

XXIV.—*A Product Obtained in the Manufacture of Natural Indigo.*

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AMONG the few points connected with the manufacture of natural indigo which do not appear to have received attention is the so-called 'seeth water,' the liquid from which the indigo precipitate settles out at the conclusion of the oxidation process. An examination of this product was suggested by Sir Lewis Hay, Bart., and also by Lieut.-Colonel Ranking, who kindly supplied samples of the evaporated material in the hope that further evidence might thus be forthcoming which would be of value in the industry.

EXPERIMENTAL.

Three samples of evaporated 'seeth water' were available for examination. The first and most important of these (*a*) was derived from water drawn from an oxidation vat in the Purtabphore factory in India, and represented 0.75 per cent. of the original liquid. In the process of manufacture, 100 parts of the plant (*Indigofera sumatrana*) underwent fermentation in the presence of 540 parts of water, so that very approximately the residue corresponded with 4 per cent. of the plant. On the other hand, the yield of cake indigo was 0.2328 per cent., but unfortunately the analytical value of this and of the plant itself could not be ascertained. Sample (*b*) consisted of evaporated drainings from the 'mahl table,' or filter, at the same factory, and formed 0.77 per cent. of the original liquid, whereas the origin of sample (*c*), supplied by Colonel Ranking, was doubtful.

These products consisted of resinous lumps varying in colour from yellowish-brown to deep brown. They were extremely hygroscopic, and when ground emitted an odour resembling that of decayed cheese.

When incinerated, the amount of ash given in each case was very similar, namely:

(*a*) 27.23, (*b*) 25.90, (*c*) 26.87 per cent.

This was not quantitatively examined, but consisted mainly of the oxides of calcium, magnesium, and potassium, traces of manganese oxide and alumina being also present.

The estimations of nitrogen in these samples were carried out by Khejdahl's method, the combustion of the substances described by means of copper oxide being very tedious. Pre-

liminary trials, employing pure indigotin, carried out some years ago by the late W. P. Bloxam and the author, indicated that if in this process 100 per cent. sulphuric acid (monohydrate) and potassium sulphate are employed, very accurate figures can be obtained. Experience, indeed, has shown that in these circumstances little or no difficulty occurs during the analysis of most organic nitrogenous materials.

Found: (a) $N=2.25$; (b) $N=2.77$; (c) $N=2.72$ per cent.

Experiment indicated that ammonium salts were absent from these products.

The samples were neutral, in the main dissolved readily in water, and these liquids on acidification emitted a strong odour of volatile aliphatic acids. These were estimated by Grimshaw's method, which consists in treating the material with sodium hydrogen sulphate solution and ascertaining the acidity before and after removal of the volatile liquids by evaporation. The percentages are calculated as acetic acid, although much butyric acid was evidently present.

Found: (a) 23.8; (b) 21.04 per cent.

A search for anthranilic acid, isatin, and other well-defined products of the indole group in these mixtures gave only a negative result, and it soon became evident that the main constituents could not be isolated in a crystalline condition.

Seventy-five grams of (a) were agitated for about half an hour with 500 c.c. of boiling water, and, after cooling, the insoluble brown residue was removed. To eliminate mineral matter it was digested with boiling 1 per cent. hydrochloric acid, and the mixture when cold rendered alkaline and subsequently acidified. This procedure was necessary to facilitate filtration, which otherwise was difficult to carry out. The precipitate (A), when collected and dried at 100° , weighed 3.292 grams, whereas in a second similar operation 3.225 grams were isolated.

In appearance this product closely resembled indigo-brown, and it was therefore examined by the methods formerly employed (T., 1907, **91**, 279) in the investigation of this material.

By extraction with hot pyridine, 0.5485 gram remained undissolved, which when dry resembled a crude cake indigo, and yielded to boiling nitrobenzene 0.135 gram of crystalline indigotin, or 0.18 per cent. of the original material.

As is well known, owing to the incomplete settlement of the indigo precipitate, some quantity is drained away by the 'seeth water,' which according to Rawson ("Report on the Cultivation and Manufacture of Indigo," 1907, p. 86) "frequently contains as

much as 20 per cent. of the total colouring matter produced." In the present case, if the 0.2328 per cent. of cake indigo yielded by the plant be given the average value of 60 per cent. purity, then the loss of indigotin or of cake indigo indicated by the above result will be 5.2 per cent. The value of this figure naturally depends upon the accuracy of the method employed for the sampling of the 'seeth water,' which in respect of the suspended matter present would be a difficult operation.

