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Contribution to the study of the bleaching of lac.

PART I.

The action of the chlorine-bleach on the resin constituents of lac.

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BY

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# CONTRIBUTION TO THE STUDY OF THE BLEACHING OF LAC.

## PART I.

### THE ACTION OF THE CHLORINE-BLEACH ON THE RESIN CONSTITUENTS OF LAC.

BY

N. N. MURTY.

#### INTRODUCTORY.

The colouring matter and impurities associated with lac preclude its use, as such, in paints and laquers, where lightness of colour is of importance. During the washing of stick lac most of the woody matter, insect remains and the water-soluble dye, laccic acid, are eliminated and, during the conversion of seed lac into shellac, the unwashed animal and woody impurities, being infusible, remain in the bag. The residual laccic acid is converted into a dark coloured constituent of the phenolic type (13) which is insoluble in water.

There is also another colouring matter, namely erythrolaccin, which is more intimately associated with the resin and which remains practically unchanged during the conversion of seed lac into shellac. Several methods have been developed to render lac colourless, of which the most important and widely used is bleaching with chlorine.

The quantity of erythrolaccin present in lac is very small, probably about 2 per cent. (5). There is present about 2 per cent. laccic acid in stick lac (17), and, hence, a far less quantity in seed lac. Nevertheless, for obtaining a white bleached lac, a far larger quantity of the sodium hypochlorite solution is required than is necessary for bleaching the colouring matter alone. It has been shown that the nitrogenous matter (11) derived from the body of the lac insect in the case of seed lac, and the orpiment in T.N. shellacs (12) consume a good proportion of the added bleach. The resin constituents of the lac itself are acted upon by the chlorine bleach and it is the purpose of this paper to show to what extent, and in what respects the resin constituents are affected.

**Available knowledge on the constitution of lac.**—In order to appreciate the nature of attack of the chlorine-bleach on the resin constituents, it will not be out of place to give here a brief review of the composition of shellac. The 'pure resin', *i.e.* the ether-insoluble portion, which forms about 75 per cent. of the lac resins, consists of various hydroxy acids among which only two, aleuretic acid (7) forming about 30 per cent. of the pure resin and shellolic acid (8) about 10 per cent. have been identified. The rest (60 per cent.) of the acids are supposed to be hydroxy acids similar to shellolic acid; but their constitutions have not been definitely established. Aleuretic acid is a (completely saturated) trihydroxy palmitic acid, and has the following formula:  $\text{HOCH}_2(\text{CH}_2)_5\text{CH}(\text{OH})\text{CH}(\text{OH})(\text{CH}_2)_7\text{COOH}$ . Shellolic acid is a dihydroxy dicarboxylic hydro-aromatic acid which has the following formula:  $\text{C}_{13}\text{H}_{16}(\text{OH})_2(\text{COOH})_2$ . The structural formula of Harries and Nagel for shellolic acid consists of a double bond in the neucliar position because, according to their observation, shellolic acid while not decolourising bromine solution, discolours permanganate solution, and also forms an ozonide. From the observation that pure shellolic acid does not give an iodine value, Bhattacharya (2) concludes that there is no unsaturation in shellolic



acid and that the structure of shellolic acid must be different from that suggested by Harries and Nagel.\* But since 'pure resin' has an iodine number the unsaturation probably exists mainly in the yet unidentified acids.

The above resin acids form the bulk of the resin constituents of 'pure resin'. No alcohol has been identified and, if present at all, may be found only in traces. It is postulated that these resin acids are present in shellac in various combinations—*Viz.* Lactide, Lactone, anhydride and either—giving rise to the different resin components. In the ether-soluble portion of lac, Tschirch and Lüdy (21) have identified aleuritic acid and mono-hydroxy palmitic acid. They have also reported the presence of dihydroxy palmitic acid. Gupta (6) was unable to confirm the above results. He has, however, demonstrated the existence of palmitic acid in the decomposition products of lac. Since the ether-soluble resin exhibits an iodine value, some unsaturated acids must also be present in this portion.

In lac, there is also present a wax (or waxes) which is a true ester consisting of saturated acids and alcohols. Verman and Bhattacharya (23) regard that the various resin constituents of lac are intimately combined, being present in a solid solution of one in the other.

**The Nature of Bleaching treatment.**—From the above summary of the constitution of lac it may be expected that oxidation, addition and/or substitution of chlorine would take place during bleaching. Also, from the fact that alkali easily hydrolyses lac to a sticky mass and hydrochloric acid converts it into an insoluble aggregate, it will be seen that bleaching such a delicate resin with sodium hypochlorite is a drastic treatment, aptly described as the 'sledge hammer method'—and calls for great caution.

In the publications of previous investigators on the subject of bleaching, some data are available which show that changes in the chemical constants of lac take place. But systematic investigation into the nature and mechanism of the action of bleach on the resin constituents of lac had not been undertaken so far. In this study an attempt has been made to follow the changes in the chemical constants of lac under all possible experimental conditions met with in bleaching. A brief description of the methods employed in evaluating the several constants such as acid value, saponification value, hydroxyl number etc. is given below:—

#### Description of Methods.

**Acid value.** (24)—1 gm. of lac is dissolved in 25 c.c. of 95% alcohol and titrated against N/10 alcoholic potash with thymol blue as external indicator, and the amount of KOH in mg. required to neutralise the acids in 1 gm. of lac is designated as the Acid Value.

