketones. This finding led to the surmise that hydroxyl, carboxyl and carbonyl groups are present in shellac as shown in the structure below[7] :



$$\begin{array}{rcl}
\mathrm{HO-CH_2-(CH_2)_5-} & \mathrm{CH} & \mathrm{-CH(OH)-(CH_2)_7-COOH} \\
 & | & \\
 & \mathrm{O} & \\
 & | & \\
\mathrm{O}\quad\; & \mathrm{C} & \mathrm{=O} \\
\|\quad\;\; & | & | \\
\mathrm{C_{15}H_{27}(OH)_4-CO-} & \mathrm{C} & \mathrm{-C_{13}H_{22}(OH)-C=O} \\
 & | & \qquad\qquad\qquad\quad | \\
 & \mathrm{O} & \rule{4cm}{0.4pt}
\end{array}$$

Structure of lac molecule

When lac is stored for a long time or heated above its melting point, it undergoes a slow process of polymerization and ultimately becomes insoluble in alcohol (spongy mass). In this way all types of lac gradually lose their life. The mechanism of heat polymerization of lac is imperfectly understood. According to the original idea polymerization involves etherification between the free hydroxyl groups of lac. Later on Nagel and Baumann[8] thought that initially a small amount of anhydride is formed, subsequent polymerization being mainly due to aggregation of lactones present. Ranganathan and Aldis[9], while agreeing with the views of Nagel and Baumann, laid more emphasis on anhydride formation. Gidvani[10] suggested that polymerization of lac involves inter-molecular esterification, followed by etherification between the free hydroxyl groups of lac.

The views that ethers or anhydrides are formed during polymerization have their basis on the observation that with the progressive polymerization of lac, its acid value is not significantly altered, although water is continuously evolved. The possibility of formation of unsaturated compounds by a process of dehydration has been discarded by the observation that the iodine value of lac does not increase with the progress of polymerization. We have made an exhaustive study on the anomalous solubility behaviour of seed lac, shellac and dewaxed shellac by heat treatment. Such a study, may be helpful in understanding, the nature of the mechanism of heat polymerization of different varieties of lac.

EXPERIMENTAL

Determination of alcohol insolubilities of seed lac, shellac and dewaxed shellac

Seed lac (5.0 gm) was taken in a porcelain crucible and heated for 3 hours at 90°C. It was then dissolved in ethanol (100 cm^3) in a beaker (250 cm^3) and stirred for 2 hours and allowed to stand overnight to dissolve all the soluble metters. The solution was filtered and the residue was washed with ethanol (50 cm^3). The residue was dried at 110±2°C for 2 hours. The percentage of alcohol insolubilities was calculated and found to be 23.11. The experiment was carried out following exactly similar procedure at 100, 110, 120, 130, 140, 150, 160, 170, 180, 190 and 200°C respectively. The results are given in Table 3.

Exactly similarly the percentage of alcohol insolubilities of shellac and dewaxed shellac were determined and the results are summarized in Table 3.

Determination of water split off from seed lac, shellac and dewaxed shellac

As moisture was found to be the only product eliminated during heat polymerization, the loss in weight of the samples on heating represented the weight of water split off. Thus the amount of water split off from different varieties of lac on heating at different temperature (from 90 to 200°C) are given in Table 4.

Table 3 : Solubility behaviour of seed lac, shellac and dewaxed shellac on heating for 3 hours at different temperatures.

Temperature (°C)	Alcohol insolubilities of seed lac (%)	Alcohol insolubilities of shellac (%)	Alcohol insolubilities of dewaxed shellac (%)
90	23.11	0.00	0.00
100	24.00	0.00	0.00
110	25.00	2.00	4.00
120	30.50	20.00	18.50
130	65.00	74.40	75.85
140	73.80	76.89	77.00
150	75.00	77.00	77.55
160	78.00	78.00	79.00
170	75.15	80.25	81.00
180	74.80	80.75	82.25
190	76.00	82.00	84.15
200	73.95	81.75	85.00

Table 4 : Water split off from seed lac, shellac and dewaxed shellac on heating for 3 hours at different temperatures.

Temperature (°C)	Seed lac (%)	Shellac (%)	Dewaxed shellac (%)
90	1.76	1.35	1.02
100	2.00	1.86	2.00
110	2.85	2.35	2.45
120	3.12	2.01	2.91
130	4.22	3.35	3.35
140	5.09	4.25	4.50
150	5.86	4.41	5.80
160	6.39	5.25	6.09
170	7.00	5.84	7.00
180	7.65	6.50	7.40
190	8.08	7.25	8.27
200	9.14	8.00	8.63

Results and Discussion

Lac when heated softens and then melts. As the temperature is raised, it gradually becomes thicker and thicker and finally turns into a rubbery product which on cooling solidifies to a hard, tough, horny mass. The original properties are changed and the final product becomes insoluble in alcohol, infusible, stone-hard and brittle. The time required just to reach this state through heating has been called "life under heat".

From Table 3, it is evident that when different varieties of lac is heated above its melting point, nearly 70-75% of the same becomes rapidly insoluble between 120° and 140°C and the speed of reaction slows down. We also observed that even when different varieties of lac are completely polymerized some 15 to 20% of the constituents always remain alcohol soluble, the presence of which may be the reason why lac does not thermoset completely. From Table 3 it is also evident that, in the case of seed lac, the higher the percentage of alcohol insolubilities in the initial stage is due to the presence of fragments of insect cells, wood-chips, sand and other minor mineral impurities which are not soluble in alcohol.

Figure 3 shows a curve of percentage of alcohol insolubilities against the heating time of seed lac, shellac and dewaxed shellac.

Table 4 shows the amount of water split off from seed lac, shellac and dewaxed shellac, when heated at different temperatures. From this table we observe that the polymerization reaction is attended with a gradual elimination of water vapour along with the gradual rise in alcohol insolubilities of the product. The elimination of water, however, continued indefinitely on further heating, Other properties of the polymer sample do not show any marked changes. Relative viscosity, on the other hand gradually increases with the progress of polymerization, indicating gradual increase in molecular size[11].

It is therefore, concluded that the possible reactions which may occur during thermal polymerization of lac with splitting off water are :

i) two carboxyl groups through elimination of water form anhydrides;

ii) carboxyl group of one molecule reacting with hydroxyl of another forming esters;

iii) two hydroxyl groups interacting with each other lead to formation of ethers and

iv) a hydrogen atom and a hydroxyl group held by two adjacent carbon atoms through an elimination reaction produce unsaturation thus giving rise to some active centres of polymerization.

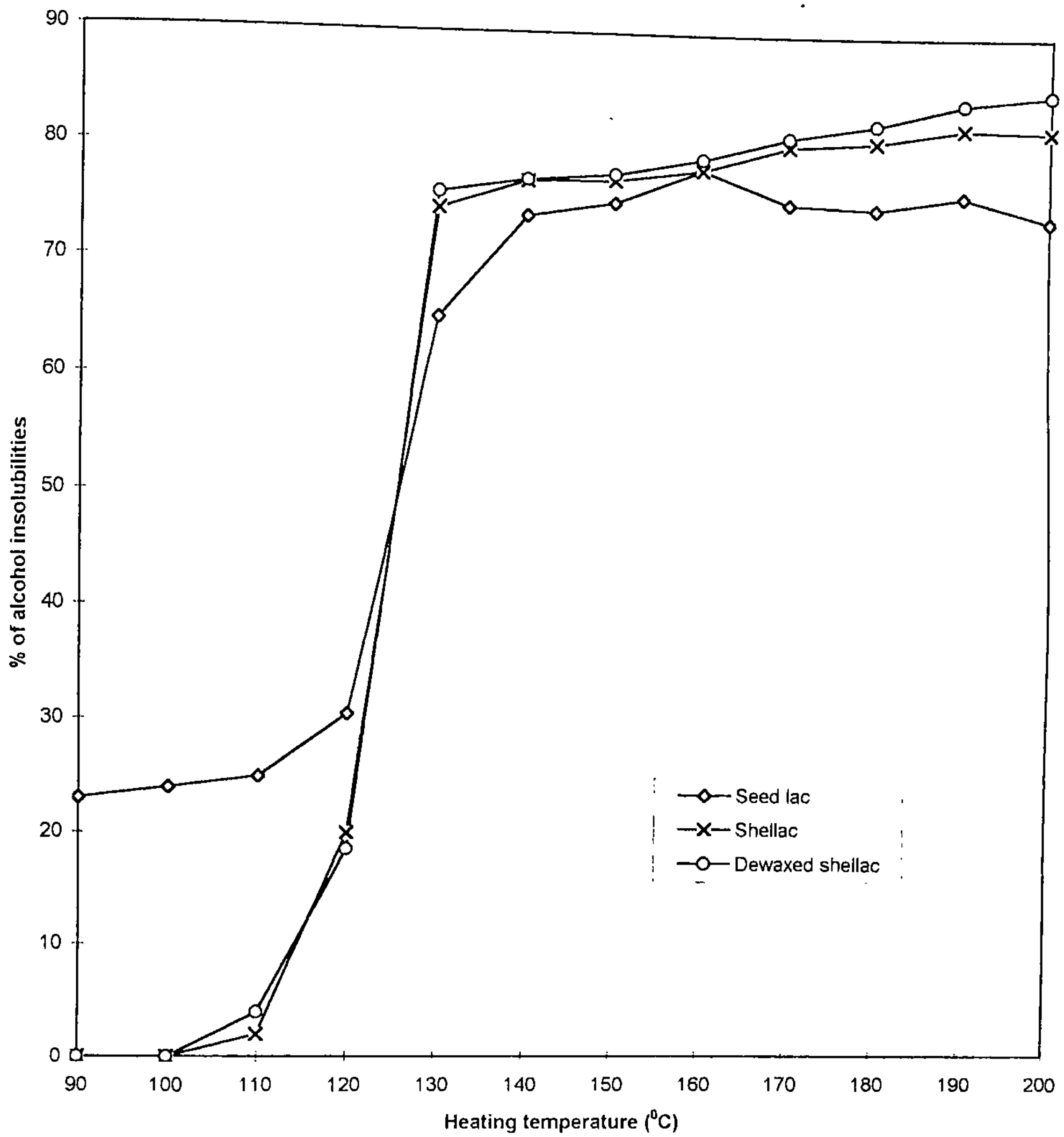


Fig. 3 : Solubility behaviour of seed lac, shellac and dewaxed shellac on heating for 3 hours at different temperatures.

1.2.b. Physico-chemical studies of polymerized seed lac, shellac and dewaxed shellac

Abstract

Lac (Shellac) has been found to undergo polymerization by heat treatment. The behaviour of polymerized lac in terms of viscosity has been studied. The relative viscosity of lac increases with the progress of its polymerization. Other properties of the polymer sample such as acid value, saponification value and iodine value have also been determined.

In continuation of the work done on the solubility behaviour of thermally polymerized seed lac, shellac and dewaxed shellac [1.2.a], we now report the physico-chemical studies of polymerized seed lac, shellac and dewaxed shellac.

EXPERIMENTAL

An exhaustive study of the thermal polymerization of Bangladeshi seed lac, shellac and dewaxed shellac has been carried out. The following physical and chemical constants of the polymerized samples were determined.

(i) **Determination of acid value :** Seed lac (2.5 gm) was taken in a porcelain crucible and heated at 125°C for 10 minutes. It was then dissolved in ethanol (50 cm^3) in a conical flask (250 cm^3) with slight warming and then titrated with standardized potassium hydroxide solution using thymol blue as indicator. The acid value of the sample was calculated and found to be 65.80. The experiment was carried out for different heating period viz. 20, 30, 40, 50, 60, 70 and 80 minutes respectively. The results are given in Table 5.

The same series of experiments were repeated using shellac and dewaxed shellac instead of seed lac and the results are summarized in Table 6 and 7.

(ii) **Determination of saponification value :** Seed lac (2.5 gm) was taken in a porcelain crucible and heated at 125°C for 10 minutes. It was then dissolved in 0.5 N alcoholic potassium hydroxide solution (50 cm^3) in a round bottom flask (250 cm^3) fitted with an upward condenser and refluxed for 2 hours. The excess of alkali was titrated with an standardized 0.5N hydrochloric acid using phenolphthalein as indicator. The saponification value was calculated and found to be 220.0. The experiment was repeated exactly similarly with seed lac heated at 125°C for various different heating period viz. 20, 30, 40, 50, 60, 70 and 80 minutes respectively. The results are given in Table 5.

The same series of experiments were carried out by changing seed lac with shellac and then again with dewaxed shellac and the results are summarized in Table 6 and 7 respectively.

(iii) Determination of iodine value : Seed lac (0.5 gm) was taken in a porcelain crucible and heated at 125°C for 10 minutes. It was then dissolved in ethanol (50 cm^3) in a 250 cm^3 iodine flask with gentle heating. To this hanus solution (20 cm^3) was added and then titrated with standardized sodium thiosulphate solution using starch as indicator. Exactly similarly a blank experiment with 50 cm^3 of ethanol and 20 cm^3 of hanus solution were carried out. It was then titrated with standardized sodium thiosulphate solution using starch as indicator. The iodine value was calculated and found to be 14.0. The experiment was carried out using seed lac heated at 125°C for different heating period viz. 20, 30, 40, 50, 60, 70 and 80 minutes. The results are given in Table 5.

The same series of experiments were carried out under exactly identical reaction conditions using shellac and then again with dewaxed shellac instead of seed lac and the results are summarized in Table 6 and 7 respectively.

(iv) **Determination of relative viscosity and specific viscosity :** The viscosity of the polymer samples (seed lac, shellac and dewaxed shellac) were determined by the Ostwald viscometer method. The relative viscosity of a polymer sample was determined by the equation,

$\eta_{relative} = \eta/\eta_o$

Where η = Co-efficient of the viscosity of a polymer solution.

and η_o = Co-efficient of viscosity of the solvent.

The specific viscosity,

$\eta_{specific} = (\eta-\eta_o)/\ \eta_o$ or, $\eta_{specific} = \eta/\eta_o - 1 = \eta_{relative} - 1$

i,e. $\eta_{specific} = \eta_{relative} - 1$.

The results are summarized in Table 5, 6 and 7.

Table 5 : Properties of seed lac heated at 125°C.

Time of heating (min.)	Acid value	Sap. value	Iodine value	Relative viscosity	Specific viscosity
00	65.50	220.0	14.0	4.77	3.77
10	65.80	222.0	16.0	4.80	3.81
20	66.00	221.0	15.6	4.82	3.82
30	65.75	220.7	14.9	4.85	3.85
40	64.40	221.5	14.6	4.85	3.85
50	63.20	223.5	15.0	4.89	3.90
60	66.20	222.4	14.0	4.92	3.91
70	66.50	222.5	14.2	4.95	3.95
80	Polymerize	-	-	-	-

Table 6. Properties of shellac heated at 125°C.

Time of heating (min.)	Acid value	Sap. value	Iodine value	Relative viscosity	Specific viscosity
00	74.0	279.0	15.5	4.64	3.64
10	74.0	277.0	15.0	4.68	3.68
20	74.2	275.8	15.7	4.69	3.69
30	74.5	277.9	14.9	4.71	3.71
40	73.5	276.5	15.2	4.81	3.80
50	73.7	275.0	14.8	4.88	3.88
60	74.6	278.0	14.0	4.91	3.91
70	75.0	277.0	14.7	4.94	3.94
80	Polymerized	-	-	-	-

Table 7. Properties of dewaxed shellac heated at 125°C.

Time of heating (min.)	Acid value	Sap. value	Iodine value	Relative viscosity	Specific viscosity
00	68.0	223.8	13.8	4.46	3.46
10	68.7	222.0	14.0	4.49	3.49
20	67.8	223.7	13.5	4.51	3.52
30	67.5	222.5	14.0	4.53	3.53
40	68.1	222.7	13.7	4.53	3.53
50	67.7	220.0	14.2	4.54	3.54
60	66.9	221.0	13.8	4.56	3.56
70	67.0	223.0	14.0	4.62	3.62
80	67.5	223.2	14.0	4.75	3.75

Results and Discussion

In these experiments, standard methods have been employed for the determination of all the specifications. From Table 5, 6 and 7, it is obvious that the properties of all the polymerized samples such as acid value, saponification value and iodine value do not show any marked changes. Relative viscosity, on the other hand, gradually increases with the progress of polymerization indicating gradual increase in molecular size.

It is, therefore, concluded that the thermal polymerization is brought about by a chemical change with the elimination of water and the reaction is inter-esterification which proceeds at a high speed followed by inter-etherification at a slow rate.

2. Effect of curing agents on life of lac (shellac) under heat

Abstract

Lac (Shellac) has been found to undergo polymerisation by heat treatment. Various chemicals, such as oxalic acid, tartaric acid, citric acid and urea have been found to play an important role in accelerating the thermal curing of shellac. The effect of these chemicals (1-5%) on life of shellac under heat at 120°, 150°, 180° and 200°C of temperatures have been determined. The degree of efficiency of the accelerators at different temperatures are also reported.

Lac (shellac) is a resinous substance secreted by an insect, Laccifer Lacca. Shellac when heated softens and then melts. As the temperature is raised, it gradually becomes thicker and thicker and finally turns into a rubbery product which on cooling solidifies to a hard, tough, horny mass. The original properties are totally changed and the final product becomes almost insoluble in alcohol, infusible, stone-hard and brittle. This phenomenon is called hardening and the polymerised product is known as cured shellac. The time required to reach the rubbery stage has been called "Life under heat" by Ranganathan and Aldis[13]. Gardner and Gross[14] designated the three stages, by analogy with thermo-setting resins, as A, B and C respectively. Ordinary shellac which is soluble and fusible was considered to be in the A-stage. The rubbery stage which is still completely soluble, is the B-stage and the cured product is in the C-stage. The rate of thermal polymerisation of shellac can be accelerated or retarded by means of various chemicals. It is well known that the curing time of shellac is high, being of the order of 20 to 60 minutes at 150°C depending upon its grade and age[15]. Accelerators may obviously play a very significant role in reducing this time compared to that of the common thermo-setting resins. Apart from these considerations, the life test is of considerable practical utility in industry. In the plastic moulding industry where hard, rigid articles have to be produced with a short time-cycle by converting lac into a semi-thermohardening resin, a shorter life would be considered to be an advantage. On the other hand, the gramophone record industry, which consumes the major portion of lac, re-uses the rejects and scraps and would, therefore, be interested in having a lac which possesses a long life[16]. The life test, therefore, is of great importance in choosing the right type of lac for any particular requirement. In general, acids, ester forming catalyst, ammonia and ammonia liberating substances behave as accelerators[17]. So, we have selected oxalic acid, citric acid, tartaric acid and urea as accelerators or curing agents in the present investigation. Our results on the effect of curing agents on life of lac (shellac) is presented here.

EXPERIMENTAL

Shellac was finely powdered, dried and stored in a stoppered bottle for further work.

2.1. Determination of life of shellac under heat at 120°C

5.0 gm shellac sample was taken in a 100 cm^3 conical flask which was immersed in an oil bath and supported by means of a clamp in such a way that the whole shellac sample was below the level of oil in the bath. It was then heated in the oil bath at 120°C and period of experiment was noted through a stop watch. The contents of the flask was stirred by a glass rod from time to time. As the shellac got more viscous, it was lifted with the rod but fell back slowly . Finally, the end point was reached when the stirrer rod is pushed back slightly owing to the resistance offered by the rubbery lac to any twisting motion and the time in minutes that elapsed was recorded as the life under heat of the sample at 120°C. In this experiment it was noted to be 110 mins.

Exactly similarly, the life of shellac under heat at 150°, 180° and 200°C were determined. The results are shown in Table 8.

2.2. Determination of the effect of curing agents on life of shellac under heat

5.0 gm shellac sample was taken in a 100 cm^3 conical flask and to it was added 1% of oxalic acid. The flask was then immersed in an oil bath and supported by means of a clamp in such a way that the whole shellac sample was below the level of oil in the bath. It was then heated in the oil bath at 120°C and period of experiment was noted through a stop watch. The contents of the flask was stirred by a glass rod from time to time. As the shellac got more viscous, it was lifted with the rod but fell back slowly. Finally, the end point was reached when the stirrer rod is pushed back slightly owing to the resistance offered by the rubbery lac to any twisting motion and the time in minutes that elapsed was recorded as the life under heat of the sample at 120°C. In this experiment it was noted to be 25 mins.

The same series of experiments were carried out under exactly identical reaction conditions using 2%, 3%, 4% and 5% of oxalic acid and the results are summarised in Table 8.

Exactly similarly, the life of shellac under heat with tartaric acid, citric acid and urea were also determined and the results are recorded also in Table 8. The degree of efficiency of the used accelerators at different temperatures were also determined and shown in Table 9. The calculating formula is given below :

$$\text{Degree of efficiency} = \frac{\text{Life (in minute) of shellac without chemicals}}{\text{Life (in minute) of shellac with chemicals}} \quad \text{(at a fixed temperature)}$$

Results and discussion

The chemistry of polymerised shellac under heat treatment has not been much studied. Recently the use of shellac as such or modified shellac in various industries is gradually increasing for the production of many useful articles of commercial interest. The results observed in the present investigation is expected to facilitate the utilisation of various modified shellac obtained through controlled experiments for specific requirements in the different industries.

From Table 8, we see that the life of lac (shellac) naturally depends on the temperature, the lower the temperature of heating, the longer the life. At a fixed temperature, the age, the quality and the method of manufacture, all have a considerable influence on the effective life of lac. Among freshly manufactured shellacs, a longer life is indicated by the better species of lac. The figure for life is therefore, a valuable indication of quality.

From Table. 8, it is evident that the life under heat were changed due to the influence of various chemicals used and it could be concluded that different chemicals act differently in accelerating the thermal curing of lac. Citric and tartaric acids increase the rate of reaction only catalytically, where as oxalic acid modify the curing process itself. The effect of urea is different from either of these. In this case, the life under heat is more or less unaffected by temperature when 3% or more is used, although at less than 3%, the characteristics of the life approach more nearly those of tartaric acid. Bhattacharya[17] and Sankaranarayanan and Sen[18] were of the view that urea forms salts with shellac from which urea can be easily removed by simply boiling with water.

