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Utilization of byproducts of lac industry part III: manufacture of total hydrolysed lac from refuse lacs

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Reprinted from *Paintindia, October 1971*

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ABSTRACT

AN economic and easy method has been developed for the preparation of total hydrolysed lac, in an yield of ∼ 102 per cent on the resin content, from refuse lacs. This consists in hydrolysing the lac resin in alcohol medium and the regeneration at room temperature of hydrolysed lac from the alcoholic hydrolysate either by neutralising with a slight excess of alcoholic sulphuric acid over that needed for exact neutralisation followed by treatment with calcium carbonate or by passing through a strong cation exchange resin. The reclaimed hydrolysed lacs are dewaxed and have better properties than those of the conventional hydrolysed lacs prepared in an yield of ∼ 75 per cent in aqueous medium.

IN the earlier communications[1,2] methods for the production of good quality bleached lac and shellac from refuse lacs were reported. In this paper, a method for the preparation of hydrolysed lac in cent per cent yield from refuse lacs is described.

Hydrolysed or saponified lac is the water insoluble dark sticky mass obtained by decomposing alkaline lac hydrolysate with mineral acid. This hydrolysed lac is a potential raw material for diversified uses, the most promising fields being cements, adhesives and glues. As such or in conjunction with shellac or other materials it is usually used for lamination of paper and fibre boards, cementing electrical instruments, production of flexible micanite,[3,4] gasket shellac compound,[3] etc. Hydrolysed lac is also an essential part in compositions for the manufacture of leather goods, bottle sealing compositions, black insulating tapes,[5] printing inks for non-porous surfaces, rubber pad ink, etch primer for aluminium surfaces[6] and varnishes for natural and synthetic rubbers etc. The butyl ester has been recommended as a plasticiser as it is compatible with nitrocellulose and polyvinyl chloride[7]. The ethylene glycol ester has been found to be remarkable for its low temperature flexibility[4]. Thus it will be evident that hydrolysed lac is a versatile material of considerable promise. Refuse lacs have practically no market in our country. The production of hydrolysed lac from refuse lacs will be another valuable outlet for its disposal which will consequently add to the overall economy of the lac industry.

In the conventional process[8,9] of preparing hydrolysed lac, lac is hydrolysed with aqueous alkali, decomposed with aqueous acid and the water insoluble precipitated soft mass collected. The yield is generally 70-75 per cent of the lac resin. The rest being highly soluble is usually lost in the aqueous portion. In connection with the manufacture of reconstituted lac from lacs other than refuse lacs, a method[10] was described for collecting **total** hydrolysed lac. This was achieved by neutralising the aqueous lac hydrolysate with sulphuric acid exactly equivalent to the alkali used for hydrolysis, evaporating the solution to dryness, heating the dry mass at 150°C prior to the gelling stage from which the reconstituted lac could be extracted with alcohol leaving behind the insoluble sodium sulphate.

This method appears to be laborious and time consuming. Moreover, in this method the reconstituted lac is obtained and not the hydrolysed lac. In order to make the method more convenient and economical, a simpler method needs to be developed which will eliminate the necessity of evaporating the large volume of water used for hydrolysis and decomposition. Since the alkaline hydrolysis of lac resin can only be achieved either in aqueous or alcoholic medium, attempts have been made to develop a method using distilled methylated spirit or isopropyl alcohol as the hydrolysing and decomposing medium which ultimately have led to a simpler method of preparing **total** hydrolysed lac.

Experimental

Preliminary experiments were carried out with seedlac. Seedlac was saponified with alcoholic alkali, either at room temperature for 24 hours or at reflux temperature for 4 hours and the saponified solution neutralised with the requisite amount of sulphuric acid diluted to 10 per cent with alcohol. The precipitated sodium sulphate, impurities and wax were separated by filtration and the total hydrolysed lac was recovered from the filtrate by distillation and finally by heating in an open pan at 120°C. The product was obtained in an yield of 102 per cent on the weight of lac resin present in seedlac which had acid and saponification values of 205 and 219 respectively.

