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## **STUDIES ON BLEACHING OF LAC**

### **I. ACTION OF SODIUM HYPOCHLORITE ON THE RESIN**

By B. B. KHANNA

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# STUDIES ON BLEACHING OF LAC

## I. ACTION OF SODIUM HYPOCHLORITE ON THE RESIN

By B. B. KHANNA

A study was made of physical and chemical changes that take place during bleaching of *Rangeeni* and *Kusmi*, the two main varieties of lac, by the improved hypochlorite bleaching process. The physical changes studied include life, flow and keeping quality. The chemical changes observed were oxidation, addition, substitution and partial hydrolysis. Fractionation and intrinsic viscosity, however, showed little overall molecular change.

### Introduction

Bleached lac forms the major share of the world's consumption of lac and the bleaching of lac is thus of considerable commercial importance. A number of methods have been reported for bleaching of lac<sup>1-15</sup> but the most important and the only one to be commercially exploited is bleaching with sodium hypochlorite.

The process of bleaching with sodium hypochlorite, though simple in outline, requires careful control. As a result of studies extending over a long period, conditions for the production of a bleached lac of satisfactory keeping quality have been derived.<sup>16-17</sup> The present paper describes studies on some of the important physical and chemical changes that occur in the resin during bleaching by this improved technique.

To clarify the nature of the reactions which could possibly take place, a brief account of the composition of lac<sup>18</sup> is given.

The colouring matter present in lac is of two types. The first is a water-soluble dye known as laccaic acid which contains three or four components which are derivatives of tetrahydroxyanthraquinonedicarboxylic acid.<sup>19-20</sup> Most of this dye is removed during the washing of sticklac into seedlac. The other colouring matter (erythrolaccin) is insoluble in water and is in more intimate combination with the resin. It is thus not removed during this washing. The pale yellow to reddish brown colour of seedlac or shellac is due to this colouring matter. It has recently been shown<sup>21,22</sup> that this is a 3,4,6,8-tetrahydroxy-1-methylanthraquinone.

Apart from this colouring matter, seedlac also contains 4.0-5.5% of wax. Bouchet-Faurot & Michel<sup>23</sup> have reported that lac wax contains a high percentage of free alcohols (77.2%) together with acids (21%) and hydrocarbons (1.8%). The alcohols present are essentially C<sub>28</sub> and C<sub>30</sub>, the acids C<sub>28</sub>-C<sub>34</sub> and the hydrocarbons C<sub>27</sub> and C<sub>29</sub>.

In addition, seedlac also contains an odoriferous principle which is probably composed of an acid, an ester and/or a lactone.<sup>18</sup>

Lac resin is, of course, the main constituent of seedlac and is believed to be made up of a number of aliphatic and hydroaromatic hydroxy acids which are present as lactones, lactides, inter-esters and ethers.<sup>24</sup> It has been suggested that an average molecule of lac consists of an equivalent of a little more than one free carboxyl, three ester and five hydroxyl groups apart from one unsaturated linkage and an aldehydic group partly free and partly combined. Aleuritic acid (9,10,16-trihydroxypalmitic acid) and an aldehyde acid (jalaric acid) are believed to be the chief building blocks of the resin, although the presence of several other acids, notably shellolic acid (sesquiterpene with the rare cedrene skeleton)

and butolic acid (6-hydroxymyristic acid) has been reported. The presence of many of these acids, however, has not been proved conclusively.

### Experimental

Seedlac was prepared by washing fresh sticklac with water and a little sodium carbonate by the conventional method. The shellac was prepared from fresh *Kusmi* or *Rangeeni* seedlac by the country process.

The bleach liquor was prepared by passing chlorine through a filtered, ice-cold, 1.5 N solution of commercial caustic soda. It was adjusted to a strength of 3 ± 0.05% and a free alkalinity of 0.02-0.04 N (pH 11.0-11.2).

Sodium carbonate and sulphuric acid were of commercial grade.

