Utilisation of by-products of lac industry

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Abstract

DURING the refining of sticklac to seedlac and seedlac to shellac, unavoidable by-products such as (i) wash water containing sufficient amount of lac, wax and dye, (ii) molamma, (iii) kunhi, (iv) kiri, etc., are obtained. The latter by-products contain 50-75 per cent of lac along with wax and other impurities. The various techniques developed for economical reclamation of the valuable end products from the by-products and their suitable utilisation have been reviewed in the present paper. It is felt that the recovery and proper utilisation of these will consequently add to the over all economy of the lac industry especially when the demand for lac has increased and the total production came down.

Introduction

DURING the refining of sticklac to seedlac and seedlac to shellac, unavoidable by-products such as **molamma, kunhi, kiri,** etc., are obtained. These by-products contain 50-75 percent of lac along with wax and impurities such as sand, woody matter and insect debris. Due to the presence of these impurities to a large extent, recovery of resin from these by products becomes very difficult by the conventional hot-filtration method of shellac manufacture. There is therefore, practically no market for these commodities in India except for a small quantity consumed in bangle making and for the production of inferior grades of shellac. Recovery and proper utilisation of these will consequently add to the overall economy of the lac industry especially during the low production of lac. A few methods for their reclamation and utilisation have been developed and are being described in the following sections.

Recovery of shellac from refuse lacs

Due to its acidic nature, lac resin is easily soluble in aqueous alkalies and alkaline salts. As the solvent extraction method involves the use of expensive esuipment and solvents, a method based on aqueous extraction would be more acceptable particularly to the small scale manufacturers. But aqueous extraction of lac with alkali and its regeneration with acids result in a resin characterised by[1] :-

(i) high colour index
(ii) poor keeping quality
(iii) poor flow and
(iv) reduced life (polymerisation time).

In order to remove the above defects, a simple method[2] has been worked out for the reclamation of lac resin from refuse lacs. In this process, the refuse lac is extracted with a hot (85-90°C) aqueous solution of 7 parts of sodium carbonate and 3 parts of sodium sulphite per 100 parts of lac resin and the extract obtained is treated with 2 parts of sodium hydrosulphite. Lac is precipitated out of the resulting solution with dilute sulphuric acid.

The yield of the reclaimed lac is nearly 80 per cent of the lac content of the refuse lac. The reclaimed lac, on sheeting had good colour and storage stability, and a hue comparable to that of ordinary shellac.

Bleached lac from molamma

Bleached lac is gaining popularity in our country and if it can be prepared from refuse lacs, the product will be cheaper than that produced from shellac. But the presence of insect debris creates a difficult problem to prepare good quality bleached lac from **molamma** by the conventional method. During the extraction, a part of the insect debris goes into solution resulting in a dark coloured extract having a very high bleach index and thus requiring larger amounts of bleach liquor for bleaching results in bleached lacs of very poor storage quality[3]. Therefore, the dissolution of the undesirable materials during alkali extraction has to be reduced, and this has been achieved by modifying the conventional extraction procedure.

The modified extraction procedure[4] consists of carrying out the initial alkali extraction of **molamma** at lower temperature (50°C) for a longer period (4 hrs.). Further processing such as dewaxing (if necessary), bleaching, precipitation and washing, may be carried out according to the conventional methods[5,6]. The yield of the bleached lac is 80-83 percent of the lac content.

The bleached lac prepared from **molamma** by this modified technique is free-flowing and its keeping quality very good. A typical sample retained its solubility in alcohol even after one year's storage in the

dry state at room temperature. Its colour index, acid value and percentage of chlorine content are 0.38, 68.00 and 1.32 respectively. It is thus almost similar in all respects if not better, than those of bleached lacs prepared from seedlac by the conventional method.

Preparation of total hydrolysed lac and its modification

Hydrolysed lac is a versatile and useful raw material for a variety of products of industrial importance,[7-11] the most promising fields being cements, adhesives and glues. The product is a resinous mixture of various water insoluble constitutent acids of the resin obtained by treating alkaline lac hydrolysate with mineral acid, and the yield is therefore only 70-75 percent. The rest being highly soluble is lost in the aqueous mother liquor. A simple and convenient method[12] to collect the total products of hydrolysis from the refuse lacs has been worked out. It consists of carrying out the hydrolysis with **alcoholic** alkali and neutralising the solution with an equivalent amount of 10 percent solution of sulphuric acid also in alcohol. The excess of sulphuric acid, if any, may be easily neutralised by adding solid calcium carbonate. Sodium sulphate, calcium sulphate (if any) and unreacted calcium carbonate being insoluble in alcohol are filtered off very easily.

Alternatively, especially if contact with sulphuric acid is to be avoided and complete freedom from inorganic radicals ensured, the hydrolysate may be passed through a column of cation exchange resin to regenerate the free acids.

The **total** hydrolysed lac is collected by distilling off the alcohol and the residue heated in an open pan at 120°C to free it from the last traces of the solvent.

