

CXCVIII.—*The Catalytic Bleaching of Palm Oil.*

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THE usual methods of bleaching palm oil are: (1) Exposing the oil in thin layers to the action of air and sunlight. This involves much time and cost. (2) Blowing air through the heated oil. This method is employed in some places. (3) Bleaching by means of bleaching powder and finally washing the oil repeatedly to remove the traces of acid. (4) By the dichromate method, which appears to be the one most generally used. The oil is stirred with 1—3 per cent. of potassium dichromate, the calculated quantity of dilute sulphuric acid added, the whole stirred for about two hours, and the emulsion left to separate. The oil is washed repeatedly to remove the chromic chloride and traces of acids.

All these methods take a good deal of time. In the last two processes it is essential to keep the temperature as low as possible, and there is the trouble of washing the oil to remove the chemicals employed to bleach it; there is also always a risk of the oil being attacked by the bleaching powder or the dichromate employed.

At the suggestion of Prof. F. G. Donnan, the author made a series of experiments with the object of bleaching palm oil by blowing air through it in the presence of various catalysts, both the oil and the air being kept at a temperature of 80—90°. The flask containing the oil was provided with a cork with two holes, through one of which passed a glass tube flush with the cork and connected to a pump. Through the other hole passed another tube almost touching the bottom of the flask and in connexion with a coil of glass tubing surrounding the flask. Both the flask and the coil were immersed in a water-bath, and a temperature of 80—90° was maintained throughout the experiments. At this temperature the oil is not attacked by air or oxygen to any appreciable extent. By this arrangement the air or oxygen was heated to the same temperature as the oil itself before it was blown through the oil.

Whenever oxygen was used it was found to be more efficient than ordinary air in the process of bleaching. The catalysts used consisted of the oxides and salts of the metals manganese, cobalt, nickel, iron, and lead. (Compare Eng. Pat. 17,784 of 1913.)

It will be found from the table given below that a very efficient bleaching effect can be obtained with a minimum of trouble. No attempt has as yet been made to study experimentally the chemical changes that take place. No doubt the lipochromes are oxidised

to colourless compounds by means of the oxygen conveyed to them by the catalysts. It is possible that the catalysts pass into a higher state of oxidation, and then bleach the colouring matter, become reduced, and so on. The presence of the catalyst intact before and after the experiment would necessarily preclude the idea of the formation of a soap with these metals. (Compare *Tech. Quart.*, 1890, **3**, 9.) The catalysts which settle down as a residue at the bottom of the flask were examined after the experiment, and found to contain no soap, and it is improbable that an intermediate formation of the soap may have occurred, except in those cases in which the oxides of the metals were employed. The question of the probable formation of any organic peroxide during this process and the bleaching action of the peroxide on the lipochromes has not been studied. (Compare also Engler, *Ber.*, 1900, **33**, 1101.)

The specimen of the palm oil used was of a deep reddish-brown colour, and was supplied by Messrs. Alexander Finlay, Ltd., Belfast. It had the following constants:

Acid value, 49.44; saponification value, 198.2; iodine value, 55.4.

TABLE I.

Weight of oil. Grams.	Catalyst.	Amount of catalyst per cent.	No. of hours that air or oxygen was passed in.	Colour after bleaching.
60	Manganese oxalate	0.3	Air 16	White
52	" "	0.6	" 16	"
52	" "	0.1	Oxygen 3.5	"
65	" borate	0.04	Air 7	"
70	Lead borate	0.01	" 12.5	"
66	Manganese borate	0.01	Oxygen 4	"
73	Cobalt oxalate	0.01	Air 19	"
58	" "	0.02	Oxygen 5	"
75	Manganese palmitate	0.01	Air 12.5	"
85	Cobalt borate	0.01	" 4	"
71	Ferrous sulphate	0.01	" 11	"
78	Ferrous oxide	0.01	" 10	"
100	Nickel oxide	0.02	" 12	Yellowish-white
75	Iron oxalate	0.02	" 10	"

In the above experiments the velocity with which the air was passed was kept constant roughly by turning the tap to the same extent every time. Later on (see table II) accurate measurements of the velocity of air were made, and some of the results of table I checked. In both sets of experiments the time of bleaching was found to be shortened with an increased quantity of the catalyst generally, or, in other words, roughly the time was inversely proportional to the quantity of the catalysts. The best catalysts were

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found to be the salts of cobalt and manganese, and borates were better catalysts than other salts.

All the results tabulated above were confirmed in duplicate experiments. After keeping the specimens for 15 months, no colour has appeared in any of them. The author has been informed that the soaps prepared from palm oil bleached by the above method are not coloured, and also that the properties of the oil for soap-making purposes are in no way interfered with. The faint odour of violets characteristic of palm oil was not destroyed in the process of bleaching.

In the experiments, the results of which are given in table II, the apparatus described before was used, and air was passed at the rate of 17,350 c.c. per hour:

TABLE II.

Weight of oil. Grams.	Catalyst.	Amount of catalyst. Per cent.	No. of hours	Quantity of air in c.c.	Colour after passing air.
72	Cobalt borate	0.01	2.0	34,700	Yellow
72	" "	0.01	3.0	52,050	Very pale yellow
64	" "	0.01	3.5	60,725	White
79	Ferrous borate	0.01	10.0	173,500	"
72	Nickel borate	0.01	8.0	138,800	Yellow
72	" "	0.01	10.0	173,500	White
69	Manganese borate	0.01	6.0	104,100	"
72	" "	0.02	4.5	78,075	"

A point of interest in the above table is that by doubling the quantity of the manganese borate used (that is, using 0.02 per cent. instead of 0.01 per cent.) the time of bleaching is reduced by one and a half hours.

Colorimetric estimations were made in order to observe the effect of bleaching. The bleached specimen (10 grams) was dissolved in a solvent (50 c.c.), the solution placed in a Nessler glass, and the colour observed against a white surface. The effect of dilution, when the quantity of the oil was kept constant, was in accordance with Beer's observation (*Ann. Phys. Chem.*, 1852, [ii], 86, 78) that the observed intensity of a coloured solution, as viewed in the above manner, does not alter during the addition of more of the solvent. The solvents used were carbon tetrachloride, tetrachloroethane, and trichloroethylene. Specimens bleached by Messrs. Alexander Finlay, Ltd., Belfast, were taken as the standard, since they showed the best appearance. A very pale straw-yellow colour was all that could be observed in the standard solution, and also in all the perfectly bleached specimens in the present investigation, dissolved in various solvents. Those

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which had a yellowish-white appearance after bleaching showed a distinct yellow tint when their solutions were examined. A solution of the original oil itself showed a deep reddish-brown tint when examined in the above manner. The shades of colour of the bleached specimens in the free state and in solutions were almost identical in intensity and of the same order.

It is clear from the foregoing account that cobalt borate constitutes one of the best materials that can be used as a catalyst in the bleaching of palm oil, and the bleaching is complete within three and a half hours under the conditions described above. Considering the quantity of palm oil used in the soap industry, this method of bleaching may very advantageously be employed in preference to the other methods now in vogue.

The author desires to express his thanks to Prof. F. G. Donnan for his many suggestions and for the continued interest which he took in this work, and also to Messrs. Alexander Finlay, Ltd., for the specimens of palm oil.

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[Received, November 22nd, 1915.]