From Table 9, it is observed that the degree of efficiency of an accelerator increases with the increase of the amount of the accelerating or curing agent.

Thus it is seen that when shellac is treated with different chemical reagents, it accelerates the polymerisation reaction of shellac. The polymerisation reaction is attended with a gradual elimination of water vapour along with the gradual rise in insolubilities of the product in alcohol. Other properties of the polymer sample do not show any marked changes[19, 20].

Table 8 : Life of shellac (in minutes) under heat and in combination with other chemicals

Accelerator/ Curator	% on lac	Life (in minute) at temperatures			
		120°C	150°C	180°C	200°C
-	-	110	42	17	7
Oxalic acid	1	25	11	5	3
	2	18	8	4	3
	3	15	7	4	3
	4	11	6	3	3
	5	8	5	2	-
Citric acid	1	70	21	8	3
	2	55	16	7	2
	3	48	14	6	2
	4	35	12	5	2
	5	30	11	5	2
Tartaric acid	1	100	38	12	6
	2	90	28	10	5
	3	75	25	9	4
	4	65	22	8	3
	5	55	18	6	3
Urea	1	90	38	18	9
	2	15	22	10	3
	3	9	13	8	2
	4	7	10	6	2
	5	6	8	6	2

Table 9 : Degree of efficiency of different accelerators at 120°C, 150°C, 180°C and 200°C.

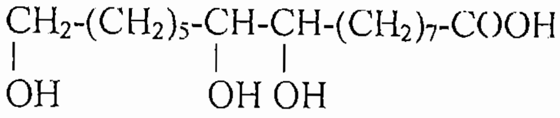
Accelerator	% on lac	120°C	150°C	180°C	200°C
Oxalic acid	1	4.40	3.81	3.40	2.33
	2	6.11	5.25	4.25	2.33
	3	7.33	6.00	4.25	2.33
	4	10.00	7.00	5.66	-
	5	13.75	8.40	8.50	-
Citric acid	1	1.57	2.00	2.12	2.33
	2	2.00	2.62	2.42	2.33
	3	2.29	3.00	2.83	3.50
	4	3.14	3.50	3.40	-
	5	3.66	3.81	3.40	-
Tartaric acid	1	1.10	1.10	1.41	1.16
	2	1.22	1.50	1.70	1.40
	3	1.46	1.68	1.88	1.75
	4	1.69	1.90	2.12	2.33
	5	2.00	2.33	2.83	2.33
Urea	1	1.20	1.10	0.94	0.77
	2	7.33	1.90	1.70	2.33
	3	12.22	3.23	2.12	3.50
	4	15.71	4.20	2.83	3.50
	5	18.33	5.25	2.83	3.50

3. Chemical Investigation on Thermally Polymerized Aleuritic Acid

Abstract

Aleuritic acid, isolated (30%) from Bangladeshi shellac has been found to undergo polymerization by heat treatment. The behaviour of polymerization from of kinetic point of view has been studied and found that the overall reaction is of third order. Other properties of the polymer sample, such as acid value, saponification value and ester value have also been determined.

From the exhaustive study on thermal polymerization of seed lac, shellac and dewaxed shellac[19,20] it appeared to be very much exciting to study the behaviour of thermal polymerization of aleuritic acid, which is one of the important and major constituent of lac. Aleuritic acid (I) is a trihydroxy carboxylic acid[21].



$$\underset{\mathrm{OH}}{\mathrm{CH_2}}\text{-}(\mathrm{CH_2})_5\text{-}\underset{\mathrm{OH}}{\mathrm{CH}}\text{-}\underset{\mathrm{OH}}{\mathrm{CH}}\text{-}(\mathrm{CH_2})_7\text{-}\mathrm{COOH}$$

(I)

Considering its structural feature aleuritic acid may undergo both inter and intra-molecular condensations leading first to the formation of fusible ethers, anhydrides, lactones and esters and ultimately to infusible and insoluble three dimensional structures. Further light may be thrown on the nature of reaction by applying Arrhenius equation[22]:

$$\mathrm{Log_e}\ \frac{k_1}{k_2} = \frac{Q}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

We get the value Q, the energy of activation to be 15.6 k. cal. mol., which is characteristic of esterification reaction (cf. 15 k. cal. mol. of esterification of ethanol). From the kinetic point of view after modifying the overall bi-molecular reaction 2A → reaction product, we come to the relevant form of the equation,

$$kt = \frac{1}{C} - \frac{1}{C_0} = C_0 (1-p)$$

Where k = Reaction constant

t = Time in hours

C_O = Initial concentration of acid = acid value of unpolymerized acid

C = Concentration of acid after time t = Co (1-p)

P = Extent of reaction.

$$\therefore C_0 kt = \frac{1}{(1-p)} - 1 \text{ .... } (1)$$

i.e. The plot of $\frac{1}{(1-p)}$ against t should be a straight line. In case of the reaction being of the third order, i.e. 3A → reaction product, the relevant kinetic reaction will be $2\,kt = \frac{1}{C^2} - \frac{1}{C_0^2}$

$$\text{or, } 2\,kt\,C_O = \frac{1}{(1-p)^2} - 1 \text{ .... } (2)$$

i.e. the plot of $\frac{1}{(1-p)^2}$ against t will be a straight line.

EXPERIMENTAL

3.1. Isolation of aleuritic acid

The required aleuritic acid was isolated from Bangladeshi shellac by the method as described in section 5.3 (p.p. 74).

3.2. Polycondensation of aleuritic acid

The isolated aleuritic acid (20 gm) was heated for a certain period of time at 160° and 180°C. It was converted into fusible and later into infusible resinous condensation products. The change was accompanied by elimination of water, lowering of acid value and increase in molecular size. The extent and rate of condensation was enhanced by increase in heating period. The acid value, saponification value and ester value of sample drawn after regular interval indicated by time in the course of reaction have been determined, from which the extent of reaction were calculated and recorded in Table 10 and 11.

Physical and chemical constants of the polymer samples

(i) Determination of acid value- Acid value of the polymer sample was determined as usual and the results are summarized in Table 10 and 11.

(ii) Determination of saponification value- Saponification value of the polymer sample was determined as usual and the results are summarized in Table 10 and 11.

(iii) Determination of hydroxyl number- Hydroxyl number of the sample was determined following the standard method[23] and the results are summarized in Table 10 and 11.

(iv) Estimation of moisture evolved during polymerization - As moisture was found to be the only product eliminated during heat polymerization, the loss in weight of the sample after definite interval of time at a particular temperature represented the weight of the water evolved. Aleuritic acid (10 gm) was heated in a thermostat at 160±1°C in a current of dry air. After definite intervals the mass was chilled and weighed. The rate of bubbling air through the molten acid was kept constant all through. The results are summarized in Table 12.

Table 10 : Properties of aleuritic acid heated at 160° C.

Heating time (in hour)	Acid value	Sap. value	Ester value (%)	P	$\frac{1}{(1-p)}$	$\frac{1}{(1-p)^2}$
0.25	161.71	192.40	15.00	0.15	1.18	1.39
0.50	148.92	191.90	25.00	0.25	1.33	1.77
0.75	130.98	192.50	28.00	0.28	1.38	1.93
1.00	122.30	193.50	33.00	0.33	1.49	2.23
1.25	115.10	195.00	40.00	0.40	1.66	2.77
1.50	108.70	194.40	41.00	0.41	1.69	3.08
1.75	99.50	193.30	45.00	0.45	1.81	3.31
2.25	91.65	192.25	48.00	0.48	1.92	3.70
2.50	88.00	191.90	50.00	0.50	2.00	4.00
3.00	85.55	192.25	56.00	0.56	2.27	5.18

Table 11 : Properties of aleuritic acid heated at 180° C.

Heating time (in hour)	Acid value	Sap. value	Ester value (%)	P	$\frac{1}{(1-p)}$	$\frac{1}{(1-p)^2}$
0.25	140.00	190.00	20.00	0.20	1.25	1.56
0.50	132.25	191.00	35.00	0.35	1.53	2.36
0.75	125.50	190.50	43.00	0.43	1.75	3.08
1.00	105.00	192.00	55.00	0.55	2.22	4.95
1.25	90.65	191.80	62.00	0.62	2.63	6.94
1.50	75.20	190.90	70.00	0.70	3.33	11.11
1.75	73.00	190.50	72.00	0.72	3.57	12.82
2.25	63.30	193.00	74.00	0.74	3.84	14.92
2.50	58.25	192.25	75.00	0.75	4.00	16.12
3.00	50.0	192.00	78.00	0.78	4.54	20.83

Table 12 : Water evolved per 10 gm of aleuritic acid heated at 160° C.

Acid value	Theoretical (gm)	Experimental (gm)
184.00	0.000	0.000
130.00	0.002	0.002
94.00	0.065	0.060
70.00	0.117	0.110
48.00	0.196	0.150

Results and discussion

From Table 10 and 11, it is seen that with the progress of the reaction under isothermal conditions, the amount of free acidity decreased with the increase of percentage of esterification and the saponification values remained practically constant. The results clearly demonstrate that the reaction is a continuous process and does not occur in stepwise manner, as would be expected in the case its formation first into a dimmer, then into a tetramer and so on.

A more detailed study of the process from the kinetic point of view has led to the results of an additional interest. We define the extent of reaction p as the ratio of the number of ester groups to the number of ester plus free carboxyl groups, when the degree of polymerization would follow as 1/ (1-p), where p is the extent of reaction. When the plots are drawn from the data mentioned in Table 10 and 11, the graph of $1/\ (1\text{-}p)^2$ against t is a straight line (Fig. 4 and 5). Therefore the overall reaction is of the third order.

Moreover, the acid value-water evolved curves are compared with the theoretical curves drawn on the assumption of inter-esterification, it is found that the water evolved is slightly less than the theoretical values (Tables 12 and Fig. 6).

Regarding the nature of final products of polycondensation of aleuritic acid, it is generally recognized that in the C-stage of polymerization, i.e. when the products become insoluble and infusible, cross-linkings develop through the union of the reactive centres and the ultimate space pattern is of three dimension. Methyl aleuritate did not undergo any condensation when it is heated at 160°C. This experimentation conclusively suggests that the polymerization of aleuritic acid does not involve etherification at all but takes place through an inter-esterification.

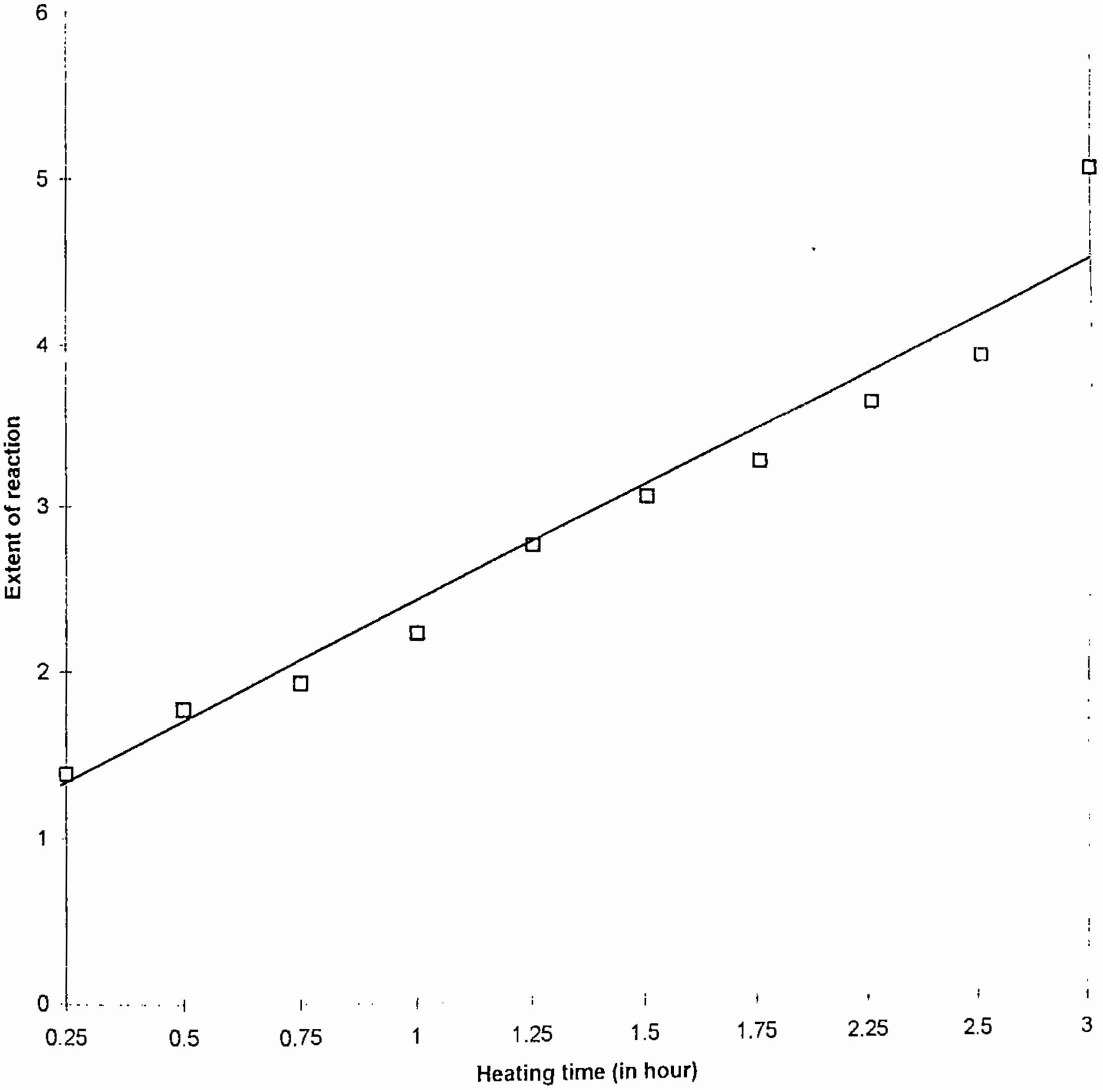


Fig. 4 : Degree of polymerization at 160°C

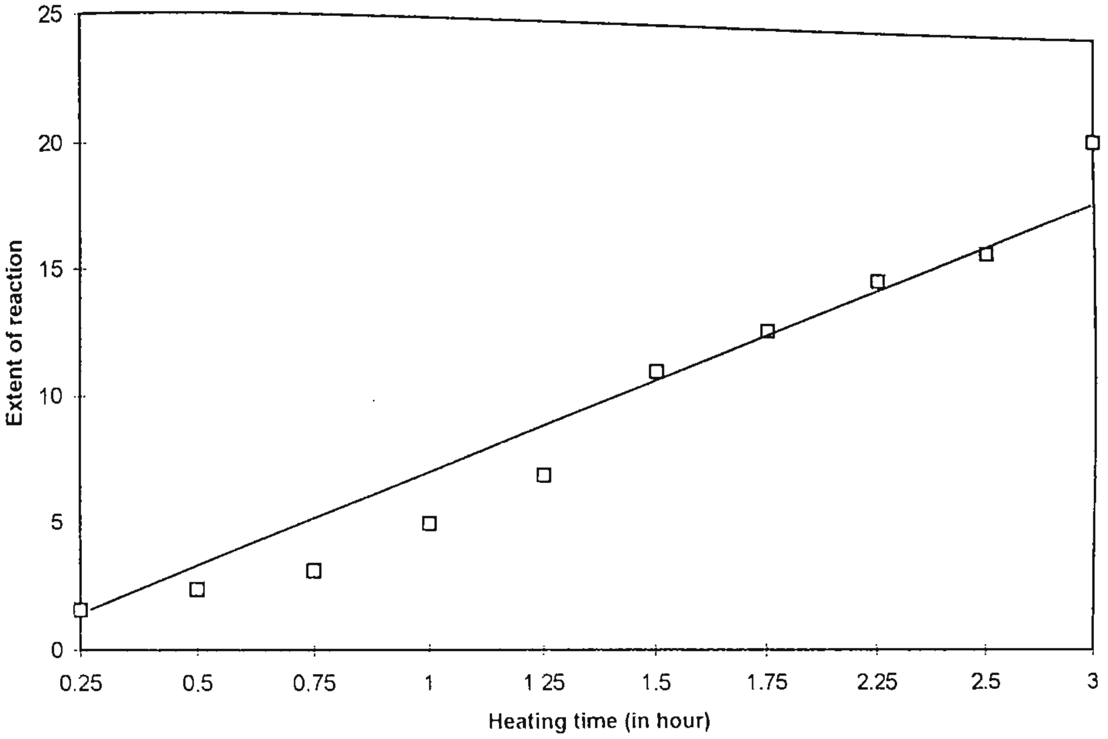


Fig. 5 : Degree of polymerization at 180°C

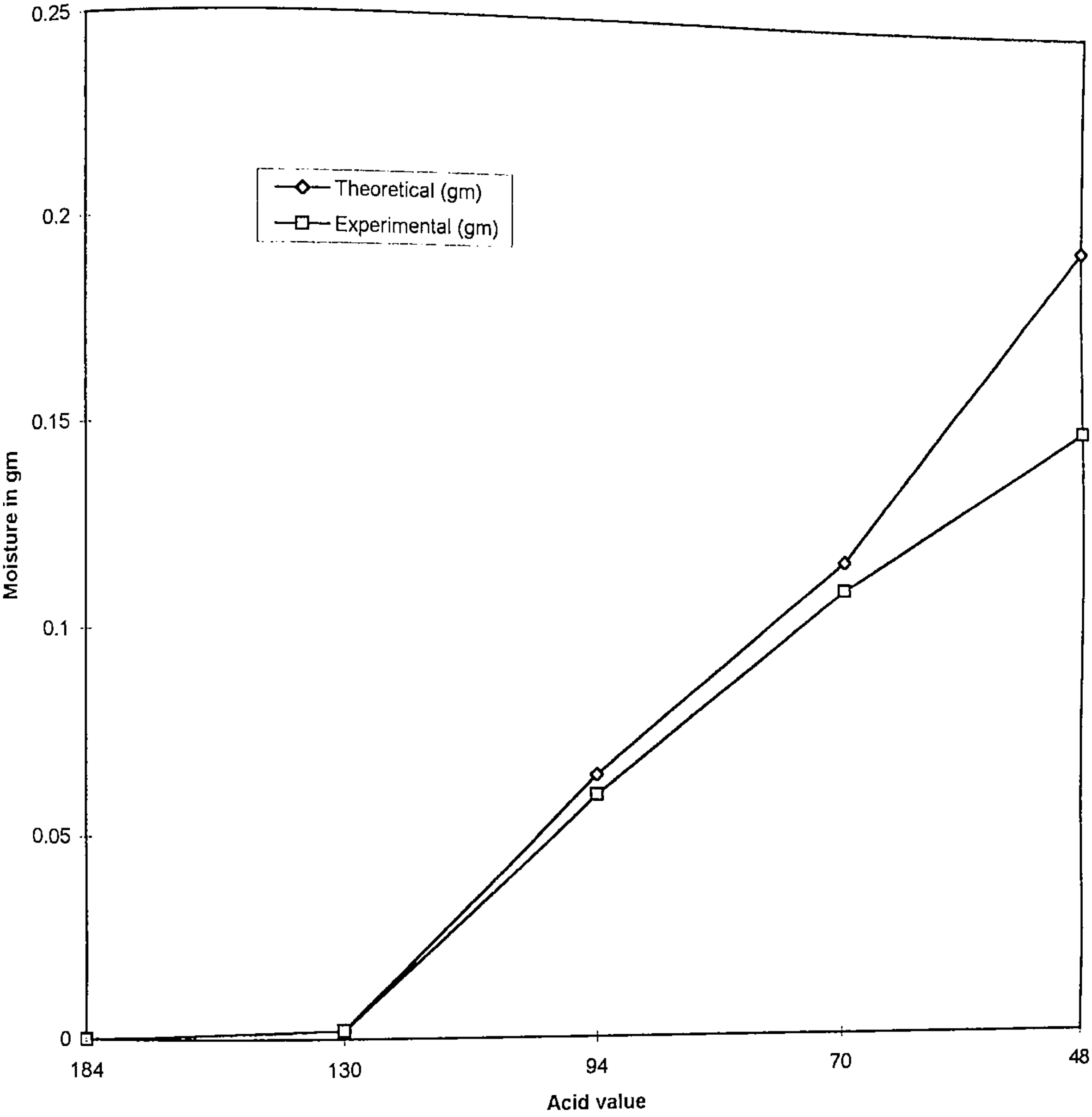


Fig. 6 : Acid value-water evolved curve.

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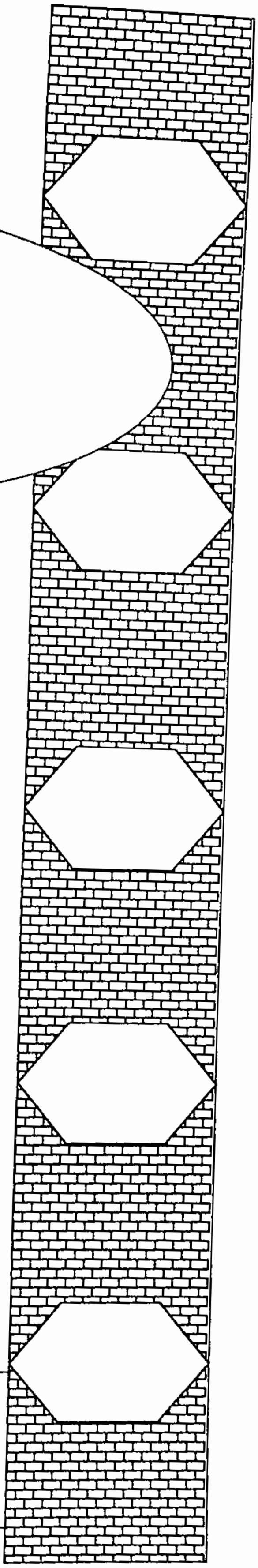
CHAPTER 4



CHEMICAL MODIFICATIONS OF LAC

1. Chemical modifications of lac

Shellac (Lac) can be modified by chemical treatment. The modified lac has better adhesion, elasticity, toughness and water resistance than the original lac. On heating, a tough, flexible resin is obtained when lac is etherified by interaction with mono or poly alcohols (of which ethylene glycol is a typical). By esterifying hydrolysed shellac with glycols, some products, flexible enough for fabric coatings can be prepared.