**Saponification value.** (26)—1 gm. of lac is treated with 25 c.c. of N/2 alcoholic potash for 2.5 hrs. on a water bath under reflux, and the excess of alkali is back titrated against N/2 HCl. The amount of KOH in mg. required to saponify 1 gm. of lac is called the saponification value. In the case of bleached lac, however, as part of the KOH is used up in reacting with the chlorine, the saponification value obtained by the above method is only apparent. The true (corrected) saponification value is obtained by employing N/2 nitric acid for titrating the excess of alkali, in place of N/2 HCl, then determining the

\* Recent work of Nagel and Mertens (14) indicates shellolic acid to be a derivative of tricyclic sesquiterpene



potassium chloride in the neutralised solution, and finally subtracting the KOH-equivalent of this chloride from the 'apparent saponification value'.

*Ester value.*—The difference between the saponification value and acid value is referred to as the ester value. It must be remembered that, since no alcohols are present in lac, the ester value refers to the lactide and other forms of interlinking of the hydroxy acids.

*Chlorine content.*—The method described by Heller (9) of treating lac with KOH in benzyl alcohol solution was found to give too high values. Hence a modification of the Stephanow's method (20) was adopted. The chlorine content is expressed as gms. of chlorine present in 100 gms. of bleached lac.

*Iodine value.*—Wijs' method as developed by Langmuir (10) for shellac was used. The iodine value represents in percentage the amount of iodine absorbed by lac. In the case of insoluble bleached lac samples, a drop of concentrated hydrochloric acid was used to bring it into solution in acetic acid. In these cases the iodine values obtained are too low by 1-2 units, possibly due to the addition of HCl at the double bond. Hence such values are only of comparative significance and have been marked with asterisks in the tables.

*Hydroxyl Number.*—The method of Normann as described in a paper (13) by Nagel and Körnchen was employed. Owing to the troublesome nature of the method and difficulty encountered in completely freeing the acetylated product from acetic anhydride, the hydroxyl number was not determined for all samples. If we assume that during acetylation, complete hydrolysis (acetolysis) would take place and that the OH group which forms a part of the carboxyl group would not be acetylated, the difference between the saponification value after acetylation (referred to in the tables as "total acetyl value") and the saponification value before acetylation, would represent the hydroxyl number. In the table it is these values that are given under hydroxyl number.

**Experimental Procedure.**—*Series I.*—A 10 per cent. cut of Kusum shellac in 1 per cent. sodium carbonate solution was prepared by dissolving at 60-65°C for 2 hrs. on a water bath. The solution was filtered, and 250 ccs. of the filtrate were taken separately in beakers and different quantities of sodium hypochlorite solution were added in small lots to these as noted in table I. The bleaching was conducted at 35°C for a total period of about 18 hours, at the end of which the lac was precipitated from all the solutions by acidifying with dilute sulphuric acid, washed thoroughly, and dried in a vacuum desiccator. The various analytical constants were determined as detailed above.

*Series II.*—In this series of experiments the same Kusum shellac was taken and the same procedure was followed as in series I, but instead of precipitating the bleached lacs all at the same time, the precipitation was done as soon as the bleach in each beaker was consumed. Thus, unlike the experiments in the first series, no chance was given for hydrolysis to proceed in absence of free chlorine. The results are summarised in table II.

*Series III.*—In this set of experiments the procedure adopted was the same as in series II but, instead of shellac, a seed lac of medium bleaching quality was chosen. The results are incorporated in table III.



TABLE I.

*(Progressive bleaching of Kusum Shellac, F 364.)*

No. of bleached sample.	Bleach (3% Cl.) added for 10 gm. lac. cc.	Acid value.	Sapon. value (apparent).	Ester value (apparent).	Chlorine content. %	Iodine value. %	Iodine value + Iodine equivalent of Cl. content. %	Colour grade.*
1	0.0 (Control)	76.6	224.0	147.4	...	14.2	14.2	...
2	13.0	83.4	243.8	160.4	0.654	10.4	12.7	G2
3	18.0	84.4	250.8	166.4	1.100	9.7	13.6	G3
4	28.0	...	268.9	...	1.550	9.2	14.8	G5

TABLE II.

*(Progressive bleaching of Kusum Shellac F 364.)*

1	Original (wax-free basis.)	74.2	229.6	155.5	...	14.6	14.6	...
2	0.0 (Control)	72.2	224.2	152.0	...	13.8	13.8	...
3	10.0	75.2	254.0	178.8	0.655	10.0	12.4	G4
4	20.0	82.9	260.0	177.1	1.035	8.6	12.3	G4
5	30.0	89.2	267.4	178.2	1.309	8.4	13.2	G5
6	30.0 (with wax)	86.4	261.4	175.0	1.206	8.7	13.0	G5
7	No. (6) on wax-free basis.	89.8	271.5	181.8	1.253	9.0	...	...

TABLE III.