### Analysis

The methods of analysis were those prescribed by the Indian Standards Institution and the International Standards Organisation in their specifications for shellac, seedlac and bleached lac.<sup>25</sup> Carbonyl values were determined by the method of Bhatt *et al.*<sup>26</sup> but the values were calculated using the correction suggested by Sengupta & Tripathi.<sup>27</sup> Vicinal OH groups were estimated by use of periodic acid.<sup>28</sup> For fractionation, the method of Seavell<sup>29</sup> for fractionating oil-modified alkyds using low-temperature fractionation with dry acetone as the solvent which was later extended by Kunhunni & Sankaranarayanan<sup>30</sup> to lac was adopted.

For determination of intrinsic viscosity, viscosity measurements were carried out at 30 ± 0.1° in 95% alcohol free from aldehyde with an Ostwald capillary viscometer.

### Bleaching procedure

Ten parts of seedlac or shellac were extracted, under mechanical stirring, with 40 parts of water containing 1 part of anhydrous sodium carbonate at 85-90° for 30 min. The hot extract was strained through a 100-mesh brass sieve and the insolubles were washed with water of the same temperature. The filtrate was diluted to 20% solids. Bleaching was carried out at 25 ± 1°. The requisite amount of bleach liquor was added in several small portions (Table I). After consumption of the bleach, the solution was cooled to 20° by the addition of ice and water, and diluted to 5% solids. The bleached lac was reclaimed from this solution by slow addition of excess dilute (5%) sulphuric acid in the form of a fine spray so as to obtain the product in a fine granular form. After the addition, the solution was agitated for a further 10 min to ensure complete precipitation. The precipitated lac was thoroughly washed with cold water (20°) until it was completely free from sulphates. It was dried in the open shade to a moisture content of ~ 2%.

TABLE I  
Properties of bleached lac

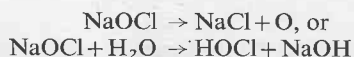
Type of lac	Bleach added to 30 g of lac, ml	No. of portions in which bleach was added	Yield of bleached lac, %	Life at 150°C, min.	Flow time for 5 in, sec	Acid value	Saponification value (apparent)	Chlorine reacting with KOH, %	Saponification value (corrected)*	Iodine value (Wij's, 1 h)	Total chlorine,** %	Iodine value,† iodine equivalent of chlorine	Carbonyl value	Hydroxyl value
<i>Kusmi</i> shellac, bleach index 60	Original shellac	—	—	64	40	70.65	221.8	—	221.8	12.6	—	12.6	16.5	255.8
	Precipitated lac (unbleached)	—	98.0	32	66	69.18	218.5	—	218.5	11.9	—	11.9	13.0	253.6
	20	1	96.0	15	115	69.36	224.6	0.36	218.9	8.6	0.45	10.21	14.5	—
	40	2	95.5	13	160	69.97	233.4	0.68	222.7	7.7	0.8	10.56	—	245.4
	60	3	95.0	13	240	70.94	240.2	0.97	224.9	6.8	1.1	10.73	20.0	240.2
	80	4	93.7	12	360	71.52	248.5	1.29	228.1	6.2	1.4	11.23	—	235.6
100	4	92.0	12	480	73.86	255.8	1.38	234.0	6.2	1.52	11.63	21.0	235.0	
<i>Rangeeni</i> shellac, bleach index 92	Original shellac	—	—	45	140	73.28	221.0	—	221.0	14.1	—	14.1	10.66	250.0
	Precipitated lac (unbleached)	—	97.0	33	265	70.94	218.6	—	218.6	13.2	—	13.2	7.00	246.5
	20	1	94.4	12	Does not flow 5 in	70.36	225.8	0.23	222.1	10.5	0.3	11.57	8.8	244.1
	40	2	94.0	11	"	70.94	231.7	0.6	222.2	9.5	0.72	12.07	11.26	—
	60	3	93.5	10	"	71.52	240.2	0.902	225.9	8.5	1.00	12.08	14.96	238.7
	80	4	92.8	10	"	73.28	249.0	1.2	230.03	7.8	1.32	12.52	—	—
100	4	92.0	10	"	75.03	254.7	1.3	234.2	7.3	1.43	12.41	—	230.2	
<i>Rangeeni</i> seedlac, bleach index 88, soda insolubles 3%	Original seedlac	(Values corrected for insolubles)	—	Not found because of the presence of insolubles		70.0	218.5	—	218.5	14.0	—	14.0	18.0	252.5
	Precipitated lac (unbleached)	—	95.0	30	250	68.7	215.8	—	215.8	13.0	—	13.0	—	—
	20	1	92.5	15	Does not flow 5 in	69.5	224.5	0.28	220.1	10.53	0.3	11.6	17.1	243.8
	40	2	92.0	14	"	70.0	233.4	0.65	223.1	9.55	0.7	12.0	—	—
	60	3	91.0	12	"	71.5	239.0	0.95	224.0	8.24	1.05	12.0	19.0	238.0
	80	4	90.6	11	Does not flow 5 in	73.0	244.5	1.15	226.3	8.03	1.25	12.5	—	—
100	4	90.0	11	"	73.0	249.9	1.25	230.2	7.6	1.37	12.5	22.2	234.5	