The above process involved neutralising the alkali used for the saponification with the exact equivalent of mineral acid. A trace of excess mineral acid, however, has been found to give a product with a shorter life at 150°C. And it was always found that the hydrolysed lac thus obtained invariably contained trace amounts of sulphuric acid which requires removal since its presence in the product is harmful.

As it is difficult to ensure, in the resulting product, complete freedom from mineral acid or alkali, especially when carried out on a large scale, the method necessitated some modification. The hydrolysate was decomposed with an excess of sulphuric acid (just acidic to congo red paper) and the excess mineral acid was effectively removed by treating the alcoholic solution with powdered calcium carbonate. Incidentally, it was noticed that the addition of calcium carbonate greatly enhanced the rate of filtration as the wax settled down readily along with it.

Another simpler process avoiding the use of mineral acid all together was also worked out. The alcoholic lac hydrolysate was passed through a column of cation exchange resin (Amberilite Resin IR-120) to regenerate the lac acids. The hydrolysed lac was recovered from the solution adopting the method mentioned earlier in an yield of 103 per cent; the acid and saponification values being 199 and 212 respectively.

The above processes were repeated a number of times with various seedlac samples and were found reproducible. These standardised methods were then extended to lac reclaimed from **molamma** and **kiri** and were found equally reproducible and satisfactory.

Recommended procedure

Lac resin from refuse lac or seedlac (100 parts) is gradually added to distilled methylated spirit or isopropyl alcohol (95 per cent; 200 parts) containing caustic soda (20 parts) in an enamelled or glass lined iron or stainless steel vessel fitted with a condenser. The saponification is allowed to proceed at reflux temperature for 4 to 5 hours or at room temperature for 18-24 hours whichever is convenient. The solution, after dilution with alcohol (200 parts) is treated, in the cold, with a slight excess of a 10 per cent alcoholic solution of sulphuric acid than needed for exact neutralisation. Afterwards the solution is treated with finely powdered calcium carbonate (precipitated chalk, 5 parts) under vigorous agitation and the whole allowed to stand overnight while unreacted calcium carbonate along with calcium sulphate, sodium sulphate, wax and impurities settle down. The clear liquid is decanted off and the residue washed with fresh alcohol under suction. The alcohol is then removed by distillation and the recovered **total** hydrolysed lac is dried finally in an open vessel by heating at 120°C with constant agitation or under vacuum.

Alternatively the saponified solution is treated with or passed through a column of strongly acidic cation exchange resin, such as Amberilite IR-120 or Zeocarb 225, so as to liberate all the lac acids. The resin is washed thoroughly with alcohol and the total hydrolysed lac recovered as mentioned above.

Preparation of total hydrolysed lac by this process has given reproducible results with batches of 10 kg of lac samples. The yield was found to vary within 102-103 per cent on the weight of lac resin in the samples. The cation exchange resin after regeneration with sulphuric acid solution may be used again and again.

Hydrolysed lacs were also prepared from **molamma** and seedlac by the conventional method in aqueous medium for comparative study.

Results and discussions

Total hydrolysed lac thus prepared is a soft, dark and sticky material. It is soluble in lower alcohols and organic acids, esters, ketones, amines and aqueous alkalies but partially soluble in ether, chlorinated solvents and aromatic hydrocarbons, while almost insoluble in aliphatic hydrocarbons. On heating it melts to a thin liquid which readily filters through muslin cloth at 100°-120°C.

The carbonyl values of the parent and hydrolysed lacs varied within the ranges of 18-20 and 56-61 respectively. The amount of vicinal hydroxyl groups, in terms of aleuritic acid, present in the resin before and after hydrolysis were found to be within 14—15 and 35-36 per cent respectively.

It will thus be evident that during alkaline hydrolysis the combined aldehyde and vicinal hydroxyl groups have been set free.