1.1. Some ethylene glycol modifications of lac and its derived products

Abstract

Lac (Shellac) and lac acids in combination with polyhydric alcohols like ethylene glycol in presence of catalyst led to the formation of lac-glycol resin. This resin on further esterification with double boiled linseed oil gave an oil soluble lac-glycol fatty acid complex. An improved varnish was also prepared from this complex. The physico-chemical characteristics of the product were ascertained.

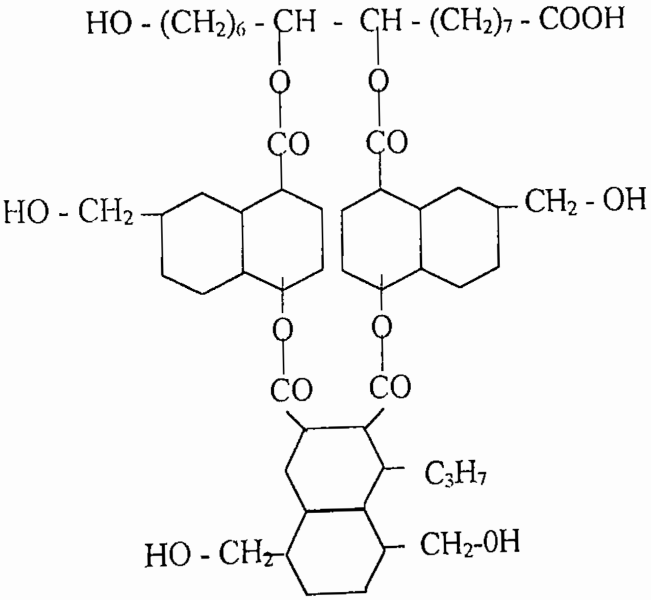
Several attempts have been made to produce lac (shellac) drying oil combinations with a view to combine the excellent film-forming characteristics of the former with the elasticity and weather-resistance of the oil. But unlike other natural resins, shellac does not readily react with drying oils because of its incompatibility and polymerisation behaviour at the high temperature of the reaction.

Bhattacharya and Gidvani[1] made an extensive study of the formation of lac-linseed oil combinations by incorporating shellac in linseed oil fatty acids in the presence of glycerol and claimed a product of very low acid value and satisfactory properties.

Compatibility of lac with linseed oil in presence of oxides of lead has been recognised from early times. Other incorporating agents are oxides and carbonates of sodium and calcium and glycerine[2].

In the present work, lac-oil new combinations are reported. In modification of the method of Bhattacharya and Gidvani[1] these combinations are prepared by using : a) ethylene glycol instead of glycerol, b) double boiled linseed oil instead of raw linseed oil and c) no metal oxide catalyst.

To modify lac, it is necessary to consider the chemistry of lac resin. A complete knowledge of the lac resin molecule is not yet available, but the following monomeric structure I formula is believed to exhibit most of the chemical properties of lac[3]. It may be noted that the hydroxyl and carboxyl groups of component acids other than aleuritic acid are arbitrarily disposed in formula 1.



(1)

It is suggested that of these five hydroxyl groups two are more reactive than the other three. When a mixture of shellac and excess of ethylene glycol is heated together in presence of an acid catalyst at 150°-200°C, etherification takes place between the hydroxyl groups of the lac and those of the glycol[4].

Heat polymerisation of the shellac-glycol compound leads to an elastic rubber like material having, a molecular weight of nearby 2200. The residual hydroxyl groups of shellac glycol resin are further esterified when the latter are heated with various lower or higher saturated and unsaturated fatty acids with or without the help of catalysts at various temperature. The nature of the products varies from soft balsams through waxy materials to hard resins and their properties and uses depend upon the esterifying acids.

Shellac, on saponification with alkali and treatment of the resulting solution with acids, gives a water-insoluble soft acidic mass to the extent of 65 to 70% by the weight of the original shellac. This product is called hydrolysed lac or lac acids. Hydrolysed lac is a useful raw material for a variety of products of industrial importance. The most promising fields being cements, adhesive and glues. Esterfication of hydrolysed lac with ethylene glycol results in sticky balsam like materials which are non drying at ordinary temperatures but dry to hard, smooth surface on baking.

The results of the present investigation on the modification of lac with ethylene glycol and its derived products are presented below :

EXPERIMENTAL

1.1.a. Preparation of dewaxed shellac[5]

The required dewaxed shellac was prepared from seed lac following the same procedure as described in section 1.4 (p.p. 40).

1.1.b. Preparation of hydrolysed lac (Lac acids)[6]

Hydrolysed lac (lac acids) was prepared by following the procedure available in the literature.

1 kg of seed lac (raw lac) was dissolved in 4 litre of water containing 0.25 kg of caustic soda in a 6 litre flat-bottom steel vessel. The solution was then boiled for 2-3 hours and allowed to cool. The shellac wax that floats to the top and forms a scum was removed by means of a laddle.

The solution was then filtered through nylon cloth to remove any impurities. The saponified lac or lac acids were precipitated from the filtrate in the form of sticky resin by the gradual addition with stirring of 1 litre of dilute sulphuric acid (20%). The precipitated lac acid was then washed several times with boiling water until the washings were free from sulphuric acid. This was tested by the addition of barium chloride solution previously acidified with hydrochloric acid to the washings until the latter showed no turbidity or precipitation. The saponified lac was then dried by heating at 100°-105°C for 1 hour. The yield of lac acids was 650 gm (65%), calculated on the basis of weight of seed lac taken.

1.1.c. Reaction of ethylene glycol with dewaxed shellac:formation of lac-glycol ether[6]

500 gm of dewaxed shellac and 187 cm^3 of ethylene glycol was taken in a 1 litre round bottom flask fitted with an upward condenser and heated in an oil bath at 120°C until all the lac dissolved. The temperature was then allowed to fall to 80°C and

concentrated H_2SO_4 (1.8 cm^3) added. The mixture was then refluxed at 180° to 190°C for 4 hours and then poured into water. The excess of glycol and acid was then washed out repeatedly with boiling water and the product dried by heating under vacuum over boiling water bath. The etherified product thus obtained was soluble in most of the usual solvents.

1.1.d. Preparation of double boiled linseed oil

200 cm^3 raw linseed oil was taken into a 1 litre three necked round bottom flask fitted at its one neck with a reflux condenser; to the middle neck with a mechanical stirrer and to the other neck with a dropping funnel and heated on an oil bath at 240-250°C with constant stirring for about 45 min. It was then cooled down to 90°C and litharge (2.0 gm), cobalt acetate (0.70 gm) and manganese acetate (0.72 gm) were added to the linseed oil as drier and again stirred for about half an hour. The temperature of the mixture was again raised to about 250-260°C and air was bubbled through a blow pipe in the reaction mixture. The product obtained was the double boiled linseed oil.

1.1.e. Esterification of lac-glycol ether with double boiled linseed oil : formation of lac- glycol fatty acid complex[6]

The prepared lac- glycol compound (100 gm) was taken in a 1 litre round bottom flask and heated on an oil bath at 200-205°C for 30 min. to remove any uncombined glycol. Double boiled linseed oil (100 gm) was then added to this hot mixture and the esterification carried out in the same open vessel by heating the mixture for 4-5 hours at 150°-200°C. The lac-glycol fatty acid complex thus obtained was soluble in castor oil, xylene, meta-cresol etc.

1.1.f. Glycol-ester of hydrolysed lac[6]

250 gm of hydrolysed lac (lac acids) was taken in a 1 litre round bottom flask and to it was added 100 cm^3 of ethylene glycol. The mixture was then refluxed in an oil bath at 195°-200°C for 24 hours, when practically a neutral product was obtained. The ester was then washed free from glycol or any other water-soluble matter by repeated washing with boiling water and dried. The product was a dark-red sticky balsam with sp. gr. 1.05 at 30°C. It was soluble in castor oil, xylene, meta-cresol, etc.

Results and discussion

It is observed in the course of our experiments that double boiled linseed oil dries more quickly than either raw and refined oil and exhibits improved drying qualities.

The chemical constants of dewaxed shellac, lac-glycol ether, lac-glycol fatty acid complex and glycol-ester of hydrolysed lac were determined and shown in Table 1..

Table 1 :. Chemical constants of dewaxed shellac and its modified products

Sample No.	Description of sample	Acid value	Sap. value	Iodine value
1.	Dewaxed shellac	70.00	232.00	18.50
2.	Lac-glycol ether	13.60	216.88	14.29
3.	Lac-glycol fatty acid complex	18.54	242.23	18.15
4.	Glycol-ester of hydrolysed lac	67.77	164.25	9.92

The resulting resinous products have been found to be of low acid value and useful in coating industry, plasticisers and adhesives. The modified lac can also be used in printing ink.

2. Preparation of varnish from lac glycol fatty acid complex

An improved varnish was prepared from the lac-glycol fatty acid complex. A brief description of the method is given below[7]:

The varnish was prepared by dissolving 100 gm of lac-glycol fatty acid complex in 300 cm^3 xylol : m-cresol (3:1), filtering the solution through fine compact cloth and refluxing the filtrate with 6.0 gm malic acid and 5.0 gm castor oil for 3 hours.

The prepared varnish was tested for its physical properties like extractable matter content, solid content, viscosity and specific gravity and the results are recorded as :

Extractable matter content	4%
Solid content	40%
Viscosity at 30°C	1.4 poise
Specific gravity at 30°C	0.95

Air drying of the films of varnish was measured by touching with finger. For this purpose test sample of the prepared varnish containing 0.1% cobalt naphthenate was used to paint the wooden surfaces and the films obtained was found to be smooth and clean. The time taken for the films to dry to touch, to hard dry and to become tack free were found to be 1-2 hours for touch dry, 4-5 hours for hard dry and 24 hours for tack free. Water resistance towards tacking was measured by dipping the panel in water. For this purpose the prepared varnish was applied to wood at 0.007" thickness, air dried for 6 days and then immersed in water. The wooden surfaces were examined at intervals of 1, 2, 4, 24 and 48 hours and found unaffected with water. The thermal resistance of air-dried films is upto 70-80°C, it can be improved upto 150°C by baking the films at 175°C for half an hour. The salient properties of the varnish is shown in Table 2 below :

Table 2 : Salient properties of the varnish

Characteristics	Synthetic varnish[8]	Prepared varnish
Drying in thin film	non-tacky not more than 4 hours	Air-dried within 1-2 hours
Dilution ability or compatibility (%)	100	100
Reaction of the varnish with copper wire	The copper will not change colour	No change in colour was observed, when it was coated with the varnish and heated at a temperature of 100°C for 24 hours.
Electrical strength (KV/mm) in air at room temperature	50	50
Resistance to tacking at 200 V	50 drops	48

The varnish may be applied on coils of electric motors, transformers etc. It can also be used as anti-tacking insulating varnish and for finishing of electrical component of instruments.

The Super Enamelled Copper Wires (SECW) were coated with the prepared varnish and tested for its technical requirements (specification) following procedures available in Brochure of Gazi Wires Ltd, Chittagong. The parameters determined are conductor size, area of cross section, electric break down voltage, abrasion resistance, elongation, cure-test, heat shock resistance and resistance to solvents. The test results of the prepared varnish in comparison to imported synthetic varnish (PVA) (supplied by the Gazi Wires Ltd) are recorded in Table 3.

Table 3 : Typical test results and technical data of super enamelled copper wire insulated with prepared varnish and imported synthetic varnish.

Type of varnish	Size (SWG)	Diameter of Bare wire in mm.	Overall diameter in mm	Break-down voltage	Abrasion Resistance	Elongation (%)	Cure test	Resistance to solvents	Heat shock Resistance	Solid content	Exractable matter content
Preapred varnish	32	0.273	0.322	5000	24, 28, 32	25	Slight Swelling	Pass	Pass	40%	4%
Imported synthetic varnish	32	0.273	0.320	6000	32, 34, 37	24	Pass	Pass	Pass	35%	4%

(i) **Resistance of the enamel cover to Abrasion :**

The test was applicable to wire of size 32 SWG. The test was performed in an automatic abrasion testing apparatus. (PVE Abrasion Tester. Furukawa Electric Co., Ltd., Tokyo, Japan, Model- 1980). The Corresponding values were 24, 28, 32.

(ii) **Heat Shock :** A sample of enamelled wire was placed for one hour in an air oven operating at 130±2°C. The covering shows no crack.

(iii) **Heat Ageing :** A specimen of the enamelled wire unstreched and unbent was heated for 72 hours in an oven at temperature 180±2°C. The specimen was then cooled to room temperature and wounded for 10 continuous turns on a polished metal mandrel having a diameter three times the diameter of the bare wire. The covering shows no crack.

(iv) **Elongation of SECW :** A specimen of the enamelled wire 25 cm long was steadily stretched at a rate of 30 cm/min. until the wire breaks. Minimum elongation of SECW was 25%.

(v) **Electric break down voltage :** The electric break down voltage was noted (by Voltage Testing Apparatus, Furukawa Electric Co. Ltd., Tokyo, Japan, Model-1965) and found 5000 volts.

(vi) Chemical Test

(a) **Cure test :** A sample of enamelled wire was conditioned by baking at 130±2°C for 10 minutes and then allowed to cool to room temperature. About 10 cm of this sample was then immersed without bending, for 5 minutes in boiling mixture containing 30% commercial grade toluene and 70% ethanol by volume. On removal from the liquid the wire shows slight visible swelling.

(b) **Resistance of the enamel to varnish solvents :** The surface of the SECW was emerged in methylated spirit for 24 hours. After removal from the solvent the specimen was allowed to dry under room condition for half an hour. At the end of this period it was not possible to remove the enamel partially.

(c) **Extractable matter :** The test was performed by extracting an appropriate specimen of SECW for two hours with pure toluene and two hours with redistilled methanol. The percentage of the extractable matter determined was 4% on the weight of SECW.

Results and Discussion

The prepared insulating varnish was tested for solid contents, viscosity, and found quite satisfactory.

The super enamelled copper wire was covered with the prepared insulating varnish. The size of the wire was generally in accordance with Standard Wire Gauge (SWG).

Super Enamelled Copper Wire popularly known as Magnet wire is a leading material for electric machinery, communication apparatus and electronics applied equipments. The function of these wires is entirely different from the ordinary electric wires which are used for transmitting electric waves to destinations. SECW are used for making coils in electric machinery and equipment for converting electric energy to magnetic energy or vice versa. SEC wires featuring space saving qualities are essential for miniaturization and sophistication of electronic equipments. Particularly demand is increasing for high quality SEC wires having enough softness to be adaptable to high speed automatic winding machine, which are capable of maintaining the above mentioned various properties even after severe winding process.

For ensuring superior quality of SECW we compare the test results to that of the imported varnish shown in Table 3.

The conductor diameter and overall diameter was checked with a precision instrument so that the value given in Table 3 may confirm.

An initial voltage not exceeding 100 volts was applied between the two twisted wires and gradually increased at a rate constant with accurate reading of the indicating instrument until the enamel was punctured. The break down voltage was noted as 5000 for prepared varnish and 6000 for synthetic varnish.

All other values given in Table 3 were comparable to that of synthetic varnish.

3. Application of some modified lac on jute fibre

Abstract

Some modified lac, such as dewaxed shellac, lac-glycol ether, lac-glycol fatty acid complex and glycol-ester of hydrolysed lac are prepared. Effect of these products on some physical properties viz. tensile strength, tenacity, elongation, moisture regain, weight gain, shrinkage etc. of jute fibre (both mordanted and unmordanted) have been studied. It is observed that the tensile strength, tenacity and moisture regain properties of the treated fibre decreases and percent elongation increases in comparison with the raw jute (control). The treated fibre containing modified lac deposit (weight gain) 12.73% are found. The nature of the shades developed on jute fibre by the application of various modified lac are also reported.

The effect of urea formaldehyde and melamine formaldehyde resin precondensates on jute fibre and fabrics were studied in detail by Amin *et al.*[9-12] In the present investigation we have treated jute fibre with some modified lac products[13] viz. dewaxed shellac, lac-glycol ether, lac-glycol fatty acid complex, glycol-ester of hydrolysed lac and thence the following physical properties of jute fibres were determined with an expectation of extension of the newer uses of jute.

3.1. Determination of tensile strength

The resistance of a material to rupture is called tensile strength. Tensile strength is expressed in kg/yarn. A jute fibre of length 25 cm and weight 0.5gm considered as a yarn in the related experiments. Tensile strength of the jute fibre was measured by "Schopper type tensile strength tester" in BCSIR laboratories, Rajshahi.

The sample (0.5gm fibre, 25 cm in length), was fixed in between the two jaw's of the instrument that were placed at a distance of 10 cm apart from each other. One twist per 2 cm was given along the length of fibre between the jaw's. Different loads were then applied successively and the operation was started in the instrument. At a certain load the sample yarn was ruptured. This breaking load of the yarn is know as its tensile strength.

3.2. Determination of tenacity

Tenacity of a yarn is defined as the strength per unit yarn number and the another term of yarn number is denier. The denier of a yarn is the weight in gms of a length of 9000 meters of that yarn and tenacity is expressed in gm/denier.

So, $$\text{denier (D)} = \frac{w(g)}{L(m)} \times 9000\ (m)$$

$$(D) = \frac{0.5}{0.25} \times 9000 = 18000$$

$$\text{and tenacity} = \frac{\text{Breaking load in gram}}{\text{denier}}$$

$$= \frac{\text{Breaking load in gram}}{18000}$$

3.3. Determination of percent elongation

Elongation is the deformation of load caused by a tensile force. The deformation strain may be measured at any specified load or at rupture. It is expressed as percent of the original length.

So, percent elongation = $\frac{L_r - L_i}{L_i} \times 100$

Where, L_r = Length of fibre in cm between two jaw's just at rupture.
L_i = Initial length in cm between two jaw's.

3.4. Determination of moisture regain in percent

The jute fibre was dried at 110±2°C to constant weight and exposed to a standard atmosphere (Relative humidity 65±2%, Temperature 25±2°C) for 48 hours and again weighed carefully in the conditioned atmosphere. The percent moisture regain was calculated from the following relation:

$$R = \frac{b-a}{a} \times 100$$

Where, R = Moisture regain percent
a = Dry weight of the sample
b = Moist weight of the sample

3.5. Determination of weight gain in percent

The jute fibre was dried with a hot air blower to a constant weight and again weighed after its treatment with a reagent. The percent of weight gain was calculated from the following relation:

$$W_g = \frac{W_f - W_i}{W_i} \times 100$$

Where, W_i = Initial weight of dried jute fibre

W_f = Final weight of treated fibre (dried)

W_g = Weight gain in percent

3.6. Determination of percent shrinkage

The jute fibre was cut to a size of 25 cm in length for the experimental purpose. It was than cleaned and converted into a yarn properly. The individual yarns were then treated separately with different chemical reagents. Each of these piece of treated fibre was then washed thoroughly with water, dried and finally length was measured again. The percent shrinkage was calculated from the following relation:

$$L_{sh} = \frac{L_f - L_i}{L_i} x100$$

where, L_i = Initial length of dried jute fibre (25cm).

L_f = Final length of the treated & dried jute fibre

L_{sh} = Length shrinkage in percent

EXPERIMENTAL

Jute fibre (Corchorus olitorius, Tossa) was collected from Rajshahi Jute Mills, Rajshahi, was cut off from both the top and the bottom end of fibre and its middle part was separated out for the present investigation. It was cleaned manually and was dried using a hot air blower. It was cut into pieces of 25 cm in length and was divided into bundles of 0.5 gm. Each of these bundles constituted a yarn for the subsequent experiments.

3.7. Mordanting of Raw Jute (RJ) with copper sulphate[14]

6% mordanting bath was prepared with copper sulphate in aqueous solution in a 500 cm^3 beaker. 10 yarns (5gm) of jute fibre (RJ) was introduced into the bath. It was heated to boiling for 30 minutes. After expiry of this time the bath was allowed to cool. The mordanted jute fibre was taken out of the bath, washed well with distilled water and dried at room temperature (25±2°C). Let this mordanted raw jute sample be called RJCu. Similarly, mordanting with ferrous sulphate, chromium sulphate and nickel sulphate are called RJFe, RJCr and RJNi respectively and alkali treated jute fibre RJA.

3.8. Treatment of different forms of jute fibre with dewaxed shellac

Each of 5 yarns (2.5gm) of the experimental sample of RJ, RJA, RJCu, RJCr and RJNi were immersed into an alcoholic solution of dewaxed shellac (20%) in separate beakers. After 24 hours, the samples were taken out of the beaker and squeezed off. The impregnated fibres were then successively washed by dilute soap solution (0.25%) and water, dried at 105°C. The physical properties of the fibre were determined and the results are summarized in Table 4.

Similar operations on the experimental yarns were carried out using other modified products of lac, viz., lac-glycol ether, lac glycol fatty acid complex and glycol-ester of hydrolysed lac. The results are summarized in Table 5, Table 6 and Table 7 respectively.

Table 4 : Effect of dewaxed shellac on jute fibre

Sample	Colour produced	Tensile strength (kg/yarn)	Tenacity (gm/D)	Elongation (%)	Moisture regain (%)	Weight gain (%)	Shrinkage (%)
Control (untreated)	Golden	40.5	2.25	2.5	11.57	-	Nil
RJ	L. violet	34.5	1.91	8.5	7.61	6.68	Nil
RJA	L. violet	32.4	1.80	5.5	10.33	5.80	Nil
RJCu	L. violet	32.6	1.81	8.0	5.71	10.23	Nil
RJFe	Brown	22.5	1.25	5.2	8.01	9.25	Nil
RJCr	Brown	15.0	0.85	5.0	7.75	9.77	Nil
RJNi	Golden	21.5	1.19	6.0	5.39	13.41	Nil

Table 5 : Effect of lac-glycol ether compound on jute fibre.