*(Progressive bleaching of Seed Lac.)*

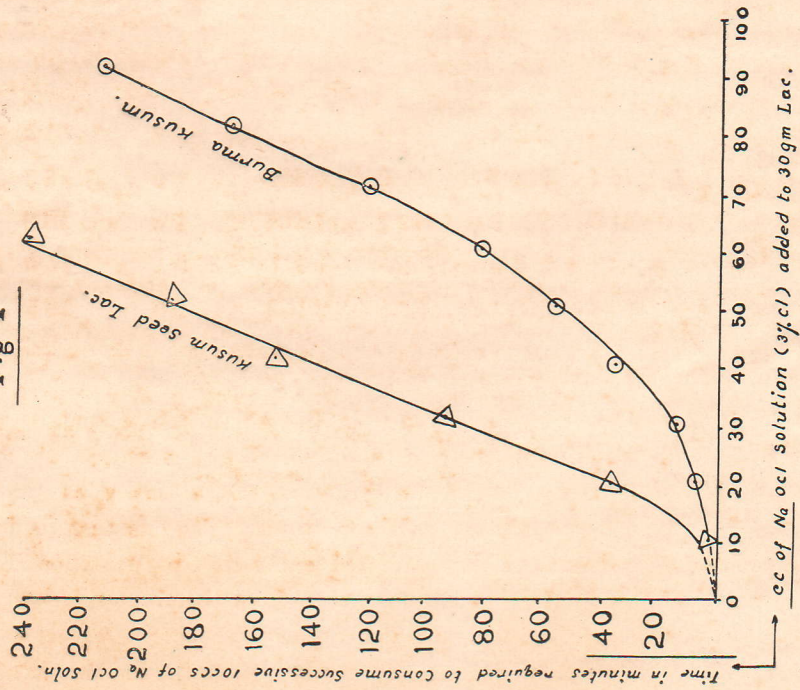
1	0.0 (Control)	71.4	232.1	154.0	...	14.9	14.9	...
2	21.0	79.1	244.1	165.0	0.932	9.9	13.2	G3
3	28.0	81.5	250.8	169.3	1.206	9.5	13.8	G4
4	35.0	...	258.5	...	1.617	9.1	14.9	G4
5	43.0	85.6	268.3	182.7	2.103	9.0	16.5	G4

\*N.B.—The bleached samples are arbitrarily divided into six grades based on their colour, and the palest sample is given the highest numerical index.

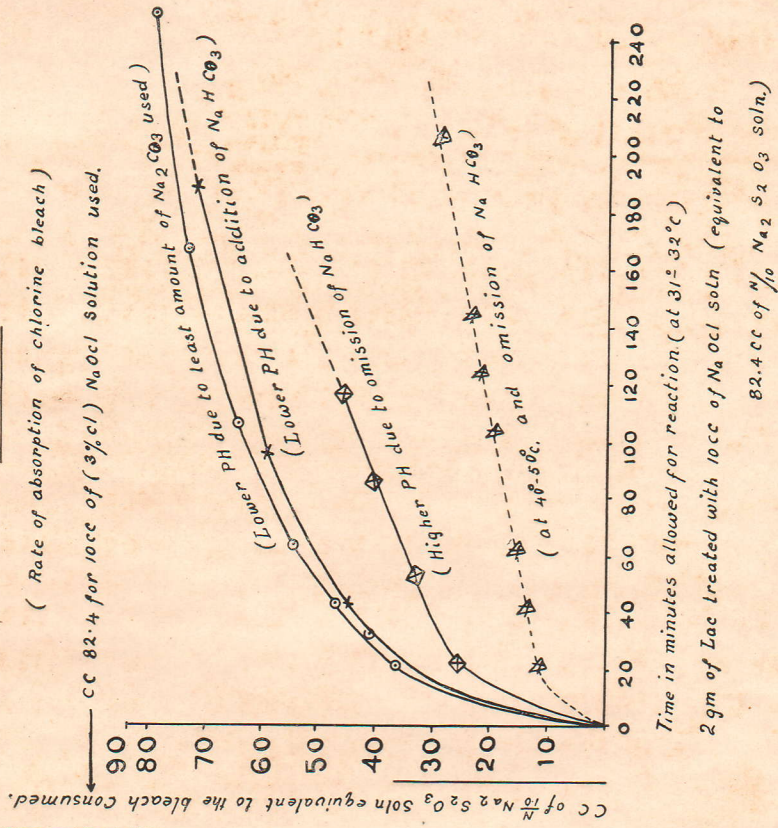
**Discussion of results.**—It will be seen from the above tables that as the lac is progressively bleached, the chlorine content goes on steadily increasing, while the iodine value drops down fairly rapidly at first, and continues to decrease slowly as the bleaching is continued and, finally, tends to attain a minimum value. The fact that the iodine value decreases shows that the molecules are getting saturated either due to oxidation, or addition of chlorine at the double bond. It will also be seen from the above tables that both the acid value and the (apparent) saponification value increase as bleaching progresses. But this increase in saponification value does not exactly correspond to the increase in acid value as reported by Whitmore and Weinberger (26), but far exceeds the increase in acid value.



**Fig 1**



**Fig 2**





Hence, contrary to their statement, the (apparent) ester number also increases. It is, no doubt, true that a part of the increase in saponification value is shown up in the increase in acid value. One of the earlier investigators has suggested that the locked up mineral acid is responsible for the increase in acid value (22). This explanation does not appear tenable because, in the bleached lac samples examined, hardly any trace of mineral acids could be detected. On the other hand, a part at least of the increase in acid value could be due to hydrolytic splitting of the lactide and other forms of linkages. The extent of this hydrolysis depends upon experimental conditions. From tables I and II it will be seen that bleached lac samples which were precipitated after long contact with the alkali of the bleaching medium show higher acid values than those precipitated as soon as free chlorine was absent in the bleaching medium. The lowering of the (corrected) ester value with progressive bleaching also supports the hydrolysis theory.

With progressive addition of bleach, the colour of the bleached lac goes on improving up to a certain stage, beyond which the improvement is not commensurate. From table III, it will be noticed that the changes undergone by seed lac during bleaching are of the same type as undergone by shellac, except for the fact that the colour of the bleached seed lac is poorer than that of bleached shellac, despite the extra bleach used. This, as has been pointed out in an earlier paper (11), is due to the impurities (the dye and the nitrogenous substances) associated with seed lac which consume a portion of the bleach.