The yield of **total** hydrolysed lac is nearly 102 percent on the weight of the lac content. Its acid, saponification and hydroxyl values, and life under heat are 205, 212, 425 and 360 (minutes) respectively; the corresponding values for the conventional hydrolysed lac being 198, 201, 370 and 240 (minutes) respectively.

Since the total hydrolysed lac obtained as above is of very dark colour and in some of its uses light coloured hydrolysed lacs are preferred, a method has also been worked out to bleach the sulphuric acid treated alcoholic lac hydrolysate at pH 3-5 by sodium chlorite or chlorine gas[13].

The first attempt to modify **total** hydrolysed lac was by application of heat only. The material obtained by heating it at 150°C for nearly 5½ hours has been termed as 'Rebulac' (for rebuilt lac)[14] and is similar to shellac in many respects and different in a few. It is a tough, dark coloured, slightly tacky matter, soluble in all the usual lac solvents and, again like shellac, in aqueous alkalies also. Rebulac has the following physical and chemical properties :

Acid value	=	82
Saponification value	=	212
Hydroxyl value	=	87
Carbonyl value	=	14
Life under heat at 150°C	=	36 mts.
Flow (by Victor method)	=	134 mm.
Melting point	=	55-66°C
Molecular weight	=	1,100

The most noteworthy deviation from shellac is its low hydroxyl value of 87 as against 260 of shellac.

Like shellac, rebulac also cures melamine resin in the cold and also readily reacts with toluene di-isocyanate. There is, however, a considerable improvement over shellac when films are prepared from its aqueous ammoniacal solution[15]. These films are glossy with good adhesion, hardness and flexibility whereas the films from aqueous lac varnishes under similar conditions crack and flake off the surface.

Aqueous rebulac varnish while pigmented with red oxide or titanium dioxide has resulted in cheap and simple water thinnable primers and gloss paints for ferrous as well as non-ferrous substrates. Hard glossy films with good adhesion and flexibility are obtained. When backed at 200°C for 5-10 minutes, water resistance and scratch hardness of these films varied from 25-30 days and 1,500-1,800 respectively.

Rebulac may also be used as an adhesive and in emulsion paints and can also be deposited by electrodeposition technique. Its dark colour can be bleached as usual[5,6] by sodium hypochlorite to give a product of colour index 0.6.

In order to make the above water thinnable paints applicable on substrates which need not be backed and or where backing facilities are not available, total hydrolysed lac has been modified by heating at 150°C with linseed oil fatty acids (LOFA)[16]. Paints formulated with these compositions, produced very hard glossy films with moderate water resistance, good adhesion and flexibility, and can be dried at room temperature in presence of a drier. Water resistance of the films can be further improved if hydrolysed lac is first converted to rebulac and then modified with LOFA.

Hydrolysed lac has also been modified with maleic and phthalic anhydrides[17] by application of heat only to tough, dark coloured and slightly tacky products

which can also be used to formulate aqueous paints with similar properties.

Reclamation of lac wax

In respect of hardness and general polishing properties, lac wax, another valuable by-products of the lac industry, ranks second only to carnauba wax. As such, it is gradually increasing in importance as a substitute for the imported costly carnauba wax.

Lac wax is present to the extent of nearly 5 percent in lac. A part of this (0.8%) is lost during washing of sticklac with water in the preparation of seedlac and another part (0.6%) remains with refuse lacs. Considering the country's annual estimated output of nearly 30,000 tonnes (average of ten years) of sticklac, about 240 tonnes of this useful lac wax are being lost every year along with the effluents of the lac factories and another 180 tonnes remain with **kiri, molamma,** etc. A method[18] has been standardised for the recovery of lac wax from these effluents and refuse lacs. Well over 90 percent of the wax can be recovered by extracting the dry sludge, obtained during the hygienic disposal of lac effluents with sulphuric acid, with n-hexane in a solvent extraction plant. It will be interesting to note that **molamma** and/or, other refuse lacs can be mixed up with an equal weight of dry sludge, and the wax of both can be extracted with ease by this method.

The melting point, acid and saponification values of the reclaimed wax are 82-83°C, 16-17 and 97-100 respectively. Its penetration value (3-3.5) is, however, higher than those of the commercial (Angelo's 2.9-3.0) and carnauba (1-1.5) waxes.

The wax from the above sources is dark in colour (colour index 7) and as such has a very limited use. A method[19] has, therefore, been standardised to obtain perfectly white wax. It consists of successive treatments with -(i) potassium permanganate and hydrochloric acid, (ii) sodium hypochlorite and (iii) activated carbon. A typical wax thus obtained had a m.p. of 81°C and penetration value of 3.0 as against 79°C and 5.5 respectively for the crude one.

Thus we find that the ever accumulating and unsaleble refuse lacs can be successfully utilised to get shellac, bleached lac and total hydrolysed lac which in turn can be modified to Repulac and a variety of other end products finding their use in many fields including water thinnable paints.

The effluents of the lac industry which are simply drained out and sometimes pose a serious problem for social hygienist, can be utilised as source for useful lac wax. If these findings can be commercialised with due publicity, it will result in successful disposal of the by-products but at the same time add to the overall economy of the industry.

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