Sample	Colour produced	Tensile strength (kg/yarn)	Tenacity (gm/D)	Elongation (%)	Moisture regain (%)	Weight gain (%)	Shrinkage (%)
Control (untreated)	Golden	40.5	2.25	2.5	11.57	-	Nil
RJ	Yellow	34.2	1.90	8.5	9.67	7.0	Nil
RJA	Yellow	28.0	1.55	5.8	10.10	5.5	Nil
RJCu	Brown	28.8	1.60	5.8	7.06	4.5	Nil
RJFe	Brown	24.5	1.36	5.0	8.92	8.0	Nil
RJCr	Orange	18.0	1.00	5.8	6.58	11.5	Nil
RJNi	G. yellow	27.0	1.50	5.7	6.66	12.73	Nil

Table 6 : Effect of lac-glycol fatty acid complex on jute fibre

Sample	Colour produced	Tensile strength (kg/yarn)	Tenacity (gm/D)	Elongation (%)	Moisture regain (%)	Weight gain (%)	Shrinkage (%)
Control (untreated)	Golden	40.5	2.25	2.5	11.57	-	Nil
RJ	Brown	24.0	1.33	6.0	9.20	6.68	Nil
RJA	Yellow	25.5	1.41	6.0	9.89	7.70	Nil
RJCu	Brown	22.5	1.25	5.9	5.40	8.25	Nil
RJFe	Yellow	21.0	1.16	5.5	7.43	9.25	Nil
RJCr	Brown	24.0	1.33	6.0	6.47	3.66	Nil
RJNi	Yellow	26.0	1.44	6.4	5.31	12.12	Nil

Table 7 : Effect of glycol-ester of hydrolysed lac on jute fibre

Sample	Colour produced	Tensile strength (kg/yarn)	Tenacity (gm/D)	Elongation (%)	Moisture regain (%)	Weight gain (%)	Shrinkage (%)
Control (untreated)	Golden	40.5	2.25	2.5	11.57	-	Nil
RJ	L. violet	31.5	1.75	6.0	7.85	4.8	Nil
RJA	L. violet	30.0	1.66	5.5	10.34	6.6	Nil
RJCu	Violet	30.0	1.66	5.5	6.36	4.39	Nil
RJFe	Brown	28.0	1.55	5.0	7.79	8.0	Nil
RJCr	Brown	27.0	1.50	6.6	7.28	11.79	Nil
RJNi	Yellow	29.0	1.61	6.0	6.72	12.0	Nil

Results and discussion

The treated jute fibre showed marked improvement in various physical properties, such as reduction in tensile strength, moisture regain and weight gain. It appears to be a simple chemical finishing process for internal deposition of different lac products within jute fibre in order to incorporate new textile properties in jute. The loss of tensile strength of the fibre (Table 4 to 7) is probably caused by the fact that lignin is dissolved in solution. Through such dissolution of the components of jute fibre, its compactness or crystallinity is partially lost resulting in decrease in its tensile strength.

The increase in percent elongation of the treated fibre is due to the increase in cell wall thickness of the treated fibre. The percent moisture regain character of each treated jute fibre is lower than that of percent moisture regain character of control (untreated). The weight gain of the fibre is due to the deposition of lac products on the fibre. The variation in absorption of water vapour (moisture regain) decreases with the increase of lac-resin deposition brings forth hydrophobic characteristics in jute fibre, for which lower regain of moisture has been exhibited by the experimental samples.

The shrinkage causes loss in fibre length and found nil in the present investigation. The different shades developed on jute fibre are shown in Table (4 -7). Crosslinking of jute fibre with modified form of lac resin involves the weight gain (resin deposit) upto 12.73%.

The treatment causes embrittlement of the fibre and this also leads to loss of strength and reduces the moisture regain properties. However, an optimum level of application in the 6-8% range of resin add-on is noticeable, which may be a reasonable compromise between loss and improvement of the treatment[13]. Furthermore, the resin add-on with the fibre may be varied from this level of application of resin depending upon the end uses of jute.

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CHAPTER 5

SYNTHESIS AND CHARACTERZATION OF SOME NOVEL THIOCARBAMIDES FROM LAC PRODUCTS AND STUDIES ON THEIR ANTI-MICROBIAL ACTIVITIES

1. Synthesis and characterization of some novel thiocarbamides from lac products and studies on their antimicrobial activities

Abstract

Certain new thiocarbamides have been synthesized by the reaction of aleurityl hydrazide (lac product) with t-butylisothiocyanate, phenylisothio-cyanate, p-tolylisothiocyanate, p-anisylisothiocyanate and tetra-acetyl-glucosyl (TAG) isothiocyanate. The structural assignments of the products have been made on the basis of their elemental analyses, spectral analyses and other physico-chemical investigations. Antibacterial activities of the products were also determined qualitatively against 16 pathogenic bacteria.

Mono-arylthiocarbamides are known to be used as starting materials for the synthesis of various substituted dithiobiurets, dithiazolidines and S-triazines which are of immense industrial and medicinal importance. Some of these compounds are used as excellent vulcanization accelerator[1-5]. Inorganic and organic salts of these compounds have been found to be active against bacteria, fungi and marine organism[6]. Recently these are shown as excellent complexing agents[7,8] and their metal complexes are found to impart a very important role in balancing environmental pollution[9,10,11]. S, N-containing heterocyclic compounds are also useful as antibacterial[12-15], anti-inflammatory[16], blood pressure depressant[17], anti-diabetic[18], hypoglycemic agents[19] and some of these are known to cure gastrointestinal hyperacidity ulceration[20] and convulsion[21]. Recent medical reports have shown some of these compounds to possess antitumour activities[22] *in vitro*.

S, N-containing thiocarbamide derivatives in acyclic or macrocyclic form are very important class of compounds due to their various chemotherapautic uses or their application in the field of agriculture and in the wide industrial horizon. It is expected that similar other compounds may impart some interesting and important role in the field of agriculture and pharmaceutical chemistry. With this end in view some new thiocarbamides are prepared by the reaction of aleurityl hydrazide (prepared from aleuritic acid, the chief constituent of lac) with different isothiocyanetes. The details of the work is described in the following experimental section.

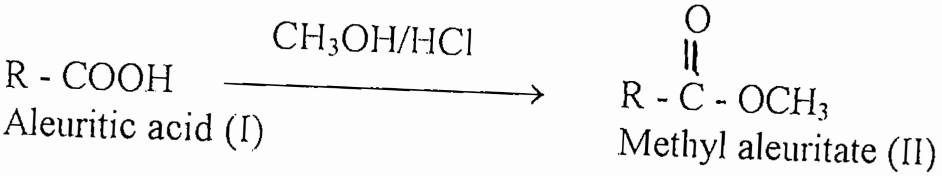
EXPERIMENTAL

1.1. Isolation of aleuritic acid from shellac

The required aleuritic acid was isolated from Bangladeshi shellac following usual procedure (section 5.3, p.p. 74).

1.2 Preparation of methyl aleuritate from aleuritic acid

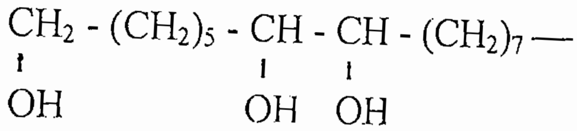
Reaction involved :



$$R-COOH \xrightarrow{CH_3OH/HCl} R-\overset{\overset{O}{\|}}{C}-OCH_3$$

Aleuritic acid (I) Methyl aleuritate (II)

Where, R =



$$\underset{OH}{\underset{|}{CH_2}}-(CH_2)_5-\underset{OH}{\underset{|}{CH}}-\underset{OH}{\underset{|}{CH}}-(CH_2)_7—$$

PROCEDURE

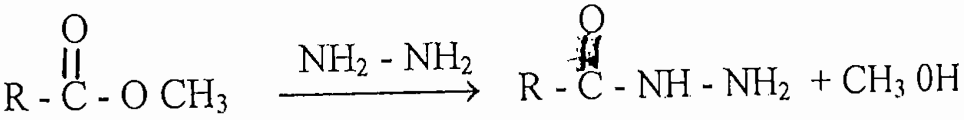
To a solution of 10.0 gm of aleuritic acid (I) in 80 cm^3 of absolute methanol, 4 cm^3 of 30% hydrochloric acid was added and the reaction mixture was allowed to stand for three days. It was then neutralized with a solution of sodium hydroxide in absolute methanol. The precipitated sodium chloride was filtered off and the filtrate poured into a large excess of cold (10°C) water with constant stirring whereby a solid product was separated out. The solid mass was filtered, washed with 10% aqueous sodium carbonate, stirred for thirty minutes and then filtered. It was washed again with distilled water and then dried. It was recrystallised from alcohol, yield 8.5 gm (85%).

It was soluble in alcohol, acetone and insoluble in water, benzene and chloroform. Its m.p. was found to be 72-73°C.

The isolated aleuritic acid and methyl aleuritate were applied on TLC plates and were run using different solvent systems amongst which ethanol : ammonia (20:1) solvent mixture was found to be more suitable. Each of the products showed a single spot and the R_f values, 0.81 for aleuritic acid and 0.68 for methyl aleuritate was measured. The authentic sample of aleuritic acid also showed a single spot at R_f value 0.81 while applied in the identifical solvent system.

1.3. Preparation of aleurityl hydrazide from methyl aleuritate

Reaction involved :



$$R-\overset{O}{\overset{\|}{C}}-O\,CH_3 \xrightarrow{NH_2-NH_2} R-\overset{O}{\overset{\|}{C}}-NH-NH_2 + CH_3\,OH$$

Methyl aleuritate (II) Aleurityl hydrazide (III)

PROCEDURE

To a solution of 10.0 gm of pure methyl aleuritate in 100 cm^3 of methanol, 30 cm^3 of hydrazine hydrate was added and the reaction mixture was refluxed for forty minutes on a water bath and then filtered while still hot to remove any insoluble impurities. The solution, on cooling, deposited white crystals of the hydrazide, which were separated by filtration. The volume of filtrate was then reduced at room temperature through a rotavapour under reduced pressure and a crude product of aleurityl hydrazide was obtained. It was then recrystallized thrice from hot (90°C) water, yield 9.5 gm (95%). Its m.p. was found to be 138-139°C. It was soluble in ethanol, acetone, xylene and insoluble in benzene, chloroform and water. The product was applied on TLC plate using ethanol : ammonia (25:1) solvent system and showed a single spot at $R_f = 0.70$.

1.3. a. Preparation of tert. butylisothiocyanate

(i) Preparation of tert. butyl choloride

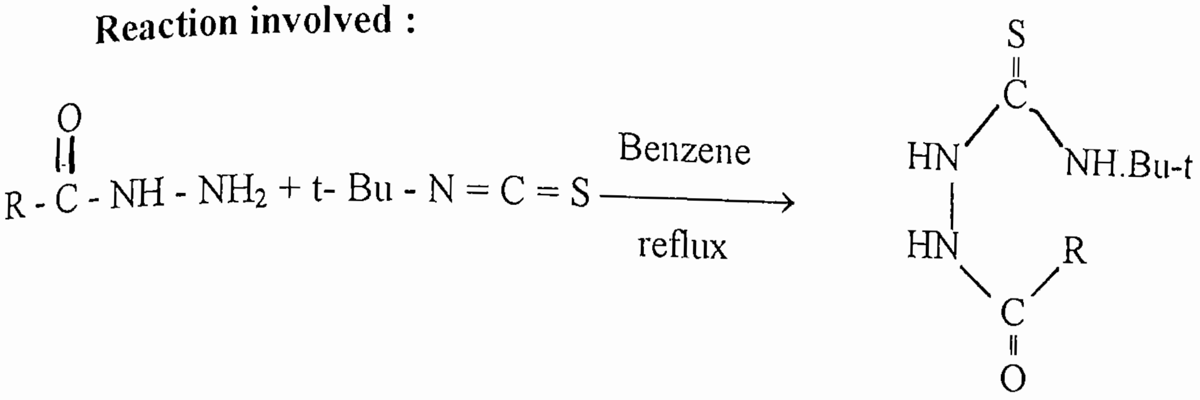
To a portion of freshly distilled tert.butyl alcohol (250 cm^3) in a separating funnel 500 cm^3 of conc. hydrochloric acid was added in installments with vigorous shaking. The mixture was allowed to stand for sometime, whereby two distinct layers were separated. The lower aqueous layer was rejected and the upper layer, consisting of ter.butyl chloride was washed first with 5% aq. sodium bicarbonate to remove any excess of acid and then several times with water and finally it was dried over anhydrous calcium chloride and then distilled. The fraction between 49-51°C was collected. Yield 150 cm^3.

(ii) Reaction of tert. butyl chloride with ammonium thiocyanate

The above prepared tert.butyl chloride (150 cm^3) was taken in a one litre flask and to this an aqueous solution of ammonium thiocyanate (90 gm) and 15 gm zinc chloride was added. This mixture was allowed to stand for one month with occasional shaking. The upper pale-yellow viscous dense layer was separated and washed several times with water. Dried over anhydrous calcium chloride. To this dense oil 15 gm of anhydrous zinc chloride was added and again it was allowed to stand for another one month with occasional shaking. Finally, it was washed several times with water, dried over anhydrous calcium chloride and distilled. The fraction between 138-140°C was collected, yield 80 cm^3.

1.4 Reaction of aleurityl hydrazide with tert. butylisothiocyanate : Formation of the related thiocarbamide of aleurityl hydrazide

Reaction involved :



PROCEDURE

To a benzene solution of aleurityl hydrazide (0.01 mole; 3.18 gm in 50 cm^3) in a 500 cm^3 round bottom flask freshly prepared tert.-butylisothiocyanate (0.01 mole; 1.15 gm) was added and the mixture was shaken gently. A few pieces of boiling chips were added to the reaction mixture and the contents of the flask was then refluxed for 2 hours. On distilling of the solvent from the reaction mixture, the desired thiocarbamide was obtained as a white solid mass, yield 1.4 gm. It was recrystallised from ethanol. It was designated as t-Bu.T.

1.4. a. Preliminary investigation on the product t-Bu.T.

(i) Melting point of the product was noted to be 85°C.

(ii) Its aqueous solution was found to be readily desulphurated while heated with alkaline plumbite solution, indicating the presence of $(-\overset{S}{\overset{\|}{C}} - NH-)$ group in the compound t-Bu.T. .

(iii) **Solubility test** : Solubility behaviour of the pure product was studied in various solvents. The result is summarized in the following Table 1.

Table 1 : Solubility chart of the product t-Bu.T.

Sl No.	Solvents	Solubility
1.	Absolute ethanol	Soluble in cold and hot
2.	Acetone	Soluble in cold and hot
3.	Benzene	Soluble in hot
4.	Water	Insoluble in cold and hot
5.	Chloroform	Partially soluble
6.	n-Hexane	Partially soluble
7.	Pet. ether (40-60°)	Insoluble in cold and hot
8.	Carbon tetrachloride	Soluble in cold and hot
9.	Di-ethyl ether	Insoluble in cold and hot
10.	Methanol	Soluble in cold
11.	Dioxane	Partially soluble
12.	DMSO	Soluble in cold and hot
13.	Xylene	Soluble in cold and hot

iv) Comparative TLC study on t-Bu-T. and aleurityl hydrazide

t-Bu.T and aleurityl hydrazide were applied on TLC plate and was run using benzene : acetone (1:1) solvent system; each of the samples showed a single spot, at R_f value 0.92 and 0.70 respectively.

iv) Estimation of nitrogen

The nitrogen content of the t-Bu.T. product was estimated by Kjeldahl method[23]. Observed : N, 9.68. Required for $C_{21}H_{43}N_3O_4S$: N, 9.70%.

v) Estimation of sulphur

The sulphur content of the t-Bu.T. product was estimated by Carius method[24]. Observed : S, 7.30. Required for $C_{21}H_{43}N_3Q_4$ S : S, 7.39%.

vi) The IR spectrum of the product t-Bu.T.

The compound showed the following characteristic absorption bands.

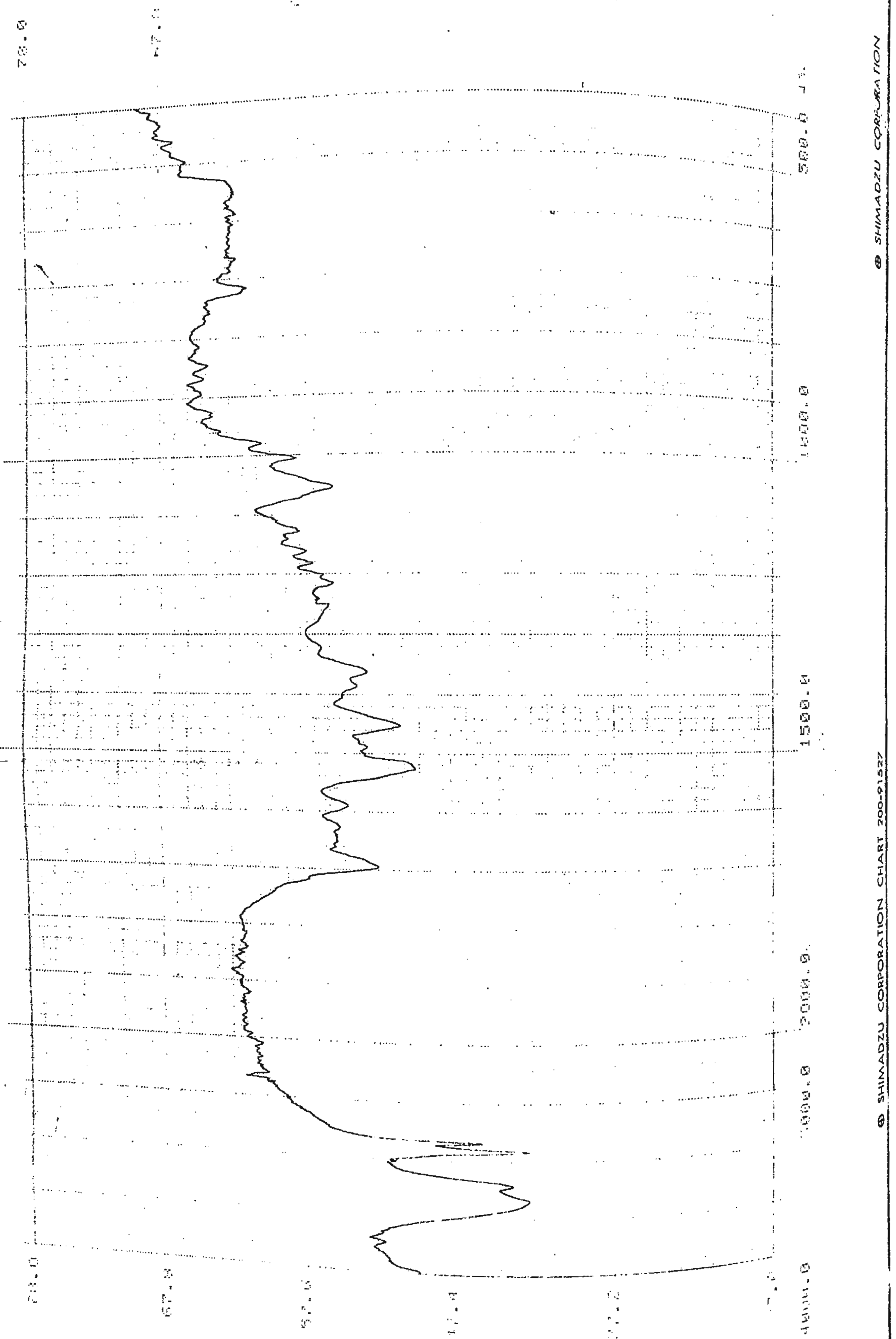


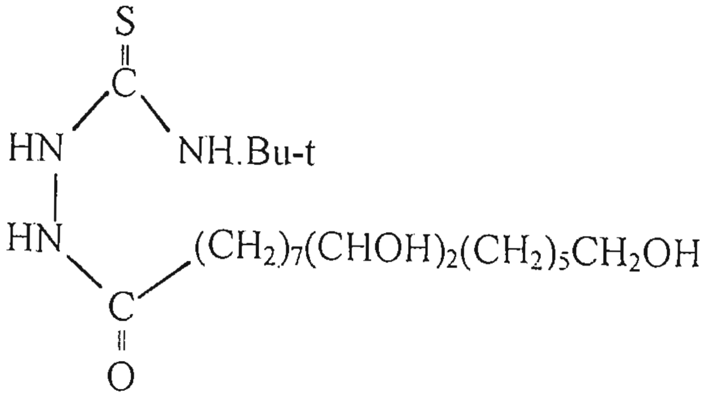
Fig. 1 : INFRARED SPECTRUM OF THE COMPOUND t-Bu.T.

Table - 2 : Important IR absorption bands of the compound t-Bu.T.

Absorption observed (cm^{-1})	Assignments	Absorption expected (cm^{-1})
3350 (s)	O-H Stretching	3400-3200[32]
3200 (m)	N-H Stretching	3400-3100[25a, 26a,27a]
2900 (s)	CH$_2$ Stretching	2960-2850[33]
1695 (s)	C=O Stretching	1775-1578[31,32]
1550 (m)	N-N Stretching	1500-1400[33]
1360 (s)	- C(CH$_3$)$_3$ Stretching	1395-1365[29]
1320 (m)	C-N Stretching	1350-1280[26c,28b]
1050 (s)	C=S Stretching	1200-1050[33]

The IR spectrum of the compound t-Bu.T. distinctly showed major absorption bands due to $\upsilon_{O\text{-}H}$, $\upsilon_{N\text{-}H}$, υ_{CH_2}, υ_{CO}, $\upsilon_{N\text{-}N}$, $\upsilon_{\text{-}C(CH_3)_3}$, $\upsilon_{C\text{-}N}$, $\upsilon_{C=S}$ (Fig. 1, Page 147)

From the above chemical investigations and spectral evidences the structure of the product, t-Bu.T was confirmed to be 1-t-Butyl-3-N-aleuritamido thiocarbamide, $C_{21}H_{43}N_3O_4S$.