**Kinetics of the chlorine-bleaching.**—When to a solution of lac in soda, hypo-chlorite solution is added in small lots (each successive lot being added after ensuring the absence of free chlorine from the previous addition with the help of starch iodide paper), the first lot is consumed with great avidity in a short time, the next lot takes much longer time, and the one subsequent to this still greater, and so on. Poor bleaching lacs consume the hypo-chlorite at a much faster rate than good bleaching ones. These results are shown graphically in Fig. I. It is to be noted, however, that although the rate of absorption materially comes down with progressive bleaching, the absorption of hypochlorite never completely ceases. The rate of absorption is also dependent on the quantity of bleach added, *i.e.* the concentration of hypochlorite present in the bleaching vat at the time; for, it has been observed that in a given time, more hypo-chlorite is absorbed when rapid additions of hypochlorite are made so that the lac is always in contact with excess of bleach.

If an excess of hypochlorite (nearly twice the quantity normally required) is added to the shellac solution in one lot, the whole of it is consumed in course of time, although the rate of consumption decreases to a more or less steady value after an initial high rate. These results are graphically illustrated in Fig. II. It will also be seen from the curves that the rate of absorption of bleach is greater at lower PH, presumably due to the greater availability of free hypochlorous acid at lower alkalinity.

**Effect of temperature.**—Two series of progressive bleaching experiments were done—one at 40°C and the other at 4°-6°C—in order to study the effect of temperature on the rate of consumption of bleach, and also on the nature of the bleached product. The procedure was the same as that adopted in previous experiments. In tables IV and V are incorporated the results of the experiments.



TABLE IV.

(Progressive bleaching of *Kusum shellac*, F428, at 40°C.)

Sample No.	Bleach (3% Cl) for 10 gm. lac. cc.	Time taken for consuming bleach. hrs.	Acid value.	Sapon. value (apparent) (corrected)	Sapon. value (corrected) (apparent)	Ester value (apparent)	Ester value (corrected)	Chlorine content %	Iodine value.	Iodine + Iodine equivalent of Cl. content. %	Colour grade.
1	0.0 (control)	...	62.2	222.8	222.8	160.6	160.6	...	13.2	13.2	...
2	13.0	4	63.8	239.1	228.0	175.3	164.2	1.003	8.3	11.9	G4.5
3	27.0	20	69.5	255.2	...	185.7	...	1.300	7.3	12.0	G5.0
4	27.0	20 (but pptd. after 80 hrs.)	77.4	245.5	235.9	168.1	158.5	0.893	8.8	12.0	G3.3

TABLE V.

(Progressive bleaching of *Kusum shellac*, F428, at 4°-6°C.)

1	10.0	49	56.0	235.8	226.5	179.8	170.5	0.760	7.2	9.9	Pinkish
2	20.0	170	59.5	244.8	229.3	185.3	169.8	1.113	6.8	10.8	Paler than (1)
3	30.0	350	66.1	255.1	231.8	189.0	165.7	1.435	6.5	11.6	Paler than (2)

N.B.—At 35°C, the corresponding times for consumption of 10, 20 and 30 cc of bleach were 3.7, 12.2 and 45.4 hours respectively.



A glance at the above tables will show that the rate of absorption at 4°-6°C is enormously slow when compared to that at 35° or 40°C. Besides, the colour of the lac is not completely discharged, the dried bleached lacs exhibiting a pinkish hue. On the other hand, in the series bleached at 40°C, it was noticed that even the partially bleached lac had attained almost the same lightness of colour as the completely bleached one. Thus, it would appear that the action of the hypochlorite solution on the colouring matter present in lac is quicker and more complete at higher temperatures than at lower temperatures. However, when bleached at lower PH or in presence of excess of the hypochlorite solution, even at lower temperatures a very light coloured bleached lac can be obtained. From the above tables it will also be observed that the acid values are lower and the (apparent) ester values are correspondingly higher when bleached at 5°C than when bleached at 40°C. Apparently, at lower temperatures, the hydrolytic action of the alkali is slower than at higher temperatures. The reason for the lower Iodine Values obtained when bleached at 4°-6°C will be given later. Except for the above differences, the action of the chlorine bleach at low temperatures is of the same type as has been observed in previous experiments.

**The rate of action of the chlorine-bleach on the resin constituents.—**

The procedure for preparing the solution was the same as in previous experiments. But, instead of adding the bleach in small lots, the required quantity was added in one lot, and aliquots were taken at definite time intervals and acidified to obtain bleached lac samples in their various stages of bleaching. The chemical character of these bleached samples was examined as before. In tables VI and VII are embodied the results of the experiment.

It is clear from the tables VI and VII that the resin constituents are the first to succumb to the action of the bleach. The maximum chlorination takes place within the expiry of fifteen minute; but the attack on the colouring matter is slower, requiring more than an hour to effect maximum bleaching. After that, the oxidative and chlorinating action cease, and the action of the alkali begins to manifest itself.

When lac is treated with hypochlorite solution in one lot as in the above experiments, the life\* of the bleached samples is very much shortened. In the above series of experiments, the samples which were precipitated earlier from the solution had lost their solubility in alcohol in a few days. But those samples which were precipitated later had comparatively long lives. The high acid values obtained in the case of the latter indicate the extent to which hydrolysis has taken place, owing to long contact with alkali during bleaching.