\* Found after subtracting KOH equivalent which reacts with the chlorine present in bleached lac from apparent saponification value.  
\*\* Determined by Stephanow's method<sup>25</sup>

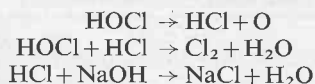
Results and discussion

The first step in the bleaching process is the reaction of the carboxyl group of the lac with aqueous sodium carbonate to form the soluble sodium salt.<sup>31</sup>

The bleaching of lac has been carried out with sodium hypochlorite in slightly alkaline medium (pH 9-9.5). Sodium hypochlorite can split by one of the following reactions :



Other reactions which may take place are:



Lac may undergo various reactions, e.g. oxidation, chlorination (by addition and substitution) and hydrolysis, owing to the evolution of oxygen, chlorine and sodium hydroxide.

Table I shows results for several types of lac.

Yield of bleached lac

When lac was dissolved in sodium carbonate solution and precipitated without the addition of bleach liquor, a 2-3% loss occurred. The loss was greater with seedlac (~5%) owing to the presence of ~3% of insolubles. The addition of bleach enhanced the loss, possibly because of the free alkali of the bleach, because when the alkalinity of the bleach was increased still further, the loss was also increased and the yield simultaneously decreased (Table II).

Life and flow

Life at 150° and fluidity of lac were adversely affected even by precipitation of the lac from sodium carbonate solution without bleaching, and addition of bleach enhanced this deterioration. As the amount of bleach used was increased,

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TABLE II

Effect of free alkalinity of bleach liquor\* on the yield and acid values of the bleached lac

Free alkalinity of the bleach, N	Yield of bleached lac based on lac used, %	Acid value of bleached lac
0.04	93.7	71.5
0.109	92.0	71.4
0.34	87.0	74.8

\* The same amount of bleach liquor, 80 ml for 30 g of lac, was added in all cases

these properties deteriorated still further. However, there was a limiting life of 10-12 min which appears to be the minimum for all bleached lac irrespective of the type of parent lac.

Keeping quality

Keeping quality (retention of alcohol solubility), Table III, deteriorated progressively with increase in the amount of bleach liquor used, which also determines the amount of chlorine in the bleached lac.

Chemical constants

Changes in chemical constants of *Kusmi* and *Rangeeni* lacs during bleaching were similar.

A slight reduction in the acid, saponification, iodine, carbonyl and hydroxyl values occurred when the lac was merely precipitated from the sodium carbonate solution, indicating removal of hydroxy, acidic, aldehydic and unsaturated constituents. Bleaching resulted in a gradual rise in acid and saponification values and carbonyl and chlorine contents, while hydroxyl and iodine values decreased, to an extent which depended on the quantity of bleach liquor used.

### Acid values

The rise in acid values was negligible (~ 5 greater than that of the control) compared with the large increase (> 20) recorded by earlier workers.<sup>32,33</sup> The latter values may have been high owing to the high alkalinity of the bleach used which would bring about hydrolysis (Table II). The high acidity may also have been due to incomplete washing of the mineral acid used for precipitation. Rigid control of these parameters are included in the improved method described in this paper. The acid value of the bleached lac becomes slightly higher than that of the parent lac only when the amount of bleach used is more than 60 ml for 30 g of lac.