Structure of t-Bu.T.

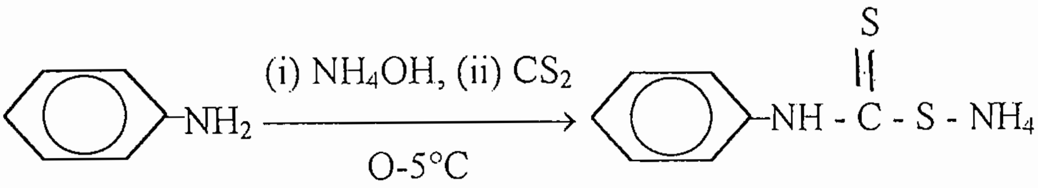
1.5 Reaction of aleurityl hydrazide with phenylisothiocyanate : Formation of the related thiocarbamide of aleurityl hydrazide

1.5.a. Preparation of phenylisothiocyanate[34]

(i) Preparation of ammonium phenyldithiocabamate

A fresh portion of distilled aniline (0.1 mole; 9.13 cm^3) was taken in a two necked 250 cm^3 round bottom flask fitted with a mechanical stirrer and to it 25% ammonium hydroxide (0.1 mole; 8.5 cm^3) was added. The reaction mixture was then cooled to 0-5°C in an ice-salt freezing bath. Freshly distilled pure carbon disulphide (0.1 mole; 6 cm^3) was then added drop-wise with constant stirring over an hour. A white crystalline solid separated out. It was then filtered and dried. Yield 17.10gm, 92%.

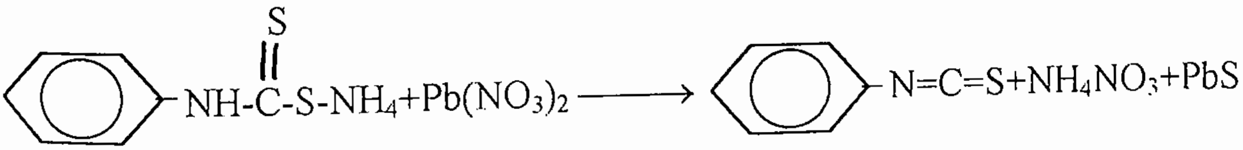
Reaction involved in the system :



(ii) Preparation of phenylisothiocyanate

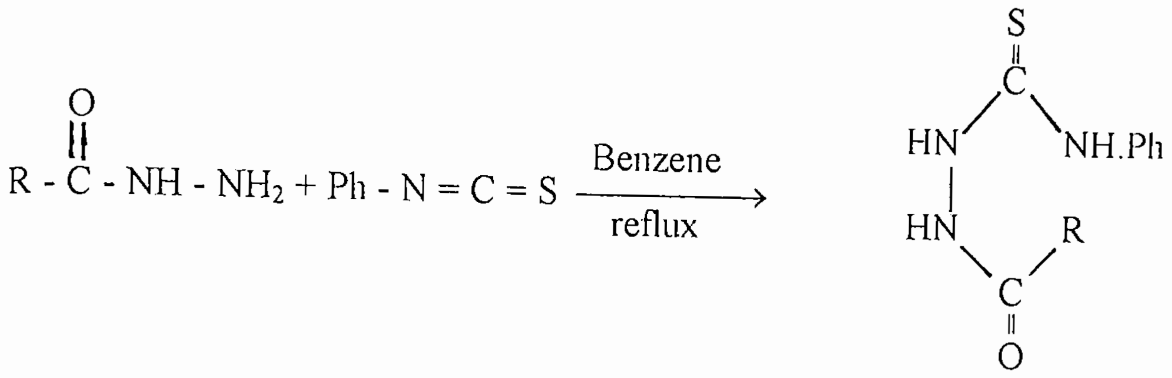
The above prepared ammonium phenyldithiocabamate was decomposed with lead nitrate, thus forming phenylisothiocyanate via lead salt intermediate. The product was collected through steam distillation. The isolated oily substance was dried over calcium chloride.

Reaction involved in the system :



1.5.b. Reaction of aleurityl hydrazide with phenylisothiocyanate

Reaction involved :



PROCEDURE

The required aleurityl hydrazide was prepared from aleuritic acid as usual.

To a benzene solution of aleurityl hydrazide (0.01 mole; 3.18 gm in 50 cm^3) in a 500 cm^3 round bottom flask freshly prepared phenylisothiocyanate (0.01 mole; 1.35 gm) was added and the mixture was shaken gently. A few pieces of boiling chips were added to the reaction mixture and the contents of the flask was then refluxed for 2 hours. On distilling off the solvent from the reaction mixture, the desired thiocarbamide was obtained as a white solid mass, yield 2.7 gm (85%). It was recrystallised from ethanol and designated as P.T.

1.5.c. Preliminary investigation on the product P.T.

(i) Melting point of the product, P.T. was noted to be 110-111°C.

(ii) Its aqueous solution was found to be readily desulphurated while heated with alkaline plumbite solution, indicating the presence of $-\overset{S}{\overset{\|}{C}}$ - NH- group in the compound P.T.

(iii) **Solubility test** : Solubility behaviour of the pure product was studied in various solvents. The result is summarized in the following Table 3.

Table 3 : Solubility chart of the product P.T.

Sl No.	Solvents	Solubility
1.	Absolute ethanol	Soluble in cold and hot
2.	Acetone	Soluble in cold and hot
3.	Benzene	Soluble in hot
4.	Water	Insoluble in cold and hot
5.	Chloroform	Partially soluble
6.	n-Hexane	Partially soluble
7.	Petroleum ether (40-60°C)	Insoluble in cold and hot
8.	Carbon tetrachloride	Slightly soluble in hot
9.	Di-ethyl ether	Insoluble in cold and hot
10.	Methanol	Soluble in cold and hot
11.	Dioxane	Partially soluble
12.	DMSO	Soluble in hot
13.	Xylene	Soluble in cold and hot

iii) Thin-layer chromatography of the product

The compound P.T. was applied on TLC plate and was run using a solvent mixture benzene : acetone (1:1). The compound showed a single spot at $R_f = 0.95$.

iv) Estimation of nitrogen

The nitrogen content of the product P.T. was estimated by Kjeldahl method[23] as usual.

Observed : N, 9.15. Required for $C_{23}H_{39}N_3O_4S$: N, 9.27%

v) Estimation of sulphur

The sulphur content of the product P.T. was estimated by Carius method[24].

Observed : S, 6.90. Required for $C_{23}H_{39}N_3O_4S$: S, 7.06%

vi) The IR spectrum of the product P.T.

The compound showed the following characteristic absorption bands.

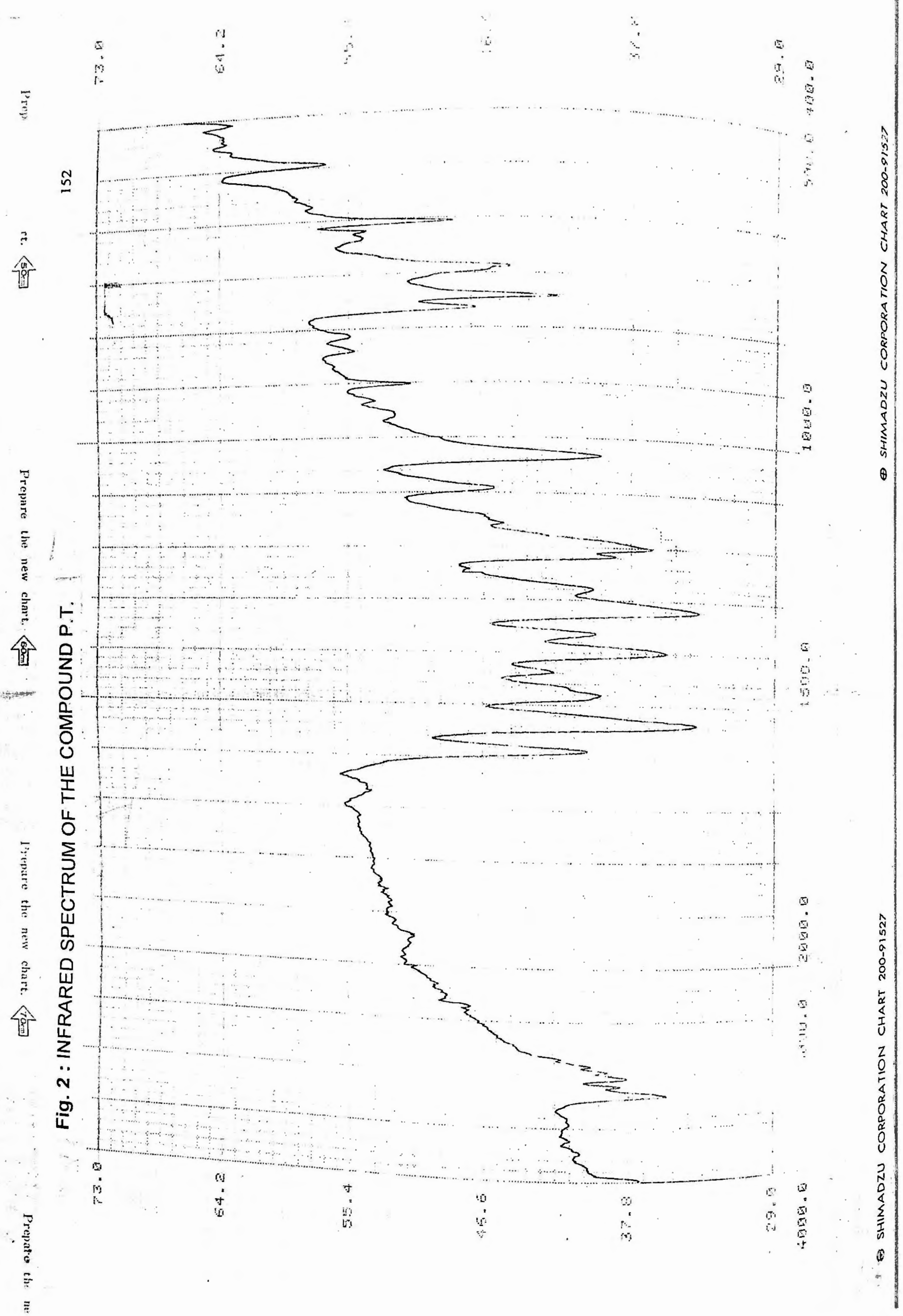


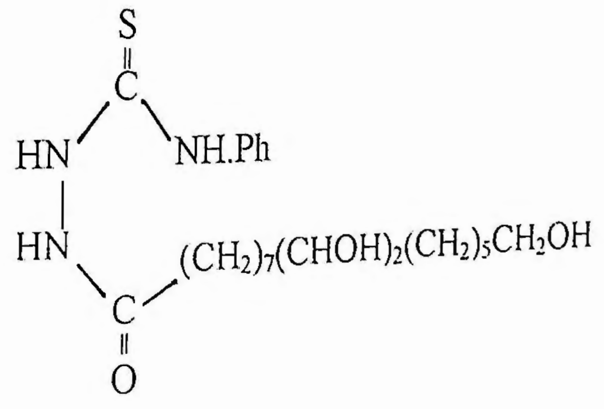
Fig. 2 : INFRARED SPECTRUM OF THE COMPOUND P.T.

Table - 4 : Important IR absorption bands of the compound P.T.

Absorption observed (cm^{-1})	Assignments	Absorption expected(cm^{-1})
3200 (s)	O-H Stretching	3400-3200[32]
3100 (m)	N-H Stretching	3400-3100[25a, 26a, 27a]
2960 (m)	CH_2 Stretching	2960-2850[33]
1590 (s)	C=O Stretching	1775-1578[31,32]
1540 (s)	Aromatic skeletal vibr.	1600-1500[33]
1400 (s)	N-N Stretching	1500-1400[33]
1320 (s)	C-N Stretching	1350-1280[26e, 28b]
1200 (s)	p-substitution to aromatic ring	1225-1175[29]
1095 (s)	C=S Stretching	1200-1050[33]
820 (w)	Two adjacent hydrogens of p-substituted aromatic ring	820-800[27d, 30]

The IR spectrum of the compound P.T. distinctly showed major absorption bands due to $\upsilon_{O\text{-}H}$, $\upsilon_{N\text{-}H}$, υ_{CH_2}, υ_{CO}, $\upsilon_{N\text{-}N}$, $\upsilon_{C\text{-}N}$, $\upsilon_{C=S}$ (Fig. 2, Page 152)

From the above chemical investigations and spectral evidences the structure of the final product, P.T was confirmed to be 1-Phenyl-3-N-aleuritamido thiocarbamide, $C_{23}H_{39}N_3O_4S$.



Structure of P.T.

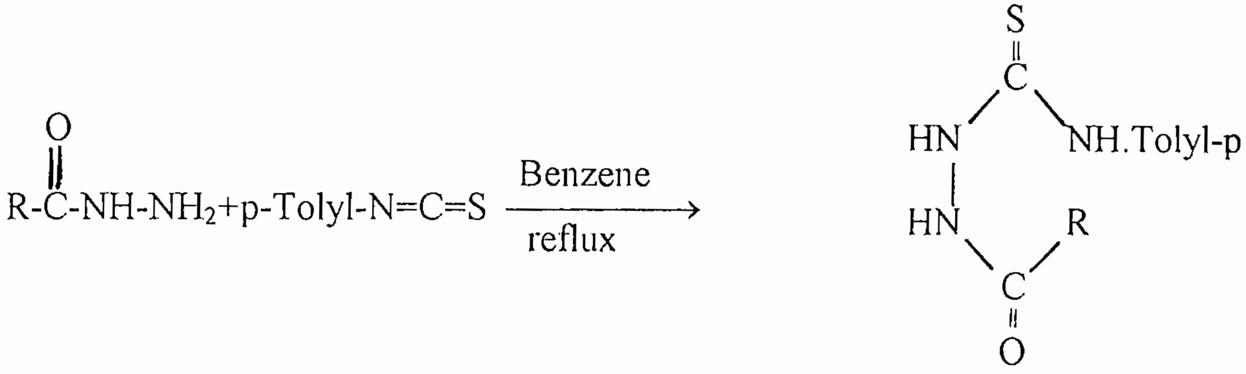
1.6 Reaction of aleurityl hydrazide with p-tolylisothiocyanate : Formation of the related thiocarbamide of aleurityl hydrazide

The required p-tolylisothiocyanate was prepared from p-toluidine following the similar procedure as described in section 1.5.a (p.p. 149).

The required aleurityl hydrazide was prepared following the usual procedure (p.p. 143).

1.6.a. Reaction of aleurityl hydrazide with p-tolylisothiocyanate

Reaction involved :



PROCEDURE

To a benzene solution of aleurityl hydrazide (0.01 mole; 3.18 gm in 50 cm^3) in a 500 cm^3 round bottom flask freshly prepared p-tolylisothiocyanate (0.01 mole; 1.49 gm) was added and the mixture was shaken gently. A few pieces of boiling chips were added to the reaction mixture and the contents of the flask was then refluxed for 2 hours. On distilling off the solvent from the reaction mixture, the desired thiocarbamide was obtained as a white solid mass, yield 2.48 gm (77%). It was recrystallised from ethanol and designated as p-T.T.

1.6. b. Preliminary investigation on the product p-T.T.

(i) Melting point of the product was noted to be 96-97°C.

(ii) Its aqueous solution was found to be readily desulphurated while heated with alkaline plumbite solution, indicating the presence of $-\overset{\overset{S}{\|}}{C}-$ NH- group in the p-T.T. compound.

(iii) **Solubility test** : Solubility behaviour of the pure product was studied in various solvents. The result is summarized in the following Table 5.

Table 5 : Solubility chart of the product p-T.T.

Sl No.	Solvents	Solubility
1.	Absolute ethanol	Soluble in cold and hot
2.	Acetone	Soluble in cold and hot
3.	Benzene	Soluble in hot
4.	Water	Insoluble in cold and hot
5.	Chloroform	Insoluble in cold and hot
6.	n-Hexane	Insoluble in cold and hot
7.	Pet. ether (40-60°)	Insoluble in cold and hot
8.	Carbon tetrachloride	Partially soluble in hot
9.	Di-ethyl ether	Insoluble in cold and hot
10.	Methanol	Soluble in cold and hot
11.	Dioxane	Sparingly soluble when heating
12.	DMSO	Soluble in cold and hot
13.	Xylene	Soluble in cold and hot

iv) **Thin-layer chromatography of the product :**

The product p-T.T. was applied on TLC plate and was run using a solvent mixture benzene:acetone (1:1). The compound showed a single spot at $R_f = 0.80$.

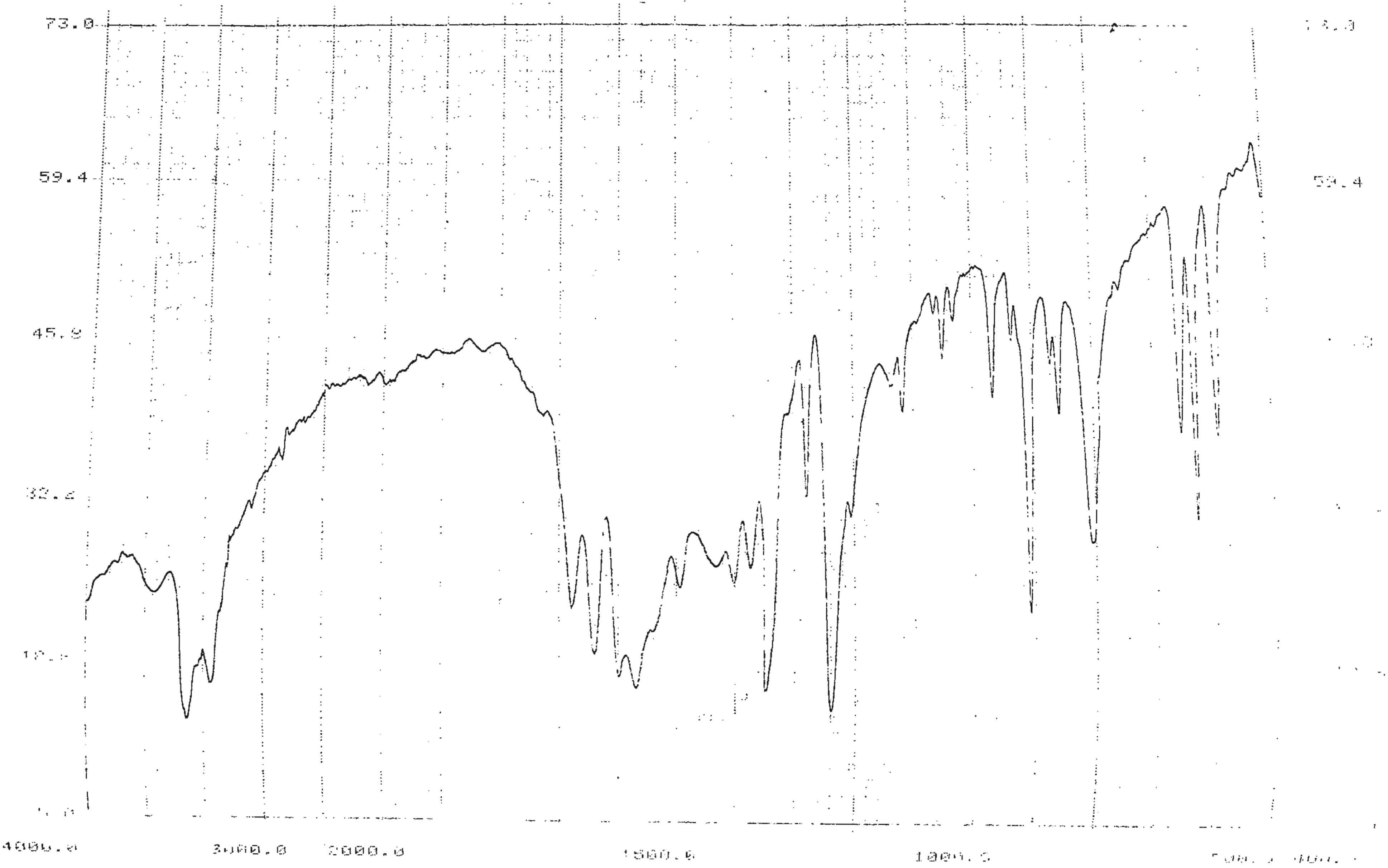


Fig. 3 : INFRARED SPECTRUM OF THE COMPOUND p-T.T.

iv) **Estimation of nitrogen**

The nitrogen content of the p-T.T. was estimated by Kjeldahl method[23]. Observed : N, 8.50. Required for $C_{24}H_{41}N_3O_4S$: N, 8.99%

v) **Estimation of sulphur**

The sulphur content of the product p-T.T. was estimated by Carius method[24]. Observed : S, 6.35%. Required for $C_{24}H_{41}N_3Q_4$ S : S, 6.85%.

vi) **The IR spectrum of the product p-T.T.**

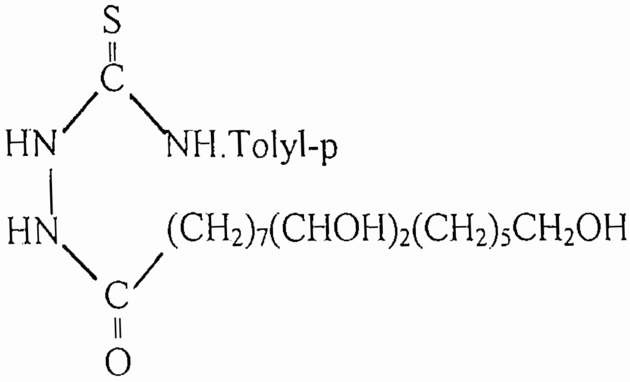
The Compound showed the following characteristic absorption bands.

Table - 6 : Important IR absorption bands of the compound p-T.T.