The properties of various hydrolysed lacs prepared under different conditions are summarised in Table I. It will be seen from the table that the acid, saponification and hydroxyl values, and life for the conventional hydrolysed lac are lower than those prepared in alcoholic medium. This is quite understandable because this **total** hydrolysed lac is totally different from the conventional one wherein a sufficient amount of water soluble acids (mostly terpenic in nature) has been lost in the aqueous portion during decomposition with mineral acid. The presence of sulphuric acid even in trace amounts has been found to affect the life of hydrolysed lac. The life is higher when sulphuric acid either is not at all used (method III) or has been effectively removed (method II). Further the estimation of sulphuric acid in various samples of hydrolysed lac showed that higher its percentage, the lower is the life.

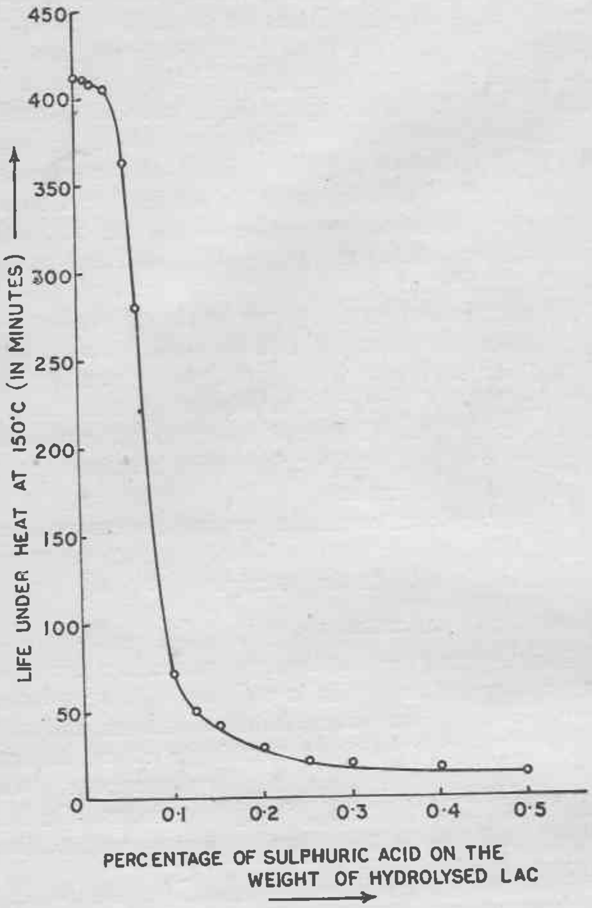

Fig. 1

In order to find out the effect of sulphuric acid on the life of hydrolysed lac and to determine the allowable percentage which will not appreciably affect the life, the life of hydrolysed lac (method III) at 150°C with different amounts of sulphuric acid was determined which, as is well known, behaved as a powerful accelerator (See Fig. 1). It will be found that the limit of sulphuric acid allowable is of the order of 0.007 to 0.030 per cent on the weight of hydrolysed lac, beyond which the life is affected.

The sulphuric acid contents in the hydrolysed lacs obtained by method I were 0.07 and 0.04 per cent, and the corresponding life of these were also lower. Though the amount of sulphuric acid in products obtained by method IV was within the non-effective limit yet the life was very low. This might be due to the fact that in the absence of the water soluble lac acids, the residual acids polymerise at a rapid rate in presence of trace amount of sulphuric acid.

It is known that the curing of conventional hydrolysed lac is accelerated or retarded by various reagents. In order to see the effect of curing agents on total hydrolysed lac the life at 150°C was determined in presence of catalysts (5 per cent on the weight of hydrolysed lac) such as oxalic, phosphoric and P-toluene sulphonic acids, urea, and maleic anhydride. The results are brought out in Table 2. It would be seen that whereas urea (which is one of the most powerful accelerators for lac) acted as a retarder as it did not polymerise hydrolysed lac even upto 30 hours of heating and maleic anhydride had no noticeable effects on the polymerisation, the other three acted as accelerators. The samples obtained by method II (calcium carbonate treatment) and by method (III) (ion-exchange resin regeneration) had almost similar lives under heat, thus indicating effective removal of the free mineral acid in the former process. No differences were observed for the hydrolysed lacs obtained either from refuse lacs or seedlac.