### Saponification value

A substantial rise apparently occurred, but 50–75% of this was due to the ionisable chlorine in the bleached lac which consumes a corresponding amount of KOH. When allowance was made for this factor, the corrected saponification value for a bleached lac was ~ 5%.

### Carbonyl value

The carbonyl value increased when lac was bleached. It is possible that during the determination of saponification value, the newly created carbonyl groups were changed to carboxyl groups which consume more alkali, which may account for the increase in the saponification value.<sup>34</sup>

### Iodine value

The decrease in iodine value on bleaching is due at least partly to the entry of chlorine into the molecule. However, as the sum of iodine value and iodine equivalent of chlorine entering was always less than the iodine value of the parent lac, oxidation may have occurred, which was confirmed by the reduction in hydroxyl value and increase in carbonyl and acid values.

TABLE III  
Keeping quality of lac bleached with different amounts of bleach liquor  
(Rangeeni shellac, bleach index 92)

Bleach (3% chlorine) added to 30 g of lac, ml	Chlorine content, %	Cold alcohol insolubles, %		
		Initial	After 1 year	Increase
Original lac	—	4.6	4.8	0.2
Precipitated lac (unbleached)	—	4.6	5.0	0.4
20	0.3	4.7	5.2	0.5
40	0.72	4.74	5.4	0.66
60	1.00	4.8	5.64	0.84
80	1.32	4.72	5.8	1.08
100	1.43	4.78	6.2	1.42

TABLE IV  
Action of bleach on aleuritic acid

Treatment	Loss, %	Acid value	Chlorine content, %	Hydroxyl equivalent of chlorine content	Hydroxyl value observed	Drop in hydroxyl value
Aleuritic acid	—	183.9	—	—	560.0	—
Precipitated from sodium carbonate solution without addition of bleach	1.0	179.9	—	—	—	—
Sodium carbonate solution of acid treated with bleach (3 g chlorine for 100 g acid)	10.0	183.9	0.264	4.17	554.8	5.2
Solution prepared as above (6 g chlorine for 100 g acid)	15.1	180.8	0.513	8.12	550.4	9.6

### Chlorine content

Chlorine was found in all bleached lacs, although the actual quantity varied widely depending on the conditions of bleaching, especially temperature. Under optimum conditions, the chlorine content was ~ 1–1.5%. Chlorine obviously enters the molecule of lac by addition and substitution.

However, the total chlorine as determined by Stephanow's method<sup>25</sup> was always higher than the quantity that could be extracted by boiling with caustic alkali, as in the determination of saponification values. This indicates that part of the chlorine is in the aliphatic chain and part in the aromatic nucleus.

### Action of bleach on aleuritic acid

Aleuritic acid is the chief constituent (30–50%) of lac and is linked with other hydroxycarboxylic acids as esters, ethers, lactones, etc., but with some of the hydroxyl groups remaining free. As the major building block of lac resin, the action of bleach on this acid under the same conditions as in the bleaching of lac was studied, and the results are given in Table IV.

A small amount of chlorine was found in the product obtained by treating aleuritic acid with hypochlorite and this was accompanied by a corresponding drop in the hydroxyl value. The percentages of vicinal hydroxyl groups in the aleuritic acid and the product from hypochlorite treatment were identical. This indicates that the chlorine has replaced the terminal and not the vicinal hydroxyl groups, which is as expected on the basis of relative reactivities of the hydroxyl groups.

As in the case of lac, there was a loss in yield, in this case 10–15%. There was evidence that oxidation had taken place since the aqueous mother liquor gave a positive test for aldehyde. The mother liquor also gave a 2,4-dinitrophenylhydrazine, m.p. 113–115° (m.p. of azealic acid semi-aldehyde is 114–115°). Oxidation of aleuritic acid should result in its cleavage at the 9:10 position, to give an acidic part (azealic acid semi-aldehyde) and a neutral part (hydroxyheptanal).<sup>35</sup> The neutral portion of the mother liquor did give a very small amount of precipitate with 2,4-dinitrophenylhydrazine, indicating its aldehydic nature, but the derivative could not be crystallised. This shows that vicinal hydroxyl groups are not completely immune to oxidation by hypochlorite and a part is evidently cleaved.