Absorption observed (cm^{-1})	Assignments	Absorption expected (cm^{-1})
3400 (s)	O-H Stretching	3400-3200[32]
3150 (s)	N-H Stretching	3400-3100[25a, 26a, 27a]
2950 (sh)	CH_2 Stretching	2960-2850[33]
1590 (sh)	C=O Stretching	1775-1578[31,32]
1550 (s)	Aromatic skeletal vibr.	1600-1500[33]
1470 (m)	N-N Stretching	1500-1400[33]
1250 (s)	C-N Stretching	1350-1280[26c,28b]
1180 (s)	p-substitution to aromatic ring	1225-1175[29]
1140 (s)	C=S Stretching	1200-1050[33]
820	Two adjacent hydrogens of p-substituted aromatic ring	820-800[27d,30]

The IR spectrum of the compound p-T.T. distinctly showed major absorption bands due to $\upsilon_{O\text{-}H}$, $\upsilon_{N\text{-}H}$, υ_{CH_2}, υ_{CO}, $\upsilon_{N\text{-}N}$, $\upsilon_{C\text{-}N}$, $\upsilon_{C=S}$ (Fig. 3, Page 156)

From the above chemical investigations and spectral evidences the structure of the product, p-T.T was confirmed to be 1-p-Tolyl-3-N-aleuritamido thiocarbamide, $C_{24}H_{41}N_3O_4S$.



Structure of p-T.T.

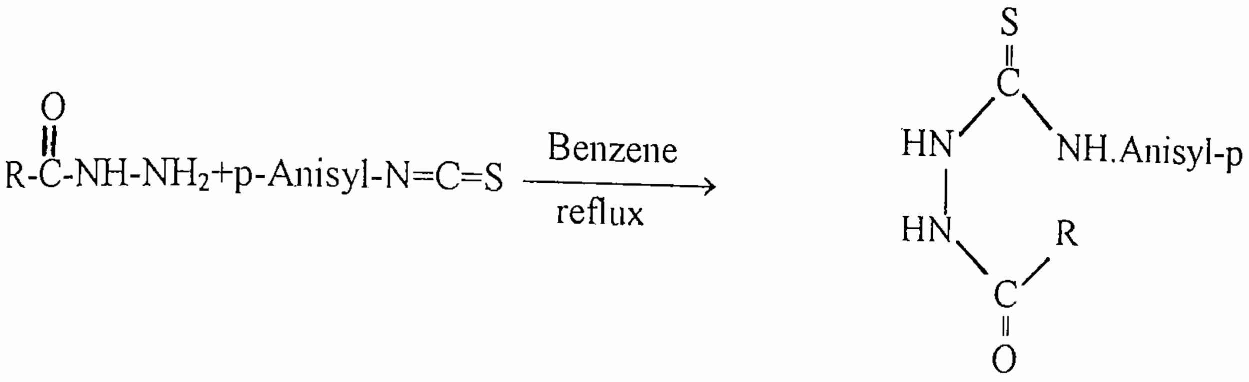
1.7. Reaction of aleurityl hydrazide with p-anisyliosothiocyanate: Formation of the related thiocarbamide of aleurityl hydrazide

The required p-anisylisothiocyanate was prepared from p-anisidine following the same procedure as described in section 1.5.a. (p.p. 149).

The required aleurityl hydrazide was prepared as usual.

1.7.a. Reaction of aleurityl hydrazide with p-anisylisothiocyanate

Reaction involved :



PROCEDURE

To a benzene solution of aleurityl hydrazide (0.01 mole; 3.18 gm in 50 cm^3) in a 500 cm^3 round bottom flask freshly prepared p-anisylisothiocyanate (0.01 mole; 1.65 gm) was added and the mixture was shaken gently. A few pieces of boiling chips were added to the reaction mixture and the contents of the flask was then refluxed for 2 hours. On distilling off the solvent from the reaction mixture, the desired thiocarbamide was obtained as a white solid, yield 5.15 gm (65%). It was recrystallised from ethanol. It was designated as p-A.T.

1.7. b. Preliminary investigation on the product p-A.T

(i) Melting point of the product was noted to be 115-116°C.

(ii) Its aqueous solution was found to be readily desulphurated when heated with alkaline plumbite solution, indicating the presence of $(-\overset{S}{\overset{\|}{C}}-NH-)$ group in the p-A.T. compound.

(iii) **Solubility test** : Solubility behaviour of the pure product was studied in various solvents. The result is summarized in the following Table 7.

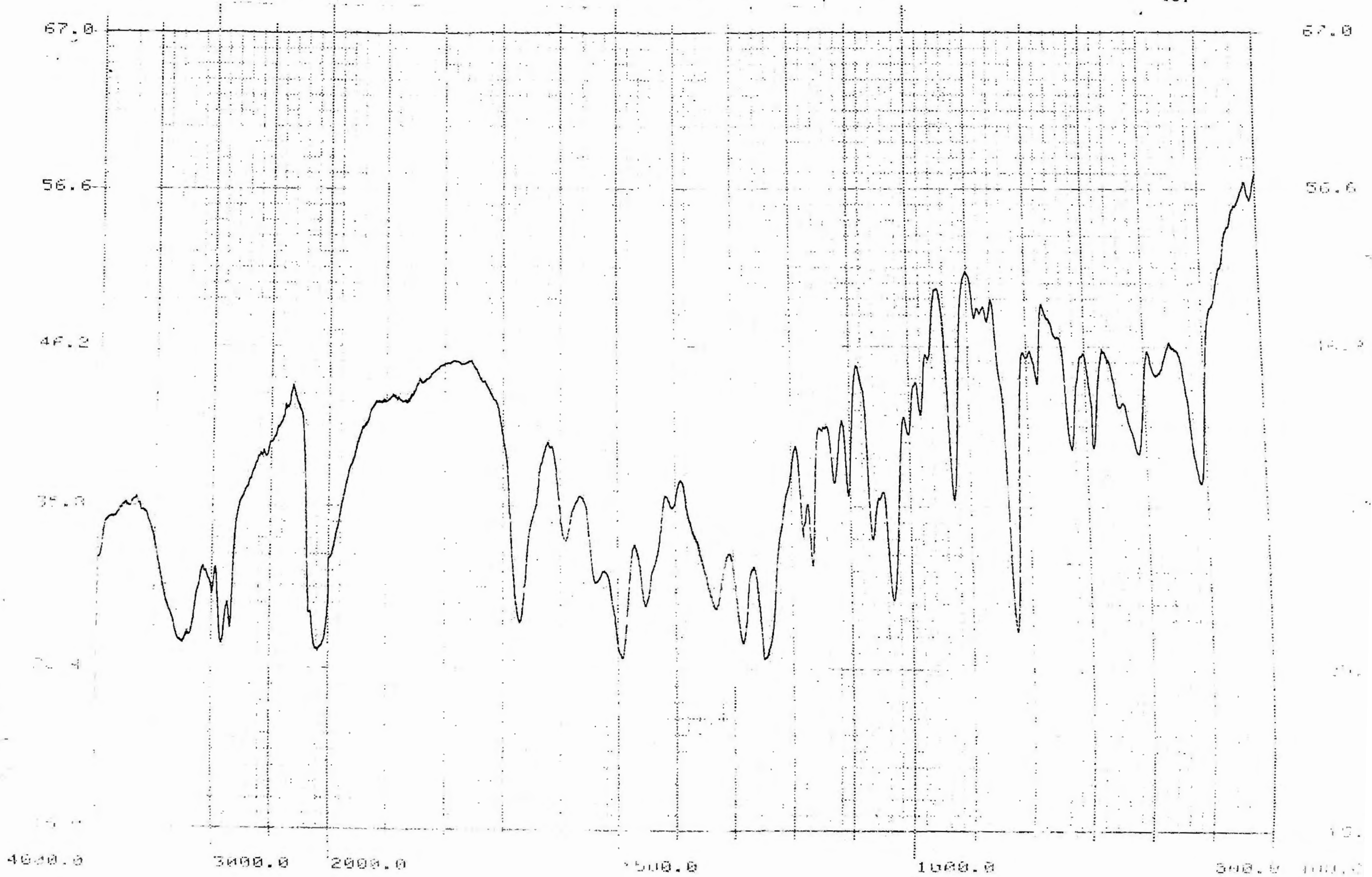
Table 7 : Solubility chart of the product p-A.T.

Sl No.	Solvents	Solubility
1.	Absolute ethanol	Soluble in cold and hot
2.	Acetone	Soluble in cold and hot
3.	Benzene	Soluble in hot
4.	Water	Insoluble in cold and hot
5.	Chloroform	Partially soluble
6.	n-Hexane	Partially soluble
7.	Pet. ether (40-60°)	Insoluble in cold and hot
8.	Carbon tetrachloride	Soluble in cold and hot
9.	Di-ethyl ether	Insoluble in cold and hot
10.	Methanol	Soluble in cold and hot
11.	Dioxane	Partially soluble in cold and hot
12.	DMSO	Soluble in cold and hot
13.	Xylene	Soluble in cold and hot

iv) **Thin-layer chromatography of the product**

The product p-A.T. was applied on TLC plate and was run using a solvent mixture benzene : acetone (1:1). The compound showed a single spot at $R_f = 0.90$

Fig. 4 : INFRARED SPECTRUM OF THE COMPOUND p-A.T.



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iv) Estimation of nitrogen

The nitrogen content of the compound p-A.T. was estimated by Kjeldahl method[23].

Observed : N, 8.55. Required for $C_{24}H_{41}N_3O_5S$: N, 8.70%

v) Estimation of sulphur

The sulphur content of the compound p-A.T. was estimated by Carius method[24].

Observed : S, 6.50%. Required for $C_{24}H_{41}N_3Q_5$ S : S, 6.63%.

vi) The IR spectrum of the product p-A.T.

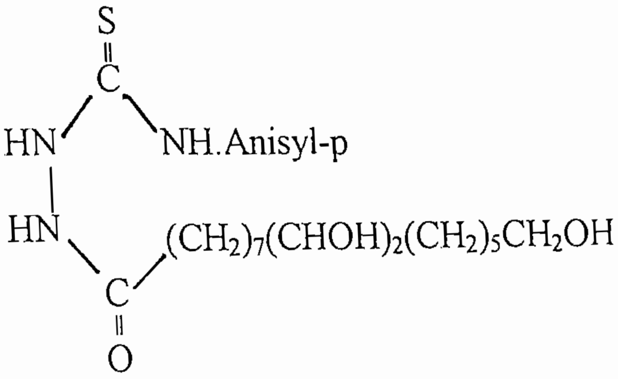
The Compound p-A.T. showed the following characteristic absorption bands.

Table - 8 : Important IR absorption bands of the compound p-A.T.

Absorption observed (cm^{-1})	Assignments	Absorption expected (cm^{-1})
3250 (s)	O-H Stretching and N-H Stretching	3400-3100[25a, 26a, 27a]
2900 (sh)	CH_2 Stretching	2960-2850[33]
1675 (s)	C=O Stretching	1775-1578[31, 32]
1500	Aromatic skeletal vibr.	1600-1500[33]
1440 (m)	N-N-Stretching	1500-1400[33]
1295 (m)	C-N Stretching	1350-1280[26c, 28b]
1180 (sh)	p-substitution to arom. ring	1225-1175[29]
1100 (sh)	C=S stretching	1200-1050[33]
815 (s)	Two adjacent hydrogens of p-substituted aromatic ring	820-800[27d, 30]

The IR Spectrum of the compound p-A.T. distinctly showed major absorption bands due to $\upsilon_{O\text{-}H}$, $\upsilon_{N\text{-}H}$, υ_{CH_2}, υ_{CO}, $\upsilon_{N\text{-}N}$, $\upsilon_{C\text{-}N}$, $\upsilon_{C=S}$ (Fig. 4, Page 161)

From the above chemical investigations and spectral evidences the structure of the final product, p-A.T. was confirmed to be 1-p-Anisyl-3-N-aleuritamido thiocarbamide, $C_{24}H_{41}N_3O_5S$.



Structure of p-A.T.

1.8. Reaction of aleurityl hydrazide with Tetra-acetyl glucosyl (T.A.G) isothiocyanate : Formation of the related thiocarbamide of aleurityl hydrazide

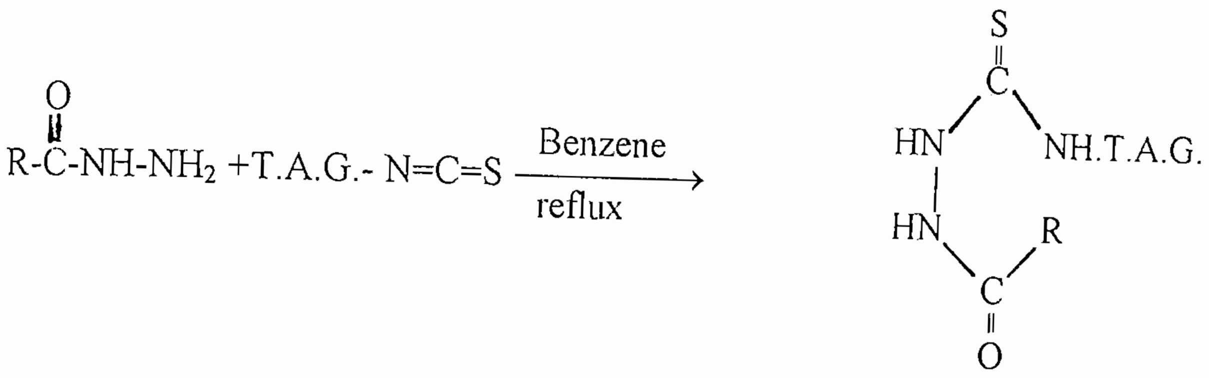
1.8. a. Preparation of Tetra-acetyl glucosyl (T.A.G) isothiocyanate

The required T.A.G. isothiocyanate was prepared starting from tetra acetyl glucosyl bromide following usual procedure.[35]

The required aleurityl hydrazide was prepared as usual.

1.8.b. Reaction of aleurityl hydrazide with T.A.G. isothiocyanate

Reaction involved :



PROCEDURE

To a benzene solution of aleurityl hydrazide (0.01 mole; 3.18 gm in 50 cm^3) in a 500 cm^3 round bottom flask freshly prepared T.A.G. isothiocyanate (0.01 mole; 3.89 gm) was added and the mixture was shaken gently. A few pieces of boiling chips were added to the reaction mixture and the contents of the flask was then refluxed for 2 hours. On distilling off the solvent from the reaction mixture, the desired thiocarbamide was obtained as a white solid mass, yield 2.25 gm (70.75%). It was recrystallised from ethanol. It was designated as T.A.G.T.

1.8.c. Preliminary investigation on the product T.A.G.T.

(i) Melting point of the product was noted to be 102-103°C.

(ii) Its aqueous solution was found to be readily desulphurated while heated with alkaline plumbite solution, indicating the presence of $(-\overset{S}{\overset{\|}{C}} - NH-)$ group in the T.A.G.T. compound.

(iii) **Solubility test** : Solubility behaviour of the pure product was studied in various solvents. The result is summarized in the following Table 9.

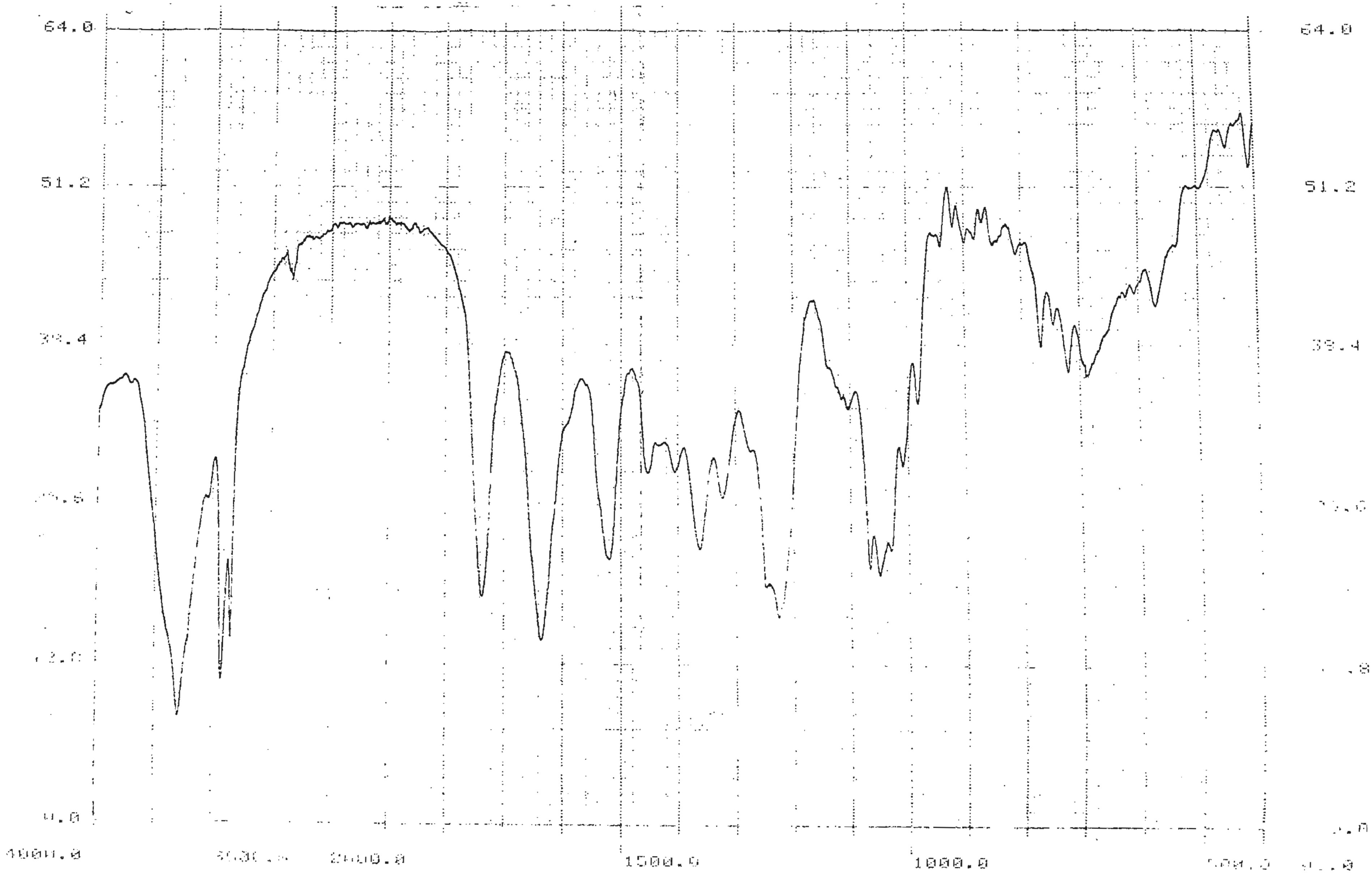
Table 9 : Solubility chart of the product T.A.G.T.

Sl No.	Solvents	Solubility
1.	Absolute ethanol	Soluble in cold and hot
2.	Acetone	Soluble in cold and hot
3.	Benzene	Soluble in hot
4.	Water	Insoluble in cold and hot
5.	Chloroform	Partially soluble
6.	n-Hexane	Partially soluble
7.	Pet. ether (40-60°)	Insoluble in cold and hot
8.	Carbon tetrachloride	Soluble in cold and hot
9.	Di-ethyl ether	Insoluble in cold and hot
10.	Methanol	Soluble in cold and hot
11.	Dioxane	Partially soluble
12.	DMSO	Soluble in cold and hot
13.	Xylene	Soluble in cold and hot

iv) **Thin-layer chromatography of the product**

The product T.A.G.T. was applied on TLC plate and was run using a solvent mixture benzene : acetone (1:1). The compound showed a single spot at $R_f = 0.90$.

Fig. 5 : INFRARED SPECTRUM OF THE COMPOUND T.A.G.T.



iv) Estimation of nitrogen

The nitrogen content of the T.A.G.T. compound was estimated by Kjeldahl method[23].

Observed : N, 5.75. Required for $C_{31}H_{53}N_3O_{13}S$: N, 5.94%

v) Estimation of sulphur

The sulphur content of the product T.A.G.T. was estimated by Carius method[24].

Observed : S, 4.30. Required for $C_{31}H_{53}N_3Q_{13}$ S : S, 4.53%.

vi) The IR spectrum of the product T.A.G.T.

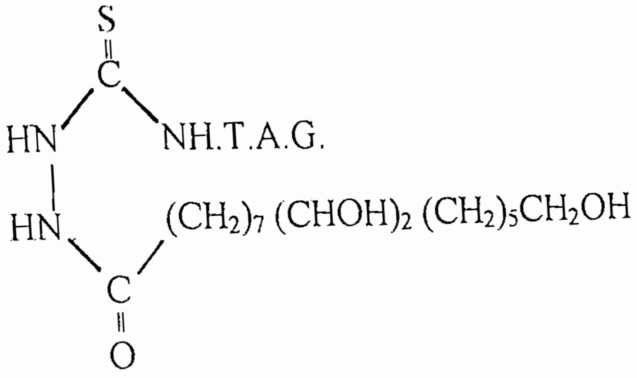
The Compound T.A.G.T. showed the following characteristic absorption bands.

Table - 10 : Important IR absorption bands of the compound T.A.G.T.

Absorption observed (cm^{-1})	Assignments	Absorption expected (cm^{-1})
3300 (s)	O-H Stretching and N-H Stretching	3400-3100[25a, 26a, 27a]
2990 (s)	CH_2 Stretching	2960-2850[33]
1740 (s)	C=O Stretching	1775-1578[31, 32]
1510 (sh)	N-N stretching	1500-1400[33]
1350 (m)	C-N-Stretching	1350-1280[26e, 28b]
1050 (m)	C=S Stretching	1200-1050[33]
775 (m)	T.A.G. ring	960-730[36, 37]

The IR spectrum of the compound T.A.G.T. distinctly showed major absorption bands due to υ_{O-H}, υ_{N-H}, υ_{CH_2}, υ_{CO}, υ_{N-N}, υ_{C-N}, υ_{C-S} (Fig. 5, Page 166)

From the above chemical investigations and spectral evidences the structure of the product, T.A.G.T. was confirmed to be 1-tetra-acetyl-glucosyl -3-N-aleuritamido thiocarbamide, $C_{31}H_{53}N_3O_{13}S$.