**The effect of alkalinity of the bleaching medium.—**In order to confirm whether or not hydrolysis accompanied bleaching, control experiments were carried out at 40°C with the addition of sodium hydroxide to the lac solution equivalent to the range of free alkalinity prevailing in bleaching liquors. In table VIII are given the results of the experiment which conclusively prove that hydrolysis is one of the factors to contend with, in bleaching.

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\* The period during which the alcohol solubility is retained.



TABLE VI.

(Time course of bleaching of *Kusum shellac*, F428, at 30°C.)

Sample No.	Bleach (3% Cl.) for 10 gm. lac. cc.	Time allowed for reaction. hrs.	Acid value.	Sapon. value (apparent).	Sapon. value (corrected).	Ester value (apparent).	Ester value (corrected).	Iodine value.	Chlorine content.	Cl. which reacts with alcoholic KOH. %	Colour grade.
1	28.0	0.25	...	265.3	234.6	...	...	...	2.064	1.938	G4.2
2	"	0.75	...	264.1	237.0	...	...	7.7*	1.957	1.710	G4.5
3	"	5.0	...	258.8	232.3	...	...	8.1*	1.847	1.672	G5.3
4	"	15.0	...	257.5	232.8	...	...	8.3*	1.778	1.558	G5.0
5	"	37 days	95.9	244.2	228.3	148.3	132.4	8.5*	1.178	1.007	G4.0

TABLE VII.

(Time course of bleaching of *Kusum shellac*, F428, at 35°C.)

1	25	0.25	...	261.5	238.6	...	...	6.2*	1.667	1.444	G4.2
2	"	2.25	...	258.8	237.0	...	...	6.3*	1.560	1.376	G4.8
3	"	15.0	78.3	254.4	236.1	176.1	157.8	7.0* (8.1)	1.378	1.157	G4.5
4	"	100.0	83.0	251.8	236.6	168.8	153.6	7.1* (8.8)	1.124	0.960	G4.5



TABLE VIII.

NaOH added for 10 gms. of shellac (F428) ... o.o. cc. (Control)	25 cc. of 0.2 N	30 cc. of 0.3 N	25 cc. of 0.4 N
Acid value of the pptd. lacs ...	63.5	66.5	71.3
lacs ...	...	...	81.3

The alkalinity of the bleaching medium brings about other changes besides hydrolysis. An examination of tables IV, VI and VII will reveal that as the action of the alkali progresses (after the cessation of the action of chlorine), a decrease in the chlorine content takes place accompanied by an increase in the iodine value. Evidently chlorine is being split off, probably initially as HCl and finally as NaCl creating again unsaturation in the resin molecules. Such a reaction is to be expected, especially in an alkaline medium. Apart from a lowering in the chlorine content, there appears to be a slight lowering in the real saponification value. It will also be noticed that as the action of the alkali proceeds, the colour of the bleached lac tends to return.

**The action of bleach on the colouring matter.**—The action of the chlorine bleach on the colouring matter of lac has not been definitely ascertained. Schwalbe and Wenzl (18) consider that in the case of cotton bleaching, the improvement in colour is due to the oxidative action of the chlorine bleach. Such an oxidative action does take place in the colouring matter of lac also as, by the action of sodium perborate, the colour of the alkaline shellac solution can be materially reduced, and an alkaline solution of laeacetic acid can be rendered colourless by the action of hydrogen peroxide alone. On the other hand, even 30 per cent hydrogen peroxide is unable to bring about any change in the colour of the erythrolaccin present in lac, although, as will be evident from table XIV, it is equally effective as sodium perborate in bringing about oxidative changes in the resin constituents of lac. Erythrolaccin, according to Tschirch and Lüdy (21), is a methyl tetrahydroxy anthraquinone.\* From the action of the perborate, it would appear that oxidation alone would be sufficient to destroy the colour due to erythrolaccin in shellac. But the ease with which chlorine bleaches the colouring matter in shellac, and the return of colour as chlorine is split off suggest that chlorine enters the molecule of erythrolaccin. The return of colour in the dry bleached lac on exposure to light and/or heat is also probably due to the splitting off of chlorine from the chlorinated erythrolaccin. It is interesting to note in this connection that the perborate bleached lac does not darken on exposure to heat, unlike chlorine-bleached lac.

The darkening or return of colour in the chlorine-bleached lac is not due to a return of the oxidation product back to the original erythrolaccin, since the alkaline solution does not exhibit the characteristic pink colour. On the other hand the reduction of erythrolaccin (with aluminium or zinc in alkaline solution) to the oxanthranol derivative is easily reversed by even atmospheric oxygen, restoring the pink colour of the shellac solution. Since the pale greenish-yellow colour of fresh lac grains changes into orange-red on exposure to light and air, it must be supposed that the lac insect secretes the reduced oxanthranol product which, on atmospheric oxidation, is converted into erythrolaccin.

\* Recent work (unpublished) of the U. S. Shellac Research Bureau throws doubt on the above constitution of erythrolaccin.



From the tables VI & VII, it will be clear that the rate of action of the chlorine-bleach on the colouring matter is slower than on the resin acids, and is more effective and more complete at higher temperatures than at lower temperatures. Also the bleaching of the colour is quicker and more complete when excess of bleach is added and the PH of the medium is kept low. Unfortunately the last two factors are not conducive to the long life of the bleached product.