### Fractionation of bleached lac

Fractionation of bleached lac into simpler components and a comparison with the fractions obtained from the parent seedlac should indicate if any changes occur in the major constituents of lac during bleaching and also how chlorine is distributed in the various fractions.

TABLE V  
Temperature phase fractionation from dry acetone of *Rangeeni* seedlac and bleached lac

Fraction	Temp. of separation, °C	Yield, % (on solubles)		Acid value		Saponification value		Bleached lac		
		<i>Rangeeni</i> seedlac	Bleached lac	<i>Rangeeni</i> seedlac	Bleached lac	<i>Rangeeni</i> seedlac	Bleached lac	Chlorine reacting with KOH, %	Saponification value (corrected)	Total chlorine, %
I	30	21.0	22.0	53.6	55.0	200.4	227.8	1.1	210.5	1.24
II	15	24.5	25.0	57.3	57.1	214.6	234.4	1.05	218.0	1.15
III	5	9.5	8.5	57.8	58.2	215.7	234.4	0.9	220.2	0.97
IV	-10	10.5	10.0	63.6	65.0	215.7	234.4	0.9	220.2	0.98
V	Retained in solution	33.0	33.5	93.4	95.0	214.0	253.5	1.46	230.5	1.58
Loss	—	1.5	1.0	—	—	—	—	—	—	—

Table V shows the percentages of different fractions obtained from *Rangeeni* seedlac and bleached lac obtained from it, and their various chemical constants.

The different fractions are present in bleached lac in similar proportions to those in the parent seedlac. Chlorine is present in all the fractions. The acid and saponification values of fractions obtained from bleached lac are higher than the values of the corresponding fractions from the parent seedlac.

#### Intrinsic viscosity

A comparison of the intrinsic viscosity of bleached lac with that of the parent seedlac should throw further light on the changes, if any, that take place in the lac molecule during bleaching.

The variation of the reduced specific viscosity with concentration is shown in Fig. 1, from which the intrinsic viscosity can be determined by extrapolation to zero concentration. The parent seedlac and the bleached lac obtained from it have similar viscosities (0.0685 and 0.0675 respectively) indicating that there is little overall molecular change and, if anything, there is a slight reduction in the molecular complexity of the lac.

#### Conclusions

It is clear that during bleaching of lac with sodium hypochlorite, apart from the change in colour owing to the reaction with erythrolaccin, the hypochlorite also attacks lac resin by addition of chlorine at the point of unsaturation, by replacing a hydroxyl group (possibly primary) by chlorine, and by oxidising other hydroxyl groups to carbonyl groups, and also possibly with rupture of the chain at the site of the free

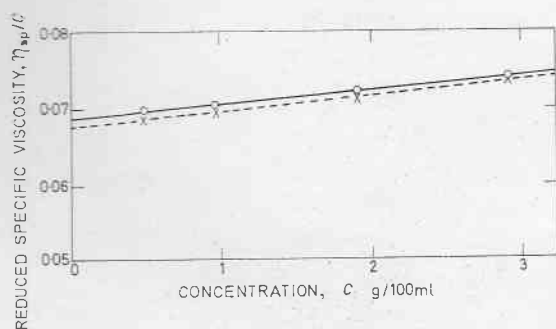


Fig. 1. Variation of reduced specific viscosity of lac with concentration  
× bleached lac; ○ seedlac

vicinal hydroxyl to give products at least some of which are water soluble. Simultaneously, the free alkali of the bleach and the alkali that is produced during bleaching partially hydrolyse the resin, thereby increasing its free acidity (although to a limited extent). There is, however, no appreciable change in the overall molecular complexity of the resin.

The principal object of bleaching is the elimination (decolorisation) of the dye erythrolaccin. The chemical reactions involved during hypochlorite treatment to achieve this objective are under investigation and will form the subject of a further communication.

