THE BLEACHING OF LAC.

By M. Venugopalan.

The bleaching of lac is a delicate process dealing with a raw material highly susceptible to physical and chemical treatment. Dry heat above 90° renders the product insoluble in alcohol, and long contact with ether or hydrochloric acid vapour produces the same result. Caustic alkalis hydrolyse the resin with great ease, alkaline carbonates with rather more difficulty, while the employment of oxidising bleaching agents such as chlorine may readily destroy the valuable properties of lac unless the process is strictly controlled. The technical manipulation of so sensitive a product naturally requires skill and scientific supervision if a standard material is to be obtained. The present work was undertaken to determine the conditions favouring economic production of bleached lac on a manufacturing scale.

There are two processes for bleaching, (1) *Physical*, in which the colouring matter is removed from the alcoholic solution of lac through adsorption by animal charcoal or by the action of sunlight on the alcoholic solution of lac, and (2) *Chemical*, in which the colouring matter is bleached by oxidising agents such as chlorine and hypochlorous acid. Reducing agents (sulphurous acid or hydrosulphites) result in the formation of green products, and as the colour is not completely removed they cannot conveniently be employed.

The physical method involves dissolution of seed-lac in alcohol and boiling the solution with well-burnt and recently heated animal charcoal until the filtrate is colourless; the alcohol is then evaporated, leaving the bleached lac. This method does not give a perfectly colourless product and, besides being very costly, the lac obtained in this way is quite altered in its physical properties. Bleaching by sunlight, recommended by some workers, is an ancient practice but is impracticable, both on account of the inefficiency of bleaching and the long period necessary to complete the process.

The essential requirements of a satisfactory method consist in attaining the maximum degree of whiteness with minimum alteration in the hardness and solubility of the product. None of the three indispensable requirements of bleached lac, namely, whiteness, solubility and a degree of hardness enabling the lac successfully to resist the atmospheric influences of temperature and moisture, are attained by any of the physical methods. These three qualities, however, can be achieved to

a maximum extent by chemical processes involving the use of oxidising agents such as chlorine, hypochlorous acid, etc. The present paper deals with this process in relation to the various factors involved, e.g., temperature, time, and concentration. Considerable experience is necessary to reach the highest standard of quality. To attain uniformity in the finished product the operations, which are numerous, distinct and equally important, should be conducted with great precision, slowly and carefully. From the crude material certain mechanical impurities such as insect bodies, fragments of wood, sand, etc., must be effectively removed before the actual bleaching begins.

The operations essential in lac-bleaching may be summarised as follows :—

1. Crushing the raw material to a fine powder to facilitate dissolution.

2. Dissolving the lac in a suitable solvent.

3. Preparing the bleaching agent in required concentration.

4. Treatment of the lac solution with the bleaching agent in optimum proportions and under conditions suitable for strict control.

5. Precipitation and recovery of the bleached lac.

6. Drying the bleached lac and preparing it for the market.

The raw material is ground in a mill to a fine powder so that it may dissolve more easily in the alkaline solution. Care must be taken that the grinding plates do not become heated by friction causing the grains to coalesce and clog the machine.

In selecting a suitable solvent many factors have to be considered. The two solvents usually employed are caustic soda and sodium salts of weak acids such as sodium carbonate, borax, etc. The solutions of the former are not suitable since lac is readily hydrolysed or saponified, losing its characteristic properties, and hence in this investigation dilute solutions of sodium carbonate have been used. The results of many experiments using different concentrations of sodium carbonate indicate that a solution of 2·5 per cent. used at a temperature of 60-70° is the most suitable. Lower concentrations tend to diminish the solubility and the rate of solution, while stronger alkali results in sticky masses due to a complete or partial hydrolysis.

Preparation of Sodium Hypochlorite for Bleaching.

The general methods for preparing sodium hypochlorite are, (*a*) Double decomposition of bleaching powder, (*b*) Electrolysis of sodium

chloride; and (*c*) Direct chlorination of sodium carbonate or caustic soda solution, using liquid chlorine.