**The mechanism of the action of sodium hypochlorite on the resin constituents.**—An examination of the tables IV, V, VI and VII will reveal that bleaching brings about an increase in the saponification value of lac. The corrected saponification value of bleached lac is between 232—238, while that of the control sample is between 222—228. This increase is probably the result of oxidation of the resin molecules by hypochlorite, by which more carboxyl groups are generated. Whitmore, Weinberger and Gardner (26) believe that these carboxyl groups are formed at the expense of the existing hydroxyl groups. According to this assumption the hydroxyl number should decrease on bleaching. In tables IX and X are given the hydroxyl numbers for bleached and control lacs.

TABLE IX.

(Hydroxyl number of bleached lac).

No.	Sample.	Bleach (3% Cl.) added for 10 gm. lac.	Total acetyl value (apparent)	Sapon. value (apparent)	Hydroxyl number.	Hydroxyl per cent.
		cc.	mg/gm.	mg/gm.	mg/gm.	%
1	Kusum, F428	0.0 (control wax-free)	468	233	235	7.13
2	„	22.0 „	481	254	227	6.88
3	„	20.0 „	476	248	228	6.91
4	Seed lac	bleached	480	240	240	7.28

TABLE X.

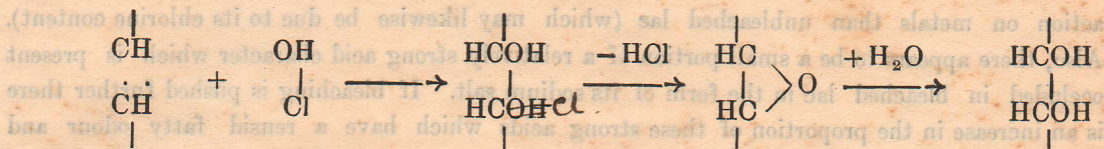
(Hydroxyl number with progressive bleaching).

1	Kusum (F428)	0.0 (control wax-free)	469	225	244	7.40
2	„	13.0 „	487	239	248	7.52
3	„	27.0 „	484	255	229	6.94
4	„	27.0 (hydrolysed)	473	246	227	6.88

From the above tables it will be seen that the hydroxyl number of bleached lac is generally somewhat lower than the control. It is probable that, as a first step in the oxidation at the double bond, fresh hydroxyl groups are generated, while, at the same time, some of the existing hydroxyl groups undergo oxidation to the carboxyl groups. That oxidation (hydroxylation) takes place at the double bond will be evident from the following considerations. If the decrease in unsaturation which takes place in the resin molecules during chlorine bleaching was only due to addition of chlorine at the double bond, then the sum of the iodine value and the iodine equivalent of the chlorine content of bleached lacs must be equal to the iodine value of the respective unbleached lacs. But, from the tables, we find that the sum is always less than the iodine



value of the unbleached lac till we reach a stage of over-bleaching. Hence the extra reduction in unsaturation must be due to oxidation (hydroxylation) at the double bond. Other bleaching agents like hydrogen peroxide, sodium perborate and potassium permanganate effect oxidation at the double bond, as will be evident from the low iodine values (table XIV). In the case of hypochlorite bleaching, the oxidation at the double bond can be pictured to take place in the following manner\* :—



The next step in the oxidation of the OH group added on to the double bond gives rise to a keto group if no rupture in the molecule takes place. Reverting to the oxidation of existing OH groups, the primary alcoholic group which is theoretically more easily susceptible to oxidation, exists in aleuritic acid, one of the known constituents of lac. But from normal bleached lac the usual quantity of aleuritic acid (21-23%) can be separated by saturating with 6 normal caustic potash†. Hence, further oxidation to carboxyl groups is probably mainly confined to freshly generated (nascent) OH groups in the case of chlorine-bleaching. This would lead to a rupture of the molecules at the double bond, giving rise to dibasic acids containing smaller number of carbon atoms.

**Molecular Weight of Bleached Lac.**—Since the unsaturation in shellac is very small, even if fission of some of the unsaturated molecules took place due to oxidation during bleaching, it would hardly have a noticeable effect on the molecular weight. Besides, the chlorine content and the polymerising conditions to which the lac is exposed during the bleaching operation, tend to raise the molecular weight of bleached lac. A comparative idea of the average molecular weights of bleached and unbleached lac can be had from table XI.

TABLE XI.

(Molecular weight of bleached lac.)

Material.	Mol. wt. modified Rast's method.	Equivalent wt. (from acid value.)	Acid value.	Reference.
(Control) soda pptd. Khair lac, (dry, wax containing) ...	891	837	67.0	Author
Bleached Khair lac (dry, wax containing) ...	949	719	78.0	"
Shellac ...	814‡	...	...	Benedict (1)
Shellac ...	983	790	70.8	Gardner (4)
Bleached lac ...	1000‡	...	...	Gardner (3)

\* Verman and Bhattacharya (Technical Paper No. 6, London Shellac Research Bureau) consider that HOCl adds to oxygen of the ether-linkages in the shellac molecule to give oxonium compounds. Since the hydroxyl number of bleached lac is not higher than that of unbleached lac this reaction probably proceeds only to a limited extent.

† Pure aleuritic acid when treated with sodium hypochlorite solution under bleaching conditions does not give any oxidation products.

‡ Method not known.