Wax content

The hydrolysed lacs prepared by the newly developed alcoholic method were almost dewaxed as these contained only 0.14 to 0.16 per cent of wax while the respective wax contents in lacs from refuse lacs and seedlac were 7.2 and 4.7 per cent respectively.

The lac from refuse lacs may be reclaimed for hydrolysis by extracting either with sodium carbonate solution and decomposing with sulphuric acid or with warm alcohol. There were hardly any differences in the properties of hydrolysed lacs prepared from reclaimed lacs obtained by the two methods as will be evident from Table I (methods III & V). In the soda extraction method, however, nearly 20 per cent of lac resin will be lost during processing resulting ultimately in a lower yield in hydrolysed lac. The alcohol extraction process, though there is some loss of alcohol during processing, is more advantageous as it involves minimum number of operations, full recovery of lac resin and the hydrolysis may be carried out straightway by the addition of alkali. The hydrolysis also may be carried out either at room temperature for 24 hrs. or at reflux temperature for 4 hrs. (vide methods V & VI).

Further there is hardly any difference in the properties of hydrolysed lacs obtained by the two regeneration procedures (methods II & III). In method II, the alcohol used should be of at least 95 per cent strength because in alcohol of lower strength a part of sodium sulphate, formed during neutralisation with sulphuric acid, will go in solution and ultimately remain in the final product. On the other hand, in method III, alcohol of even 80 per cent strength may be suitably used and incidentally most of the wax, being insoluble at this concentration of alcohol, will be left behind with the insoluble residue during alcohol extraction. Moreover, in this method isopropyl alcohol, which is at present available as a commercial solvent in our country at a comparable rate (Rs. 2/-kg), of even 70-80 per cent has been successfully used in place of methylated spirit for hydrolysis and regeneration.

TABLE I

PROPERTIES OF HYDROLYSED LACS FROM REFUSE LACS AND SEEDLAC

Sl. No.	Raw material	*Method of preparation of hydrolysed lac	Yield on the weight of lac content %	Acid value	Saponification value	Hydroxly value (gravimetric)	Life at 150°C (min)	Ash content (%)	Sulphuric acid present %
1.	Molamma (70% lac content)	I	104.1	204.0	212.3	427.3	250	0.71	0.041
2.	—do—	II	103.4	204.3	214.9	417.0	370	0.70	0.007
3.	—do—	III	102.6	202.9	210.4	433.7	410	0.12	Nil
4.	—do—	IV	76.6	197.2	199.3	374.5	255	0.19	0.015
5.	—do—	V	102.0	201.0	212.0	427.0	398	0.11	Nil
6.	—do—	VI	103.0	199.0	207.0	428.5	395	0.13	Nil
6a.	Reclaimed lac from 1.	—	—	79.8	210.4	243.5	57	—	—
7.	Kiri (bhatta, 50% lac content)	V	102.5	210.0	214.0	425.6	342	0.12	Nil
8.	Seedlac (Rangeeni)	I	103.5	204.8	219.3	402.2	275	0.65	0.070
9.	—do—	II	102.0	203.5	211.4	409.3	395	0.65	0.009
10.	—do—	III	102.4	201.4	212.3	440.9	380	0.11	Nil
11.	—do—	IV	73.8	198.1	201.0	370.4	230	0.23	0.014
12.	Seedlac (control)	—	—	67.2	214.9	224.3	42	—	—

*I — Lac hydrolysate in alcohol medium neutralised with equivalent amount of alcoholic sulphuric acid.

II — Lac hydrolysate in alcohol medium neutralised with excess alcoholic sulphuric acid and excess sulphuric acid removed by treating with calcium carbonate.

III — Lac hydrolysate in alcohol medium passed through cation exchange resin (Amberilite IR-120).

IV — Lac hydrolysate in aqueous medium neutralised with aqueous sulphuric acid (conventional method).

V — Lac extracted from refuse lac by alcohol, hydrolysed and proceeded as per method III.

VI — Lac hydrolysed at room temperature for 24 hrs and proceeded as per method III.