Where large quantities of sodium hypochlorite are required, the first process is undesirable because commercial chloride of lime varies in quality and produces much calcium carbonate sludge. In this country bleaching powder is disadvantageous because it has to be imported from foreign countries and on reaching India has lost an appreciable amount of chlorine; moreover it deteriorates further on storage.

The adoption of the electrolytic method depends upon cheap electric power and sodium chloride being available. The conditions of electrolysis also require very careful control during every stage of the reaction and we have not found this method particularly convenient.

With the advent of liquid chlorine on the market the two processes described above have largely disappeared, the direct chlorination method being the most practical one for producing hypochlorite solutions, it being most easily controlled, while the hypochlorite can be readily produced on a commercial scale. For the purpose of bleaching lac a solution of high concentration is not essential, 5-7 per cent. available chlorine being the most convenient strength. Such a concentration of sodium hypochlorite is easily obtained by using the method adopted by Harper F. Zoller (*J. Ind. and Eng. Chem.*, 1923, **15**, 845) based on a strict control of the reaction. The solution of hypochlorite required for this investigation has been prepared in accordance with this method which has been found to be the most convenient one. The materials used are commercial caustic soda, anhydrous sodium carbonate and liquid chlorine. The method is briefly as follows.

The first step is to prepare a solution of caustic soda containing sodium carbonate. The latter acts as a buffer material and must be present in such a quantity as to hold the hydrogen ion concentration in the region of P_H 10-10·5 to conserve stability in the sodium hypochlorite produced. Such a solution is obtained by using a mixture of 12·5 per cent. caustic soda and 2·5 per cent. sodium carbonate. Chlorine from a cylinder is diffused slowly into the well-stirred solution at a rate followed by determining the available chlorine in the solution at regular intervals until a concentration of 6-8 per cent. available chlorine is reached. Practical experiments have shown that a litre of such hypochlorite solution can be obtained by passing chlorine at the rate of 100 bubbles per minute for about 1½ hours; it is not necessary to cool the alkali below 40° during chlorination and the solution does not require to be stored in a cold place.

PREPARATION OF LAC-SODA SOLUTION.

One pound of finely powdered lac, grown on *Shorea talura* in Mysore, was dissolved in 2·5 per cent. sodium carbonate solution heated to about 60-70° and filtered; the residue when dried and weighed showed an average loss of 8-10 per cent. due to sand, woody debris, etc., originally present in the crude lac. The loss can also be calculated by precipitating the lac from a known volume of the solution and weighing the precipitate after washing and drying.

QUANTITY OF CHLORINE REQUIRED FOR BLEACHING.

The exact amount of lac in the soda solution having been determined previously, definite volumes of the solution were taken in different bottles, and varying volumes of sodium hypochlorite added, after the free alkali had been almost completely neutralised with acid. If the free alkali was not neutralised the excess of alkali in the solution tended to hydrolyse the lac and resulted in the production of a sticky mass of bleached lac. Moreover the efficiency and rate of bleaching were very much lessened. The temperature of the lac-soda solution and the time of reaction were kept constant at that of the laboratory. The bleached lac was then precipitated from the solution by neutralising with a mineral acid, washed and dried. The same experiments were made twice in duplicate, each time using both seed-lac and shellac and the results obtained were in close agreement. The respective results are given in tables I and II.

TABLE I.

Twenty c.c. of lac-soda solution containing 2·5718 *gms.*

No.	Vol. of NaClO	Available chlorine	Colour	Time	Cl per cent.	Yield per cent.
1	5·0 c.c.	0·0463 gms.	Dark	20 Hrs.	—	—
2	10·0 ,,	0·0900 ,,	,,	,,	3·5	98
3	20·0 ,,	0·2124 ,,	Brown	,,	8·3	96
4	30·0 ,,	0·2674 ,,	Wine-yellow	,,	10·4	95
5	40·0 ,,	0·3525 ,,	Almos. colourless	,,	13·9	95
6	50·0 ,,	0·4333 ,,	,,	,,	16·7	92

TABLE II.