It will be seen that bleached lac has a higher molecular weight than unbleached (control) lac. The equivalent weight of bleached lac, on the other hand, is smaller. This indicates that dibasic acids are probably generated in the process of bleaching. There is also indirect evidence to show that bleached lac is richer in dibasic acids. From the metal content of heavy metal soaps of bleached lac Gardner, Whitmore and Harris (3) conclude that bleached lac behaves as a dibasic acid. Bleached lac is characterised by a slightly stronger corrosive action on metals than unbleached lac (which may likewise be due to its chlorine content). Also, there appears to be a small portion of a relatively strong acid character which is present occluded in bleached lac in the form of its sodium salt. If bleaching is pushed further there is an increase in the proportion of these strong acids which have a rensid fatty odour and which remain in a dissolved or suspended condition even on acidifying, unless acidification or salting out is carried further. Under these circumstances, there is a considerable loss in the yield of the bleached product, and the lac may be said to be over-bleached.

**Loss in the yield of bleached lac.**—In normal bleaching, the loss is about 3 per cent, as will be seen from table XII.

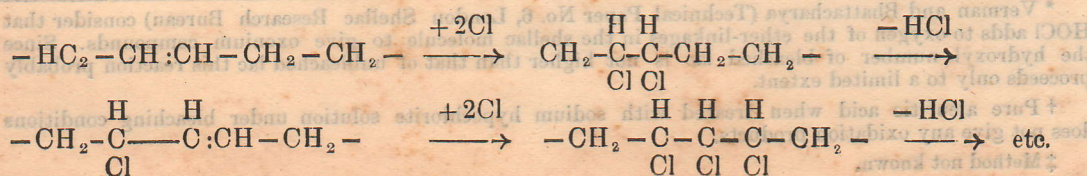
TABLE XII.

(Loss during bleaching.)

No.	MANNER OF BLEACHING.	Loss.	
			%
1.	Desiccated Khair shellac dissolved in soda & pptd. (control) ...	...	3.80
2.	Desiccated Khair shellac bleached at 35°C ...	...	3.55
3.	Desiccated Khair shellac bleached at 35°C ...	...	2.80
4.	Desiccated Khair shellac bleached at 70°C towards the end ...	...	2.75

It can, therefore, be assumed that normal bleaching does not involve any characteristic removal of some of the resin constituents during washing and thus render the bleached lac unrepresentative of the unbleached (control) lac. In the case of considerable over-bleaching or hydrolysis, however, the above assumption does not hold good.

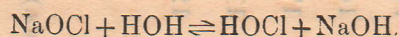
**Mechanism of the entry of chlorine into the Resin Molecules.**—It would appear from the foregoing discussions that oxidation would take place at the double bond, and that all the chlorine found in bleached lac cannot be present as addition product. Since, with progressive bleaching, chlorine content continues to increase, substitution should have taken place side by side. The mechanism of the entry of chlorine into the molecules, without assuming direct substitution can be explained on the analogy of the chlorination of rubber (16) as follows:—





The chlorine enters the molecule at the double bond. Then, through loss of HCl in presence of alkali, a new double bond is created with the neighbouring carbon atom and chlorine again adds to this new double bond; thus, through alternate addition of chlorine and splitting off of hydrochloric acid, there results a product which is in effect, a substituted compound. If the entry of chlorine into lac takes place according to this theory, then a momentary existence of free chlorine, derived secondarily from HOCl, should be assumed.

As bleaching progresses, and HOCl is removed by reacting with lac, the alkalinity of the bleaching medium increases according to the following equation :



If the bleached lac is allowed to remain in this increased alkaline medium in absence of HOCl, the iodine value of the bleached lac begins to increase and the chlorine content begins to decrease (*vide* tables IV, VI and VII). From table XIII it will be seen that in the case of lac treated with NaOH during bleaching, the chlorine content becomes very low and the iodine value exceeds the normal value of unbleached lac. These changes may take place due to either of the two reasons: (i) elimination of Cl in the form of HCl, the hydrogen being derived from the neighbouring carbon atom and thus creating fresh unsaturation as explained above (ii) Production of ethylene oxide types (as pictured on page 12) which are capable of showing pseudo-unsaturation. (19).

Towards the end of bleaching when the alkalinity of the medium is very high, this creation of unsaturation through splitting off of HCl more or less counter balances the saturating effect of the addition reaction of HOCl, thus offering an explanation as to why the iodine value of lac cannot be made to disappear completely by bleaching. Experimental conditions determine the minimum iodine value obtainable during bleaching. With low alkalinity or by carrying out the bleaching at low temperatures, so as to mitigate the action of alkali, the iodine value can be very much lowered.

Apart from an increase in unsaturation, the alkalinity appears to cause a small reduction in the carboxyl content of the bleached resin molecules as will be noticed from the (real) saponification values shown in tables VI and VII. It is probable that during the washing of the precipitated bleached lac a portion of the bleached lac constituent of a strongly acid character is washed out. It is also likely that carbon dioxide is split off from the carboxyl groups in a manner similar to the splitting off of HX and CO<sub>2</sub> from  $\beta$ -halogenated acids in presence of alkali, or, if more than one carboxyl group is attached to the same carbon atom, it is not unlikely that carbondioxide is split off. Wolff (25) has observed a reduction in the saponification value and a more marked reduction in the acid value on merely dissolving and precipitating shellac from alkaline solutions. Experiments done in this laboratory, the results of which are recorded in table XV, confirm the above observation. The same explanations as offered in the case of bleached lac probably hold good, even here.



TABLE XIII.