Structure of T.A.G.T.

1.9 ANTI-BACTERIAL ACTIVITY

1.9.a PRINCIPLE

The susceptibility of the micro-organism to antimicrobal agents may be measured *in vitro* by utilising agar diffusion technique. Dried filter paper discs containing the test materials are usually applied to the test plates containing the culture of micro organisms.

Experiments on several filter paper discs were carried out simultaneously. The dried discs absorb water from the agar medium and the test material is dissolved. Then the test material migrates through the adjacent agar medium according to the physical law that govern diffusion of the molecules through an agar gel. As a result there is gradual change of drug (test material) concentration in the agar surrounding each disc. Activities of the test sample are expressed by measuring the zone of inhibition around the area. The zone of inhibition is effected by various factors e.g. by the growth rate of the micro-organisms, also by the rate of diffusion drug through the agar gel. The diameter of the inhibition zone is usually measured to understand the extent of inhibition in different concentration.

1.9.b TEST IN VITRO : RANGE OF ANTIMICROBIAL ACTIVITY

Choice of organism

To detect the antimicrobial activity of the compounds newly prepared during the course of this study, these compounds were applied *in vitro* against 16 pathogenic bacteria Details of the techniques adopted are as follows :

1.9.c PREPARATION OF THE MEDIA : NUTRIENT BROTH AND NUTRIENT AGAR.

NUTRIENT BROTH

Compositions

Name of the ingredients	Amounts
Meat extract	3 gm
Peptone from meat	5 gm
NaCl	5 gm
Distilled water	1000 cm^3

Laboratory method

The above ingredients (13 gm) were taken in 1000 cm^3 distilled water, thoroughly mixed and the pH was adjusted to 7±0.2. The resulting solution was transferred in *equal portions* (100 cm^3) *into 10 different 250 cm*^{3} conical flask. The conical flasks were autoclaved at 120°C under a pressure of 15 lb/sq. inch for 20 minutes.

NUTRIENT AGAR

Compositions

Name of the ingredients	Amounts
Meat extract	2%
Peptone from meat	05%
NaCl	0.5%
Agar	2%
Distilled water	1000 cm^3

Laboratory method

The above ingredients (5 gm) were taken in 250 cm^3 conical flask and to the 100 cm^3 distilled water were added. The mixture was gently heated to make it a clear solution and adjusted its pH to 7±0.2. The media were then autoclaved in a similar fashion (120°C, 50 Ib/sq. inch). The flask was then removed from the autoclave and placed on a water bath at 50°C.

1.9.d PREPARATION OF THE CULTURE

A small bottle containing 10 cm^3 sterile nutrient broth was taken and the test 16 pathogenic bacteria from the pure culture were transferred to this bottle with the help of an inoculation loop in an aseptic condition. After inoculation the bottle was subjected to incubation at 37°C for 24 hours to provide sufficient time and temperature for the growth of the test organisms (The culture must be used within two or three days or it must be kept in a refrigerator).

1.9.e PREPARATION OF THE CULTURE PLATE

To 100 cm^3 of the nutrient agar, 1 cm^3 of the prepared culture was added and was mixed thoroughly with shaking. A 25 cm^3 portion of this culture was poured into a petridish and in order to facilitate a homogeneous distribution of the test organisms the petridish was related several times, first in clockwise direction and then in anticlock-wise direction. The media were poured into petridish on a level horizontal surface. So as to give a uniform depth of approximately 4 mm. The petridish was kept undisturbed for about 15 minutes during which it was solidified. After complete solidification of the media 4-5 holes were made inside it with the help of a borer. Just before using plates with lids agar were placed in an incubator (25°C) for about 10-15 minutes until the excess of surface moisture was lost by evaporation. There should be no droplets of moisture on the surface of the media or on the petridish plate cover. Then applied the compounds for observing their antibacterial activities.

1.9.f OBSERVATIONS

Antibacterial activities were qualitatively determined against 16 pathogenic bacteria and the results of these experiments are summarized in the following Table 11.

Table 11 : Antibacterial activities of the prepared compounds

Test organism	Zone of inhibition (mm) of action of the prepared compounds				
	A	B	C	D	E
1. *Bacillus substilis* (BTCC 17)	12	10	13	11	8
2. *B. Cereus* (BTCCC 19)	10	11	9	7	10
3. *B. megaterium* (BTCC 18)	13	8	10	9	9
4. *Sarcina lutea* (ATCC 9341)	14	10	9	7	13
5. *Streptococcus β-haemolyticus* (BTCC525)	9	7	6	8	6
6. *Staphylococuss aureus* (ATCC 25923)	10	12	8	7	6
7. *Shigella dysenteriae* (BTCC 526)	9	6	4	7	5
8. *Sh. shiga* (BTCC 27)	6	-	4	9	-
9. *Sh. flexneriae*	11	8	5	7	4
10. *Shigella boydii* (13147)	10	6	5	-	7
11. *Sh. sonnei* (BTCC 528)	9	5	6	5	-
12. *Escherichia coli* (ATCC 25922)	-	-	9	7	10
13. *Salmonella typhi* A (CRL)	8	10	7	-	8
14. *Salmonella typhi* B (CRL)	7	5	-	4	5
15. *Salmonella typhi* B-56 (CRL)	9	7	-	-	7
16. *Klebsiella species*	-	8	6	7	5

A = t-Bu.T., B = P.T., C = p-T.T., D = p-A.T., F = T.A.G.T. and " - " No inhibition

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APPENDIX

LIST OF PUBLICATIONS

1. Isolation and purification of aleuritic acid and its esters from Bangladeshi shellac (Lac). M. Zahurul Haque, M. Omar Faruq and M. Umar Ali, Journal of Bangladesh Chemical Society, 10 (1), 93-97, 1977.

2. Investigation on lac : Effect of curing agent on life of lac (Shellac) under heat, M. Zahurul Haque, M. Omar Faruq and M. Umar Ali, Journal of Bangladesh Chemical Society, 11 (1&2), 123-127, 1998.

3. Investigation on Bangladeshi lac dye. Part I - Isolation and purification of laccaic acid A_1 from stick lac. M. Zahurul Haque, M. Omar Faruq and M. Umar Ali, Journal of Bangladesh Chemical Society, 11 (1&2), 129-134, 1998.

4. Chemical modificaion of lac. Part I - Some ethylene-glycol modifications and its derived products. M. Zahurul Haque, M. Omar Faruq and M. Umar Ali, Journal of Bangladesh Chemical Society, Vol. 12, No. 1, 1999.

5. Investigation on lac : Solubility behaviour of thermally polymerized seed lac, shellac and dewaxed shellac. M. Zahurul Haque and others, Bangladesh J. Sci. Ind. Res. In press - 1998.

6. Investigation on lac : Physico-chemical studies of polymerized seed lac, shellac and dewaxed shellac. M. Zahurul Haque and others, Bangladesh J. Sci. Ind. Res. In press - 1998.

7. Chemical investigation on thermally polymerized aleuritic acid. M. Zahurul Haque, M. Umar Ali and M. Omar Faruq, Journal of Bangladesh Academy of Sciences, In press- 1999.

8. Chemical modificaion of lac. Part II - Application of some modified lac on jute fibre to improve its serviceability. M. Zahurul Haque, M. Umar Ali and M. Omar Faruq, Journal of Bangladesh Chemical Society, Communicated 1998.

Journal of the Bangladesh Chemical Society. 10 (1). 93-97. 1997

ISOLATION AND PURIFICATION OF ALEURITIC ACID AND ITS ESTERS FROM BANGLADESHI SHELLAC (LAC)

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Abstract

Shellac (lac) resin contains aleuritic acid combined with other ingredients. Is was isolated to an extent of 30% and purified. Some derivatives of the isolated aleuritic acid were prepared. Thin layer chromatography of the acid and its derivatives revealed some notable information. Aleuritic acid may be used in making super quality adhesive to join glass to glass binding.

Introduction

Lac is an important natural resinous product secreted by an insect, *Laccifer lacca*, which lives on the sap of some host trees. India is the major lac producing country in the world. Thailand and some other countries also produce lac. In Bangladesh, it is cultivated by the local people of Nawabganj district. Feasibility report[1] has revealed that its cultivation can be extended throughout the northern part of Bangladesh.

Shellac (Lac) is known to comprise of several hydroxy acid units. But in spite of several decades' work on the chemistry of lac, only about 65 percent of its constituent acids have been isolated in pure form. The isolation of the various acids has been carried out by a number of investigators using different methods with the consequence that divergent results both as regards the presence of some acids and the yields thereof have been reported[2].

Aleuritic acid and its esters have great importance in industrial domain. Aleuritic acid has been found to be a valuable starting material for the preparation of transparent water-clear adhesive, plasticizers and resins in combination with other chemicals[3]. The esters of aleuritic acid may be incorporated in plastic composition containing cellulose derivatives and these compositions may be moulded, rolled or extended into any desired shape such as sheets, rods, tubes and the like. Filaments, yarns and other textile materials may be made from solutions containing organic derivatives of cellulose and an ester of aleuritic acid by extrusions through

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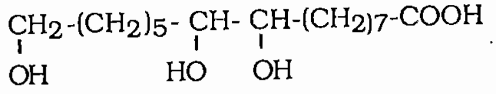
* Author to whom correspondence should be made

orifices into an evaporative atmosphere as in dry spinning or into a precipitating bath as in wet spinning[4].

In order to obtain further insight into the chemistry of lac, chemical investigation has been employed for the isolation and purification of the hydroxy acid (aleuritic acid) and its esters obtained from hydrolysed shellac (Bangladeshi). The result of this study are presented in this paper.

According to Nagel the structural formula of aleuritic acid is :



$$\underset{OH}{CH_2}\text{-}(CH_2)_5\text{-}\underset{HO}{CH}\text{-}\underset{OH}{CH}\text{-}(CH_2)_7\text{-}COOH$$

Experimental

Melting points were determined on an electrothermal melting point apparatus, Gallenkamp, Cat. No. AZ6512 and are uncorrected. For thin layer chromatography, Kieselgel GF_{254} was used and spots were developed in an iodine chamber or viewed under UV light.

Collection of lac

A research project on cultivation of lac is going on in the experimental garden of BCSIR Laboratories, Rajshahi. Lac was collected from this experimental garden for the present investigation.

Preparation of dewaxed shellac

500g of semi-powdered seed lac was taken in a 6 litre flat bottom flask and to it added 2 litre rectified spirit and kept over night at room temperature with occasional shaking. The lac solution thus obtained was filtered through nylon cloth. The filtrate was distilled on a water bath to recover the solvent as far as possible (85% recovery). The residue was transferred to a porcelain basin and was heated on a hot plate at 110°C so as to remove the residual solvent. The molten mass was cooled to 50°C and made into flakes. The yield obtained was 90% calculated on the weight of seed lac used.

Isolation of aleuritic acid[5]

100g of finely powdered dewaxed shellac was dissolved in 100 ml of 20% sodium hydroxide solution by warming on a steam bath. After 14 days the mixture was diluted with 150 ml of 20% sodium hydroxide solution and filtered through celite and the residue was washed with 20% sodium chloride solution (50 ml). The filtrate together with washing was concentrated to 75 ml on the water bath and kept over night at room temperature until no further precipition occurred. The sodium salt on the filter was dissolved in hot water (100ml) and filtered. On acidification with 2N sulphuric acid, it yielded aleuritic acid along with other acids as a pasty mass. The pasty masss was repeatedly shaken up with ether. Aleuritic acid was left undissolved while other acids went into the solution. It was then recrystallized from hot water and dried at 40°C, yield 30g (30%). Its melting point was found to be 100-01°C and the mixed m.p. with authentic sample was 100-100. 5°C. It is soluble in hot water and in alcohol, acetone and ammonia in cold. It is insoluble in ether, petroleum ether and carbon disulphide.

Preparation of ester of aleuritic acid

The following alkyl esters of aleuritic acid were prepared and purified. For this purpose standard methods were followed[6].

Methyl aleuritate

A solution of 10g of the isolated aleuritic acid in 80 ml of 5% hydrogen chloride in absolute methanol, was allowed to stand for 3 days, then was neutralized with a solution of sodium hydroxide in absolute methanol, the precipitated sodium chloride filtered off and the filtrate poured into a large excess of cold (10°) water. The solid was filtered, washed with 10% aqueous sodium carbonate. It was recrystallized from ethanol. It was soluble in alcohol, acetone and insoluble in water, benzene and chloroform.

Ethyl aleuritate, butyl aleuritate and amyl aleuritate were prepared following exactly the same procedure by dissolving the prepared aleuritic acid in the desired alcohol (e. g. ethyl alcohol for ethyl aleuritate, butyl alcohol for butyl aleuritate and amyl alcohol for amyl aleuritate). Melting points of the esters were determined to be : methyl aleuritate, 72-73°C: ethyl aleuritate, 56-57°C; butyl aleuritate, 59-60°C: amyl aleuritate, 61-62°C.

The isolated aleuritic acid and its esters were applied on TLC plates and were run using different solvent systems amongst which ethanol : ammonia (20:1) solvent mixture was found to be more suitable. The products showed a single spot and the R_f values were 0.81, 0.68, 0.75, 0.72 and 0.73 for aleuritic acid, methyl aleuritate, ethyl aleuritate, butyl aleuritate and amyl aleuritate respectively. The authentic sample of aleuritic acid was also run on TLC plate in the same solvent system and showed single spot at R_f value 0.81 which was identical to that of the isolated acid.

Results and Discussion

The composition and specification of lac vary with the nature of lac producing insects, nature of the host plants and climatic features. A survey of the available literature on the chemical nature of the shellac have shown that a different interpretation of the published data is possible. Various workers have reported the isolation of aleuritic acid which is shown in Table 1.

Table 1 Aleuritic acid contents of shellace resin.

Investigator[7]	Year of Publication	Source of Shellac	% of aleuritic acid in shellac
Tschirch and Farner	1899	Indian lac	10.5
Harries and Nagel	1923	"	21.0
Gidvani	1944	"	43.0
Wright	1949	"	26.6
Sen Gupta	1956	"	23.0

The yield of aleuritic acid which has been isolated from Bangladeshi shellac during the present study (30%) is satisfactory and conforms with the chemical literature.

Aleutritic acid was first isolated by Tschirch and Farner from the hard resin portion of lac[7]. Harries and Nagel also isolated this acid from lac and observed that the acids from lac resin could be separated into ether soluble ones consisting of shellolic and other acids and ether insoluble consisting of aleuritic acid. In no case did he succeed in isolating aleuritic or any other acid direct from pure resin before hydrolysis. He therefore concluded, like Tschirch and Farner, that aleuritic acid was present in shellac not in the free state but only in a combined form.

Recently the use of aleuritic acid as such or its esters in various industries is gradually increasing for the production of quality transparent water clear adhesive to join glass to glass binding and lacquer for coating metal. These products have great demand in our country but none are produced locally. The isolated acid and its esters are expected to facilitate better utilisation for the production of these articles of commercial interest.

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Short Communication

INVESTIGATION ON LAC: EFFECT OF CURING AGENTS ON LIFE OF LAC (SHELLAC) UNDER HEAT

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Abstract

Lac (shellac) has been found to undergo polymerization by heat treatment. Various chemicals such as oxalic acid, tartaric acid, citric acid and urea have been found to play an important role in accelerating the thermal curing of shellac. The effect of the chemicals (1–5%) on life of shellac under heat at 120°, 150°, 180° and 200°C of tempera-tures have been ascertained. The degree of efficiency of the accelerators at different temperatures have also been determined.

Introduction

Lac (shellac) is a resinous substance secreted by an insect, *Laccifer Lacca.* Shellac when heated softens and melts. As the temperature is raised, it gradually becomes thicker and finally turns into a rubbery product which, on cooling, solidifies to a hard, tough, horny mass. The original properties are changed and the final product is insoluble in alcohol and infusible, stone hard and brittle. This phenomenon is called hardening and the polymerized product is known as cured shellac. The time required to reach to rubbery stage has been called "Life under heat" by Ranganathan and Aldis[1]. Gardner and Gross[2] designated the three stages, by analogy with thermo-setting resins, as A, B and C respectively. Ordinary shellac, which is soluble and fusible was considered to be in the A-stage. The rubbery stage, which is still completely soluble, is the B-stage and the cured product is in the C-stage. The rate of thermal polymerization of shellac can be accelerated or retarded by means of various chemicals. It is well known that the curing time of shellac is high, being of the order of 20 to 60 minutes at 150°C depending upon its grade and age[3]. Accelerators may obviously play a very significant role in reducing this time compared to that of the common thermosetting resins. Apart from these considerations, the life test is of considerable practical utility in industry. In the plastic moulding industry where hard, rigid articles have to be produced with a short time-cycle by converting lac into a

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*Author to whom correspondence to be made semi-thermohardening resin, a shorter life would be considered to be an advantage. On the other hand, the gramophone record industry, which consumes the major portion of lac, re-uses the rejects and scraps and would, therefore, be interested in having a lac, which possesses a long life[4]. The life test, therefore, is of great importance in choosing the right type of lac for any particular requirement. In general, acids, ester forming catalyst, ammonia and ammonia liberating substances behave as an accelerator[1]. So, we have selected oxalic acid, citric acid, tartaric acid and urea as accelerators or curing agents in the present investigation. Our results on the effect of curing agents on life of lac (shellac) is presented in this paper.

Experimental

Shellac was finely powdered, dried and stored in a stoppered bottle for further work.

Determination of life of shellac under heat at 120°C

5.0g shellac sample was taken in a 100 cm^3 conical flask, which was immersed in an oil bath and supported by means of a clamp in such a way, that the whole shellac sample was below the level of oil in the bath. It was then heated on a heating mantle at 120°C with stirring by a glass rod from time to time. As the shellac got more viscous, it was lifted with the rod but fell slowly back. Finally, the end point was reached when the rod twisted back slightly owing to the resistance offered by the rubbery lac to any twisting motion and the time in minutes that elapsed was recorded as the life under heat of the sample at 120°C.

Similarly, the life of shellac under heat at 150°, 180° and 200°C were determined. The results are shown in Table 1.

Determination of the effect of curing agents on life of shellac under heat

For determining the effect of oxalic acid on life of shellac under heat, it was mixed with 1, 2, 3, 4 and 5% of its weight of oxalic acid separately. Then, the life under heat at different temperatures of each sample was determined by adopting the same procedure as described above. The results are recorded in Table 1.

Similarly, the life of shellac under heat with tartaric acid, citric acid and urea were also determined and the results are recorded also in Table 1.

The degree of efficiency of the used accelerators at different temperatures were also determined and shown in Table 2. The calculating formula applied is:

$$\text{Degree of efficiency} = \frac{\text{Life (in minute) of shellac without chemicals}}{\text{Life (in minute) of shellac with chemicals}}$$

(at a fixed temperature)

Results and Discussion

The chemistry of polymerized shellac under heat treatment has not been much studied. Recently the use of shellac as such or modified shellac in various industries is gradually increasing for the production of many useful articles of commercial interest.

Table 1. Life of shellac (in minutes) under heat and in combination with other chemicals

Accelerator/curator	% of lac	Life (in minutes) at temperatures			
		120°C	150°C	180°C	200°C
-	-	110	42	17	7
Oxalic acid	1	25	11	5	3
	2	18	8	4	3
	3	15	7	4	3
	4	11	6	3	3
	5	8	5	2	-
Citric acid	1	70	21	8	3
	2	55	16	7	2
	3	48	14	6	2
	4	35	12	5	2
	5	30	11	5	2
Tartaric acid	1	100	38	12	6
	2	90	28	10	5
	3	75	25	9	4
	4	65	22	8	3
	5	55	18	6	3
Urea	1	90	38	18	9
	2	15	22	10	3
	3	9	13	8	2
	4	7	10	6	2
	5	6	8	6	2

From Table 1, we see that the life of (lac) shellac naturally depends on the temperature, the lower the temperature of heating, the longer the life. At a fixed temperature, the age, the quality and the method of manufacture, all have a considerable influence on the effective life of lac. Among freshly manufactured shellacs, a longer life is indicated by the better species of lac. The figure of life is therefore, a valuable indication of quality.

From Table 1, it is evident that the life under heat were changed due to the influence of various chemicals used and it could be concluded that different chemicals act differently in accelerating the thermal curing of lac. Citric and tartaric acids increase the rate of reaction only catalytically, whereas oxalic acid modify the curing process itself. The effect of urea is different from either of these. In this case, the life under heat is more or less unaffected by temperature when 3% or more is used, although at less than 3%, the characteristics approach more nearly those of tartaric acid. Bhattacharya[5] and Sankaranarayanan and Sen[6] were of the view that urea forms salts with shellac from which urea can be easily removed by simply boiling with water.

Table 2. Degree of efficiency of different accelerators at 120°, 150°, 180° and 200°C

Accelerator	% of lac	120°C	150°C	180°C	200°C
Oxalic acid	1	4.40	3.81	3.40	2.33
	2	6.11	5.25	4.25	2.33
	3	7.33	6.00	4.25	2.33
	4	10.00	7.00	5.66	-
	5	13.75	8.40	8.50	-
Citric acid	1	1.57	2.00	2.12	2.33
	2	2.00	2.62	2.42	2.33
	3	2.29	3.00	2.83	3.50
	4	3.14	3.50	3.40	-
	5	3.66	3.81	3.40	-
Tartaric acid	1	1.10	1.10	1.41	1.16
	2	1.22	1.50	1.70	1.40
	3	1.46	1.68	1.88	1.75
	4	1.69	1.90	2.12	2.33
	5	2.00	2.33	2.83	2.33
Urea	1	1.20	1.10	0.94	0.77
	2	7.33	1.90	1.70	2.33
	3	12.22	3.23	2.12	3.50
	4	15.71	4.20	2.83	3.50
	5	18.33	5.25	2.83	3.50

From Table 2, it is observed that the degree of efficiency of an accelerator increases with the increase of the amount of the accelerating or curing agent.