Five hundred c.c. of shellac-soda containing 94·58 *gms.*

No.	Vol. of NaClO	Available chlorine	Colour	Time	Cl per cent.	Yield per cent.
1	250 c.c.	4·75 gms.	Dark Brown	20 Hrs.	5·02	98
2	350 ,,	6·65 ,,	Brown	,,	7·03	97
3	450 ,,	8·55 ,,	,,	,,	9·04	96
4	550 ,,	10·45 ,,	Wine-yellow	,,	11·11	96
5	650 ,,	12·35 ,,	Colourless	,,	13·03	95

Keeping the amounts of sodium hypochlorite constant, the same series of experiments were repeated varying the concentration of the lac solution. The results are given in table III. From the above experiments it is concluded that for complete bleaching of lac, the amount of chlorine required lies between 10 and 14 per cent. Since the amount of colouring matter in the lac varies with the season the percentage of chlorine required for bleaching also varies between these limits. In all cases the yield obtained was about 93–95 per cent.

TABLE III.

No.	Vol. of lac	Weight of lac	Vol. of NaClO	Available chlorine	Chlorine per cent.
1	100 c.c.	28·6 gms.	250 c.c.	1·112 gms.	3·7
2	100 ,,	14·3 ,,	,,	,,	7·7
3	100 ,,	7·15 ,,	,,	,,	14·2

The bleached lac was precipitated by dilute sulphuric acid (1 : 20). During the process of precipitation the acid was added slowly drop by drop, just enough being used for neutralisation, and the whole solution was kept well stirred. Otherwise the copious evolution of carbon dioxide from the sodium carbonate led to some loss of solution; moreover the precipitate formed hard lumps which adsorbed some acid not easily removed by simple washing. The precipitate of bleached lac was filtered quickly through a Buchner funnel and washed as free as possible from acid. It was then dried in thin layers over sulphuric acid in a vacuum desiccator, the product being white and easily fusible under hot water. The melted mass has a white, glossy appearance resembling ivory.

All the samples obtained were freely soluble in cold 97 per cent. alcohol, and the solubility does not alter on prolonged storage; it was also found that to retain solubility it is not necessary to store bleached lac under water.

Determination of moisture.

The factor of water-content is important because a high percentage of water depresses the melting point and the solubility in alcohol. The moisture-content was determined according to the official method worked out by a committee of the American Chemical Society (*J. Ind. and Eng. Chem.*, 1915, **7**, 633). All the samples contained moisture varying from 2·3 to 3·1 per cent.

The important constants of bleached lac such as acid-value saponification-value and iodine-value (Hubl's) were also determined for all the samples. The results are given in table IV.

TABLE IV.

Sample	Moisture per cent.	Chlorine per cent.	Saponification-value	Acid-value	Iodine-value
A	3·1	0·98	236·3	70·68	4·9
B	2·7	1·28	256·7	80·98	5·0
C	2·8	1·64	249·8	83·52	4·1
D	2·3	2·56	236·0	75·86	3·9
E	2·36	3·52	246·4	73·52	3·9

The dried samples of bleached lac were then examined for wax, ether-soluble resin, and alcohol-soluble resin by extraction in a Soxhlet successively with low-boiling petrol, ether and 97 per cent. alcohol. It was found that the samples contained very little wax, while the ether and alcohol extracts varied from 16·5 to 22·6 per cent. and 63·6–75·4 per cent. respectively. These are recorded in table V.

TABLE V.

Percentage extracted by solvents.

Sample	Petrol	Ether	Alcohol
A	0·30	20·5	75·4
B	0·38	20·0	74·9
C	0·80	19·7	73·6
D	1·40	18·7	72·9

The high acid-values may be due to free mineral acid adsorbed by the bleached lac during precipitation and not completely removed by simple washing. It was also noticed that every sample of bleached lac contained chlorine in combination with the lac, and hence the iodine-adsorption was materially modified.

The relative costs of the various processes investigated have been estimated and showed the use of sodium hypochlorite prepared by the use of liquid chlorine to be the most economical as well as giving the best results.

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