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#### References

- Venugopalan, M., *J. Indian Inst. Sci.*, 1927, **11A**(2), 17
- Stuhlmann, P., U.S.P. 1,809,738
- Mylo, O., Ger. P. 517,096; 521,292
- Murty, N. N., *J. Univ. Bombay*, 1933, **2**, 301
- Gibson, A. J., *Oil Colour Trades J.*, 1934, **86**, 1416
- Hituki, M., Jap. P. 111,607/1935
- Faucett, P. H., *Drugs Oils Paints*, 1937, **52** (9), 364; (10), 405
- Gidvani, B. S., & Kamath, N. R., *Ind. Chemist*, 1946, **22**, 414
- Baba, M., Jap. P. 173,566/1946
- Vincent, G. P., U.S.P. 2,397,389
- Hampel, C. A., U.S.P. 2,429,317; 2,430,674; 2,433,661
- McIntosh, W. J., U.S.P. 2,448,320
- Van Allen, L. R., U.S.P. 2,454,796
- Takahashi, S., Jap. P. 1,179/1950
- Ubukata, K., Jap. P. 1,492/1954
- Khanna, B. B., *Paintindia*, 1963, **13** (4), 28
- Khanna, B. B., & Sankaranarayanan, Y., *Res. & Ind., New Delhi*, 1965, **10**, 1
- Bose, P. K., Sankaranarayanan, Y., & Sengupta, S. C., 'Chemistry of lac', 1963 (Indian Lac Res. Inst., Ranchi, India)
- Burwood, R., Read, G., Schofield, K., & Wright, D. E., *J. chem. Soc.*, 1965, p. 6067; *Tetrahedron Lett.*, 1966, p. 3059; *J. chem. Soc., C*, 1967, p. 842
- Padhare, E. D., Rama Rao, A. V., & Shaikh, I. N., *Indian J. Chem.*, 1969, **7**, 977
- Yates, P., Mackay, A. C., Pandey, L. M., & Amin, M., *Chem. Ind.*, 1964, p. 1991
- Bhide, N. S., Rama Rao, A. V., & Venkatraman, K., *Tetrahedron Lett.*, 1965, p. 33, *Indian J. Chem.*, 1969, **7**, 996

- <sup>23</sup> Bouchet-Faurot, E., & Michel, G., *J. Am. Oil Chem. Soc.*, 1964, **41**, 418
- <sup>24</sup> Christie, W. W., Gunstone, F. D., Prentice, H. G., & Sengupta, S. C., *J. chem. Soc.*, 1964, p. 5833
- <sup>25</sup> Indian Standards Institution, IS, 15-17, 1956, & International Standards Organisation, ISO/R 55-57, 1957 (E)
- <sup>26</sup> Bhatt, H. A., Kamath, N. R., & Nadkarni, J. M., *J. scient. ind. Res.*, 1955, **14B**, 273
- <sup>27</sup> Sengupta, S. C., & Tripathi, S. K. M., *J. scient. ind. Res.*, 1959, **18B**, 535
- <sup>28</sup> Sengupta, S. C., *J. scient. ind. Res.*, 1955, **14B**, 537
- <sup>29</sup> Seavell, A. J., *J. Oil Colour Chem. Ass.*, 1959, **42**, 5, 319
- <sup>30</sup> Kunhunny, P., & Sankaranarayanan, Y., *Rep. Indian Lac Res. Inst.*, 1959-60, p. 23
- <sup>31</sup> Kamath, N. R., & Mainkar, V. B., *J. scient. ind. Res.*, 1955, **14B**, 337
- <sup>32</sup> Whitemore, W. F., Weinberger, H., & Gardner, W. H., *Ind. Engng Chem. analyt. Edn*, 1932, **4** (1), 48
- <sup>33</sup> Murty, N. N., *Bull. Indian Lac Res. Inst.*, 1937, No. 29
- <sup>34</sup> Kamath, N. R., & Mainkar, V. B., *J. scient. ind. Res.*, 1955, **14B**, 555
- <sup>35</sup> Raudnitz, H., Petru, F., & Schindler, H., *Ber. dt. chem. Ges.*, 1935, **68B**, 1675