TABLE II

LIFE UNDER HEAT OF HYDROLYSED LACS IN PRESENCE OF 5 PER CENT OF THEIR WEIGHTS OF CURING AGENTS

			Life in minutes at 150°C of				
				Conventional (water insoluble) hydrolysed lac	Total hydrolysed lac prepared by method		
Sl. No.	Source of raw material	Curing agents	Parent lac (control)		I	II	III
1	2	3	4	5	6	7	8
	Molamma						
1.		None	57	255	250	370	410
2.		Oxalic acid	8	18	23	245	275
3.		Phosphoric acid	10	13	17	89	98
4.		p-toluene-sulphonic acid	6	5	10	16	15
5.		Maleic anhydride	57	235	245	370	385
	Seedlac						
1.		None	42	230	275	395	380
2.		Oxalic acid	5	18	32	230	268
3.		Phosphoric acid	8	12	25	78	83
4.		p-toluene-sulphonic acid	4	5	12	15	11
5.		Maleic anhydride	41	220	250	365	370

Considering all the above facts, it will thus be evident that 80 per cent methylated spirit or 70-80 per cent isopropyl alcohol will be most suitable and economical for extraction of lac resin from refuse lacs, hydrolysis and regeneration of hydrolysed lac by passing over cation exchange resin.

Raw material cost of total and conventional hydrolysed lacs from different sources:

A. BY THE PRESENT METHOD (YIELD 102 PERCENT)

Raw material	**Quality**	**Rate (Rs)**	**Cost (Rs) for 102 kg from** **Molamma**	 **Kiri**	 **Seedlac**
Molamma (70% lac content)	143 kg	1.25/kg	178.60	—	—
Kiri (50% lac cont.)	200 kg	50.00/75kg	—	150.00	—
Seedlac (98% lac content)	105 kg	340.00/75kg	—	—	476.00
Caustic soda	20 kg	80.00/50kg	32.00	32.00	32.00
Sulphuric acid	25 kg	3.00/kg	75.00	75.00	75.00
Calcium carbonate	2.5 kg	1.20/kg	3.00	3.00	3.00
Methylated spirit (95%)	25 l.	330.00/205 l.	40.00	—	—
Loss	40 l.	330.00/205 l.	—	64.00	—
	20 l.	330.00/205 l.	—	—	32.00
Cost per 102 kg. of total hydrolysed lac			328.60	324.00	618.00

Cost per kg of total hydrolysed lac from **molamma** ... ... Rs. 3.29
Cost per kg of total hydrolysed lac from **Kiri** ... ... Rs. 3.24
Cost per kg of total hydrolysed lac from Seedlac ... ... Rs. 6.18

B. BY THE CONVENTIONAL METHOD (YIELD-75%)

Molamma (70% lac content)	191 kg	1.25/kg	238.75	—	—
Seedlac (98% lac content)	133 kg	340.00/75kg	—	—	604.50
Caustic soda	30 kg	80.00/50kg	48.00	—	48.00
Sulphuric acid	37.5 kg	3.00/kg	102.50	—	102.50
Cost per 100 kg of hydrolysed lac			389.25	—	755.00

It will be evident from above that by the new process the cost of production of hydrolysed lac especially from refuse lacs is much cheaper. Of course, the cost of cation exchange resin has not been taken into consideration as the resin after regeneration with the same amount of sulphuric acid to be used for decomposition of alcoholic lac hydrolysate, will be used repeatedly without incurring any loss.

Conclusion

The hydrolysed lacs prepared from refuse lacs or seedlac by the new process described above are obtained in an yield of nearly 102-103 per cent on the resin content, superior in properties to and cheaper than those obtained by the conventional method. The manufacture of this total hydrolysed lac and its utilisation in industries will be another useful outlet for consumption of the unsalable and ever accumulating by-products of lac industry ultimately adding to the overall economy of the industry.

Acknowledgements

The authors are thankful to Shri A. K. Ghosh for carrying out some preliminary experiments, to Dr. G. S. Misra and Shri Y. Sankaranarayanan, Ex-Directors and Dr. T. Bhowmik, Retired Senior Scientific Officer (Utilisation) for their keen interest and valuable suggestions during the progress of the work.

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