Thus it is seen that when shellac is treated with different chemical reagents, it accelerates the polymerization reaction of shellac. The polymerization reaction is attended with a gradual elimination of water vapour along with the gradual rise in insolubility of the product in alcohol. Other properties of the polymer sample do not show any marked changes[7,8].

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Short Communication

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INVESTIGATION ON BANGLADESHI LAC DYE. PART 1: ISOLATION AND PURIFICATION OF LACCAIC ACID A_1 FROM STICK LAC

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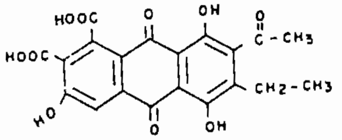
Abstract

Lac dye (10%) was isolated from stick lac of Bangladesh origin. Chromatographic studies shows that it contains three closely related components; however chromato- graphic separation led to the isolation of the major component, laccaic acid A_1 in the pure state. The physico-chemical properties and spectral analysis of the component were also determined.

Introduction

The insect *Laccifer lacca* Kerr found on the twigs of certain trees native to India and South-East Asia, produces a resin known as stick lac. When stick lac is washed with water, a pinkish solution results. This is due to water-soluble dye dissolving out in the water. The isolation of the dye has been reported by various investigators[1-3]. Schmidt[4] obtained the pure dye to the extent of 10.4-13.2% from commercial dye cakes by treatment with mineral acids. He designated the product as "Laccaic acid". Tschirch and Farner[5] also isolated this dye and identified it by spectral analysis with Schmidt's laccaic acid; Dimroth and Goldschmidt's[6] methods were slightly different. They isolated laccaic acid by extracting powdered stick lac with water. Chemical studies summarized by Thomson[7] led Dimroth and Goldschmidt to a partial formulation of laccaic acid as a polysubstituted anthraquinone. This was elaborated by Mayer[8] to the expression, **I**.



$C_{20}H_{14}O_{10}$

I

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Helen Mitrea[9] has shown that lac dye is not a single entity but consists of at least two components. It is of interest to note that depending on the region, host tree, type of insect and harvesting season the relative proportions of the various ingredients vary widely. So, the purpose of this paper is to report work carried out on laccaic acid, isolated in pure form from Bangladesh stick lac.

Experimental

Isolation of laccaic acid

Laccaic acid was isolated following the Kamath and Potnis[6] method as described below.

Stick lac (1kg) was coarsely ground by hand and freed from twigs and then powdered in a grinding mill. The powdered material was stirred with distilled water (5 litre). The suspension was allowed to settle for 1 hour. Decantation from the sludge, filtration through coarse cloth gave a clear wine red solution. This aqueous solution was then treated with a solution of calcium chloride as result of which the colouring matter precipitated out as calcium salt. The calcium salt was filtered, repeatedly washed with water until free from water solubles and then treated with 3N hydrochloric acid (100 cm^3). On standing, the dye separated out in the form of needle shaped red crystals. These were separated by filtration, washed with small quantity of water and dried at 50°C. It was recrystallised by dissolving the dye in ethanol and pouring the alcoholic solution into aqueous hydrochloric acid. The yield of dye (laccaic acid) was 10% calculated on the weight of stick lac taken. It was acidic in nature. The dye decomposed at 220°C and gradually got charred at higher temperature. It was soluble in methyl alcohol, amyl alcohol, acetic acid and formic acid and sparingly soluble in ether, chloroform and benzene. It dissolved in alkalis when a deep violet colour developed.

On TLC plates developed in n-butanol: acetic acid; water (4:1:5) a major spot at R_f 0.75 for laccaic acid A_1 and a minor spot at R_f 0.85 for laccaic acid (B+C) were observed.

Column chromatographic separation of the component of the dye

Column chromatography of 1.0g of the isolated laccaic acid dissolved in 15 cm^3 of ethanol was carried out over silica gel 60 (70-230 mesh ASTM, 50g) in ethanol. The flow rate of the elution was controlled at a rate of 2.0 cm^3/minute. Three different bands with three components were observed. One of the components was readily eluted by ethanol, while the second and third components were eluted by ethanol containing hydrochloric acid (90:10). Each fraction was evaporated at reduced pressure at room temperature and the residues were dried to constant weight. The results of a typical run are given in Table 1.

The purity of separated fraction was checked by TLC using n-butanol : acetic acid : water (4:1:5) solvent system and showed single spots at R_f values 0.85, 0.80 and 0.75 for fraction 1, 2 and 3 respectively. The third fraction was the major component (Laccaic acid A_1) and recrystallised from 85% formic acid.

Table 1. Chromatographic separation of crude lac dye

Fraction	Vol. of eluent (cm^3)	Fraction of dye (%)	Component	Eluent
1	100	15.0	Laccaic acid C	Ethanol
2	20	5.0	Laccaic acid B	Ethanol : HCl
3	150	80.0	Laccaic acid A_1	Ethanol : HCl

The infrared spectrum of the three components showed the following absorption bands.

For first fraction (orange band), (KBr disc); ν_{max} 3080, 2990, 1690, 1530, 1080 and 790 cm^{-1};
for second fraction (violet band), (direct); ν_{max} 3080, 2990, 1650, 1460, 1280 and 1020 cm^{-1};
for third fraction (red band), (direct); ν_{max} 3080, 2990, 1640, 1450, 1360 and 710 cm^{-1};

Aetylation of laccaic acid A_1[10]

Laccaic acid A_1 (0.5g) was shaken with acetic anhydride (25 cm^3) and conc. sulphuric acid (10 drops). The red suspension quickly gave an orange solution which on standing (18 hours) became yellow. The liquid was poured on ice water (150 cm^3) and the yellow solution was extracted continuously with ethyl acetate. The solvent was removed and the residue was freed from traces of solvent by storage in a desiccator over NaOH. The yellow froth was crystallised from acetic acid (3 cm^3), giving the tetraacetate as yellow prisms, yield 90%, m. p. 175°C; $R_f = 0.65$ in n-butanol : acetic acid : water (4:1:5) solvent system.

Benzoylation of laccaic acid A_1[10]

Laccaic acid (0.5g) was dissolved in 0.5N sodium hydroxide solution (25 cm^3). Benzoyl chloride (50 cm^3) was added to it with vigorous shaking for 30 minutes. Benzoyl derivative of laccaic acid A_1 precipitated out was filtered and washed with distilled water, yield 65%, m. p. 125°C; $R_f = 0.60$ in ether : benzene (1:3) solvent system.

Mordanting of silk with potassium dichromate

Mordanting bath was prepared with 0.5% potassium dichromate in a 250 cm^3 beaker. 1g of stock sample of silk was dipped into the mordanting bath in cold and heated to boiling for 30 minutes with occasional stirring. The bath was allowed to cool. The mordanted silk was taken out, squeezed and dried at room temperature (28 ± 2°C). In the similar way, silk sample was mordanted with copper sulphate, ferrous sulphate, chrominum sulphate and stannous chloride.

Dyeing of mordanted potassium dichromate-silk, copper sulphate-silk, ferrous sulphate-silk, chromium sulphate-silk and stannous-chloride silk

A dye-bath (250 cm^3 beaker) was prepared by dissolving 5g. of lac dye in 1cm^3 formic acid and diluted by adding distilled water to make its volume 100 cm^3. Then the solution was heated for 30 minutes with occasional stirring. The bath was allowed to cool. Then it was filtered. Now the mordanted silk sample (1g) was dipped into the filtrate and again heated to boiling for 30 minutes. 1g of sodium chloride was added and heating continued for further 10 minutes. The dyeing bath was allowed to stand overnight. It was then washed well with water and soaped and allowed to dry. In the similar way, dyeing of mordanted copper sulphate-silk, ferrous sulphate-silk, chromium sulphate-silk and stannous chloride-silk were completed. The dying of unmordanted silk was carried out following the same procedure.

The dyeing of wool, jute and cotton both mordanted and unmordanted were carried out as described above. The shades produced on samples of silk, wool, jute and cotton fibre using different mordants are shown in Table 3.

Light fastness test

A sample of size 2"x 1" from all the dyed samples were cut off. Half of these samples were shaded with the help of hard board of size 1"x 1" and the rest half of the dyed samples were exposed to sunlight for 100 hours. Any change of shades was measured with the help of Grey scale. The results are shown in Table 3.

Wash fastness test

All the dyed samples of silk, wool, jute and cotton fibres were separately washed with soap for several times, squeezed and allowed to dry in defused sunlight. The dried samples were compared with the controlled samples by means of Grey scale. The results are shown in Table 3.

Results and Discussion

The methods employed by earlier investigators for the isolation of lac dye were very elaborate and time consuming. The aqueous extract starts degenerating even if it is left over night. So, it is essential to have a rapid method for the isolation of the dye. In the present investigation, we have isolated laccaic acid through its calcium salt prepared from a water extract of stick lacs. Excess of calcium chloride was avoided in order to prevent the precipitation of proteinous or other materials. For obtaining pure dye from the washings of stick lac, optimum conditions were studied.

The dye appears to consist of at least three components on the basis of their absorption on activated silica gel column. The first fraction was orange band, yield 15% of the mixture. The second fraction was violet band, yield 5% of the mixture and the third fraction was the main red band, afforded laccaic acid A_1, yield 80% of the mixture.

The infrared spectra of laccaic acid A_1 shows band in the carbonyl stretching region at 1640 cm^{-1}. This is consistent with a 1,4 quinone in which both carbonyl groups are chelated by a total of two or three peri-hydroxyl groups.

On the basis of the foregoing physico-chemical investigations, spectral analyses etc., the isolated product conformed with the properties of laccaic acid A_1[8,10].

Different investigators have recorded different crystalline structures and colour characteristics for laccaic acid as shown in Table 2.

Table 2. Different investigators with crystalline structures of laccaic acid

Investigators	Crystalline structure
John[2]	Different granular crystals of acid taste.
Schmidt[4]	Brownish red crystallisable powder.
Tschirch and Farner[5]	Red-brown coloured matter.
Mitrea[9]	Amorphous or crystalline; brown red to bright-red or carmine red.
Spoerri et al.[10]	Dark red rectangular crystals.

The isolated laccaic acid was red crystalline solid. The variation in the observations might be due to the mode of crystallisation. The dye thus obtained was attempted for utilization as a dye for dyeing silk, wool, cotton and jute fibre and found fast colour with different shades[11] (Table 3).

Table 3. **Shades produced on silk, wool, jute and cotton fibre and fastness test data of laccaic acid**

Mordant used	Silk			Wool			Jute			Cotton		
	Shade	L.F	W.F	Shade	L.F	W.F	Shade	L.F	W.F	Shade	L.F	W. f
$K_2Cr_2O_7$	Maroon	4	4	Maroon	4	3	Light Maroon	4	4	Reddish yellow	2	3
$SnCl_2$	Reddish Pink	4	4	Reddish Pink	3	3	Light Brown	3	4	Ash	2	2
$CrSO_4$	Light Violet	4	4	Light Violet	4	3	Steel gray	3	4	Light berry	3	3
$FeSO_4$	Steel grey	4	4	Ash	4	3	Violet black	3	3	Light pink	4	4
$CuSO_4$	Reddish Pink	4	4	Reddish Tinge	4	3	Reddish orange	4	4	Light brown	3	3
None	Deep Violet	4	4	Light Chocolate	3	3	Violet	3	4	Violet	3	3

L. F = Light fastness test grade; W. F = Wash fastness test grade

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CHEMICAL MODIFICATIONS OF LAC. PART 1: SOME ETHYLENE GLYCOL MODIFICATIONS OF LAC AND ITS DERIVED PRODUCTS

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Abstract

Investigations were made to improve or modify the properties of lac (shellac) and lac acids by combination with polyhydric alcohols like ethylene glycol in presence of catalyst. The prepared lac-glycol resin on further esterification with linseed oil fatty acids gave an oil soluble lac-glycol fatty acid complex. An improved varnish was also prepared from this complex. The physico-chemical characteristics of the product were ascertained.

Introduction

Several attempts have been made to produce lac (shellac)-drying oil combinations with a view to combine the excellent film-forming characteristics of the former with the elasticity and weather resistance of the oil. But unlike other natural resins, shellac does not readily react with drying oils because of incompatibility and polymerization at the required high reaction temperatures.

Bhattacharya and Gidvani[1] made an extensive study of the formation of lac-linseed oil combinations by incorporating shellac in linseed oil fatty acids in the presence of glycerol and claimed to have obtained a product of very low acid value and satisfactory properties.

Compatibility of with linseed oil in presence of oxides of lead has been recognized from early times. Other incorporating agents are oxides and carbonates of sodium and calcium and glycerine[2].

In the present work, lac-oil combinations were prepared following the method of Bhattacharya and Gidvani[1]. But we modified their method in respect of the following: a) ethylene glycol instead of glycerol, b) double boiled linseed oil instead of raw linseed oil and c) no metal oxide catalyst used.

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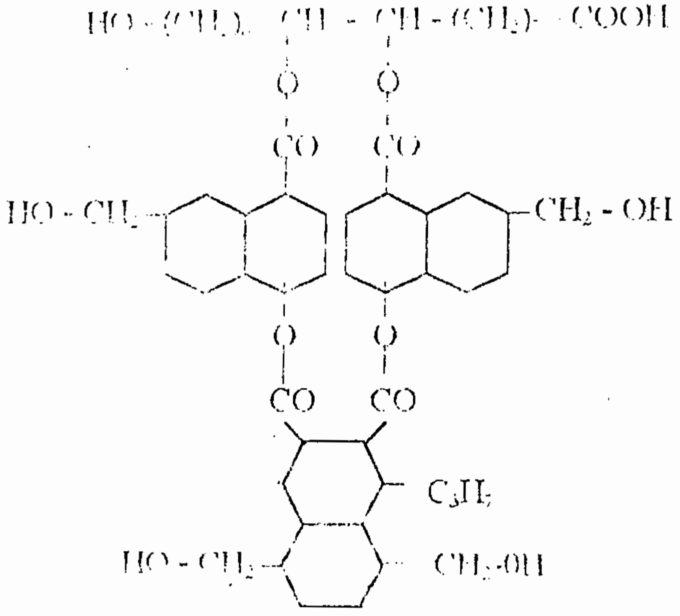
To modify lac, it is necessary to consider the chemistry of lac resin. A complete knowledge of the lac resin molecule is not yet available, but the following monomeric formula is believed to exhibit most of the chemical properties of lac[3]. It may be noted that the hydroxyl and carboxyl groups of component acids other than aleuritic acid are arbitrarily disposed in formula 1.



(1)

It is suggested that of these five hydroxyl groups two are more reactive than the other three. When a mixture of shellac and excess of ethylene glycol is heated together in presence of an acid catalyst at 150°- 200°C, etherification takes place between the hydroxyl groups of the lac and those of the glycol[4].

Shellac, on saponification with alkali and treatment of the resulting solution with acids, gives a water insoluble soft acidic mass to the extent of 65 to 70% by the weight of the original shellac. This product is called hydrolysed lac or lac acids. Hydrolysed lac is a useful raw material for a variety of products of industrial importance, the most promising fields being cements, adhesive and glues.

Esterification of Hydrolysed lac with ethylene glycol results in sticky balsam like materials which are non drying at ordinary temperatures but to dry hard smooth surface on baking.

Our results on the modification of lac with ethylene glycol and its derived products are presented in this paper.

Experimental

Preparation of dewaxed shellac[5]

1kg of semi-powdered seed lac was taken in a 6 litre flat-bottom flask and to it added 4 litre rectified spirit and kept over night at room temperature with occasional shaking. The lac solution thus obtained was filtered through nylon cloth. The filtrate was distilled on a water bath to recover the solvent as far as possible (85% recovery). The residue was transferred to a porcelain basin and was heated on a hot plate at 110°C so as to remove the residual solvent. The molten mass was cooled to 50°C when it turned into flakes. The yield was 90%, calculated on the weight of seed lac used.

Preparation of Hydrolysed lac (lac acids)[6]

Hydrolysed lac (Lac acids) was prepared by following the procedure available in the literature.

1kg of seed lac (raw lac) was dissolved in 4 litre of water containing 0.25kg of caustic soda in a 6 litre flat-bottom steel vessel. The solution was then boiled for 2-3 hours and allowed to cool. The shellac wax that floats to the top and forms a scum was removed by means of a laddle.

The solution was then filtered through nylon cloth to remove any impurities. The saponified lac or lac acids were precipitated from the filtrate in the form of sticky resin by the gradual addition with stirring of 1 litre of dilute sulphuric acid (20%). The precipitated lac acid was then washed several times with boiling water until the washings were free from sulphuric acid. This was tested by the addition of barium choride solution previously acidified with hydrochloric acid to the washings until the later showed no turbidity or precipitation. The saponified lac was then dried by heating at 100°-105°C for 1 hour. The yield of lac acids was 65%, calculated on the weight of seed lac taken.

Reaction of ethylene glycol with dewaxed shellac: formation of lac-glycol ether[6]

500g of dewaxed shellac and 187cm^3 of ethylene glycol was taken in a 1 litre round bottom flask and heated in an oil bath at 120°C until all the lac dissolved. The temperature was then allowed to fall to 80°C and concentrated H_2SO_4 (1.8 cm^3)

added. The mixture was then refluxed at 180° to 190°C for 4 hours and then poured in to water. The excess of glycol and acid was then washed out repeatedly with boiling water and the product dried by heating under vacuum over boiling water bath. The etherified product thus obtained was soluble in most of the usual solvents.

Preparation of double boiled linseed oil

200 cm^3 raw linseed oil was taken into a three necked round bottom flask and heated at 240-250°C with constant stirring for about 45 minutes. It was then cooled down to 90°C and liharge (2.0g), cobalt acetate (0.70g) and manganese acetate (0.72g) were added to the linseed oil as drier and again stirred for about half an hour. The temperature of the mixture was again raised to about 250-260°C and air was passed through blow pipe in the reaction flask. The product obtained was the double boiled linseed oil.

Esterification of lac-glycol ether with double boiled linseed oil fatty acid: formation of lac-glycol fatty acid complex

The prepared lac-glycol compound (100g) was heated on an oil bath at 200-205°C for 30 minutes to remove any uncombined glycol. The fatty acids, e.g. double boiled linseed oil fatty acids (100g) was then added and the esterification was then carried out in the same open vessel by heating for 4-5 hours at 150°-200°C. The lac-glycol fatty acid complex thus obtained was soluble in castor oil, xylene, meta-cresol etc.

Glycol-ester of hydrolysed lac[6]

The glycol-ester of lac acids was prepared by refluxing 250g lac acids with 100cm^3 ethylene glycol without any catalyst for 24 hours in an oil bath at 195-200°C, when practically a neutral product was obtained. The ester was then washed free from glycol or any other water soluble matter by repeated washing with boiling water and dried. The product was a dark-red sticky balsam with sp. gr. 1.05 at 30°C. It was soluble in alcohols, esters and ketones but insoluble in ether, paraffin and coal-tar hydrocarbons and chlorinated hydrocarbons.

An improved varnish was prepared by dissolving 100g of lac-glycol fatty acid complex in 300 cm^3 xylol : m–cresol (3 : 1 vol./vol.), filtering the solution through fine compact cloth and refluxing the filtrate with 6.0g malic acid and 5.0g castor oil for 3 hours.

Results and Discussion

The reaction between lac and ethylene glycol has been studied by Gidvani who postulated the formation of lac-glycol ethers. Later work by Gidvani and Kamath has shown that the major reaction that occurs is one of esterification, as practically neutral derivatives could be obtained if the temperature of reaction is increased or the time is prolonged[8]. It is observed in the course of our experiments that double boiled linseed oil dries in less time than either raw and refined oil and exhibits improved drying qualities.

The chemical constants of dewaxed shellac, lac-glycol ether, lac-glycol fatty acid complex and glycol-ester of hydrolysed lac were determined and shown in Table 1.

Table 1. Chemical constants of dewaxed shellac and its modified products

Sample No.	Description of sample	Acid value	Sap. value	Iodine value
1.	Dewaxed shellac	70.00	232.00	18.50
2.	Lac-glycol ether	13.60	216.88	14.29
3.	Lac-glycol fatty acid complex	18.54	242.23	18.15
4.	Glycol-ester of hydrolysed lac	67.77	164.25	9.92

The resulting resinous products have been found to be of low acid value and useful in coating industry, plasticisers and adhesives. The modified lac can also be used as printing ink. The prepared varnish was tested for its physical properties like extractible matter content, solid content, viscosity and specific gravity and the results are recorded as: Extractable matter content 3%; Solid content 40%; Viscosity at 30°C 1.4 poise; Specific gravity at 30°C 0.95.

Table 2. Salient properties of the varnish[9]

Characteristics	Requirement of IS: 10026 -1982	Property of the varnish
Drying in thin film	Non-tacky in not more than 4 hour	Air-dried within 1-2 hour
Dilution ability or compatibility (%)	100	100
Reaction of the varnish with copper wire	The copper will not change colour	No change in colour was observed, when it was coated with the varnish and heated 100°C for 24 hours.
Electrical strength (KV/mm) in air at room temperature	50	50
Resistanceto tacking 200V	50drops	48

Air drying of the films of varnish was measured by touching with finger. For this purpose test sample of the prepared varnish containing 0.1% cobalt naphthenate was used to paint the wooden surfaces and the films obtained was found to be smooth and clean. The time taken for the films to dry to touch, to hard dry and to become tack free were found to be 1-2 hour for touchdry, 4-5 hour for hard dry and 24 hour for tack free. Water resistance towards tracking was measured by dipping the panel in water. For this purpose the prepared varnish was applied to wood at 0.007" thickness, air dried for 6 days and then immersed in water. The wooden surfaces were examined at intervals of 1, 2, 4, 24 and 48 hours and found unaffected with water. The thermal resistance of air-dried films is upto 70-80°C, it can be improved upto 150°C by baking the films at 175°C for half an hour. The salient properties of the varnish is shown in Table 2.

The varnish may be applied on coils of electric motors, transformers etc. It can also be used as anti-tacking insulating varnish and for finishing of electrical component of instruments

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