*(The effect of alkalinity of the bleaching medium on the nature of bleached lac.)*

No.	Sample.	Bleach (3% Cl) added for 10 gm. lac. cc.	Acid value.	Sapon. value (apparent).	Ester value (apparent).	Chlorine content. %	Iodine value. %	Iodine value + I. equivt. of Cl. content. %	Colour grade.	Remarks.
1	Kiri ...	52.0	82.8	254.4	171.6	1.342	10.7	15.5	G2	
2	Burma Kusum seed lac ...	45.0	81.6	249.7	168.1	0.690	11.6	14.1	G2	
3	Shellac ...	20.0 + Na <sub>2</sub> SiO <sub>3</sub>	86.6	250.9	164.3	1.123	10.3	14.3	G4	
4	Shellac (Kusum)	Bleach + NaOH	115.5	210.7	105.2	0.326	16.5	17.7	G0.5	(highly hydrolysed)
5	" ...	"	99.7	247.5	147.6	0.907	8.5	11.8	G1	
6	" ...	19.0 + 5% Na <sub>2</sub> CO <sub>3</sub>	88.1	250.1	162.0	0.833	9.3	12.3	G1	

TABLE XIV.

*(The nature of changes brought about by other oxidising agents.)*

Number.	Bleaching treatment.	Acid value.	Sapon. value.	Ester value.	Iodine value. %	Colour.
1	Control (Kusum shellac, F509)	...	225.8	156.0	13.3	Orange
2	KMnO <sub>4</sub> (mild treatment)	...	238.2	164.5	12.0	Brown
3	Na BO <sub>3</sub> ...	...	258.8	154.0	7.3	Lemon yellow
4	H <sub>2</sub> O <sub>2</sub> (30%) ...	...	251.8	167.0	8.4	Orange



TABLE XV.

*(Effect of precipitating shellac from sodium carbonate solution.)*

Sample.	Acid value.	Sapon. value.	Ester value.
Kusum (F364) original, (wax free basis) ...	74.2	229.6	155.4
„ „ (pptd., wax-free) ...	72.2	224.2	152.0
„ (F509) original ...	69.8	225.8	156.0
„ „ pptd. ...	67.9	222.7	154.8
Khair original ...	71.6	.....	.....
„ pptd. ...	67.0	.....	.....

A separation of the resin constituents of bleached lac and a study of their constitution will throw further light on the changes brought about by the chlorine bleach. Ether extracts nearly the same quantity (25-30%) of soft resin from bleached lac as from unbleached lac, and chlorine is found to be present in both soft and hard resin portions, with consequent reduction in the iodine values of both portions. As already mentioned, the normal quantity of aleuritic acid obtainable from unbleached lac can also be obtained from bleached lac, thus indicating that this constituent remains unaffected during bleaching. When a complete knowledge of the constitution of the various components of lac is available it will be easier to obtain a clear conception of the action of chlorine-bleach on lac. A study of the oxidative changes brought about by the chlorine-bleach would itself help in understanding the nature and constitution of lac, besides helping to place the industry on a scientific footing.

It would also be of interest to study the changes brought about in the physical properties of lac as a result of bleaching. Carbon decolorised shellac solution has a specific (dextro) rotating power at 25°C equal to 63°, 8'. On chlorine-bleaching the rotation is not very much altered, being 51°, 11'. Unbleached lac exhibits ultraviolet fluorescence on account of the colouring matter present in it. Bleaching destroys this colouring matter, hence bleached lac does not exhibit any fluorescence. Also, unlike unbleached shellac, it appears to have lost the property of acquiring static electricity. Its use in the electrical industry for superior insulation is ruled out on account of its chlorine content. But a study of the film properties indicates that bleaching has done very little damage to lac as a material for protective coating.

### Summary.

1. A study of the chemical changes undergone by the resin constituents of lac during bleaching with hypochlorite solution has been made.
2. Bleaching is accompanied by an increase in the acid value and an apparent large increase in the saponification value and ester value of lac. On making due allowance for the reaction between the chlorine present in bleached lac and the alcoholic potash used in



saponification, (corrected) saponification and ester values can be calculated. The corrected saponification value of shellac is about five per cent. higher than that of unbleached lac, thus indicating an increase in the carboxyl groups due to oxidative changes brought about by the chlorine bleach. Aleuritic acid, a constituent of lac, does not appear to have been affected in the normal bleaching treatment with hypochlorite. The hydroxyl number generally decreases slightly on bleaching.

3. Chlorine enters into the resin molecules, and its content increases steadily as the lac is progressively bleached, while the iodine value decreases rapidly in the beginning, and then tends to attain a minimum value. The chlorine in bleached lac exists only partly as an addition compound, the excess entering the molecule through substitution.

4. The chemical changes, *viz.* oxidation and chlorination, are brought about in the resin molecules almost immediately after the addition of the bleached agent. But the changes in the colouring matter, although proceeding simultaneously, take some time to attain completion. The rate of absorption of bleach is quicker in poor bleaching lacs than in good Kusum lac, and is further enhanced by employing a higher temperature and lower PH.

5. When bleached lac is allowed to remain in the alkaline solution after all the hypochlorite added has been consumed, the following changes take place, the extent of these changes depending upon the duration, temperature and PH.

- (a) The chlorine content decreases, the unsaturation increases due to splitting off of HCl and the colour of the bleached lac tends to return.
- (b) The acid value increases due to hydrolysis, consequently the ester value decreases.
- (3) The saponification value appears to decrease slightly due, probably, to the splitting off of carbon dioxide from the carboxyl groups or due to removal of some acid constituent of lower molecular weight during washing.

6. A slower rate of attack on the resin molecules by a gradual addition of the bleaching liquor gives a product which is less prone to become insoluble than a rapidly bleached product. Higher alkalinity of the bleaching liquor and other conditions which bring about hydrolysis give a bleached lac which will have a longer life, but which will have the disadvantages of high acid value and poor colour.

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