The pyridine filtrate on treatment with excess of boiling alcohol yielded a deposit of the main bulk of the brown matter (A), and this was well washed and dried at 160°. To ascertain the effect of subsequent purification, it was submitted to analysis.

Found: C=63.59; H=5.07; N=7.39 per cent.

Extraction with boiling acetic acid removed a small amount of a soluble compound evidently possessing a low nitrogen content, and the residue was now dissolved in pyridine and precipitated with alcohol.

Found: C=65.70; H=5.07; N=8.03 per cent.

It consisted of a dark brown, amorphous powder, indistinguishable in general property from the main constituent of indigo-brown. The composition assigned to the latter is: C=68.57; H=4.28; N=10.0 per cent. (*loc. cit.*), whereas the very similar product derived from the decomposition of indoxyllic acid (T., 1909, 95, 848) gave: C=67.35; H=3.68; N=9.94 per cent. This 'seeth water' brown is thus more highly oxygenated. By digestion with boiling 50 per cent. potassium hydroxide solution, a trace of anthranilic acid was produced.

The filtrate from A on treatment with ether gave some quantity of brown precipitate, which was well washed and dried at 160°.

Found: C=64.70; H=5.00; N=4.57 per cent.

The brown matter in 'seeth water' thus consists of a mixture of compounds of variable nitrogen content.

A somewhat similar precipitate can be obtained from the aqueous extract of *Indigoferae* leaves, which in the case examined (*loc. cit.*) contained 5.67 per cent. of nitrogen, and this was presumably derived in part from the indican present.

It has been previously shown (T., 1908, 95, 803) that by the action of hydrochloric acid, indican gives indoxyl-brown, and the yield is such that the main bulk of the original nitrogen is contained by this product. A further experiment showed that by nearly neutralising the acid filtrate obtained when isolating this substance, and evaporating to dryness, a further quantity of a brown material can be recovered by means of water, in which

almost all the nitrogen previously unaccounted for is present. The latter itself contained but 2.5 per cent. of nitrogen, so that evidently here a decomposition of the dextrose had also taken place.

2.442 Grams of indican gave 1.112 of indoxyl-brown ($N=9.42$) and 0.3187 of brown matter ($N=2.5$). The nitrogen present in these decomposition products was thus 97.4 per cent. of that contained by the indican.

From this result it suggested itself that by a comparison of the leaf brown and 'seeth water' brown, as regards nitrogen content, it would be possible to ascertain what amount of the latter was due to the alteration of indoxyl during the process of manufacture. Such an experiment, however, proves to be impracticable outside the actual factory, for numerous samples of the air-dried leaf kindly supplied for this purpose by Sir Lewis Hay had so deteriorated in transit that they contained little or no indican on arrival.

Moreover, again, Prof. E. R. Watson, of Dacca, was good enough to investigate the effect of air-drying on the indican of the leaf, with the result that a disappearance of some quantity of this compound was thus found to occur.

The neutral filtrate (*B*) from the crude brown matter was now treated with 300 c.c. of *N*-sulphuric acid, an amount found necessary by the titration of the ash residue alluded to above, the product evaporated until syrupy, and then stirred with boiling alcohol to precipitate mineral matter. Addition of ether to the supernatant liquid, which possessed a greenish-blue fluorescence, caused the separation of a brown, viscous mass, which was washed two or three times with ether. The product was treated with water, and a trace of brown matter removed from the solution, which on evaporation yielded 19 grams of residue. By re-resolution in alcohol and precipitation with ether, an almost colourless material was ultimately isolated. When dry it consisted of a friable mass, and to the presence of this substance the very hygroscopic nature of the dried 'seeth' residue was evidently due. If strongly heated it yielded a vapour possessing the odour of burnt feathers in which ammonia was present, and in general property closely resembled the so-called indigo gluten of crude indigo. Allowing for a trace

rated were evaporated to dryness, the residue treated with water, the solution freed from a trace of brown matter, and concentrated.

Crystals (1.66 grams) separated, and were purified by recrystallisation from water. (Found: C=40.67; H=5.14. $C_4H_6O_4$ requires C=40.67; H=5.08 per cent.)

These melted at 185—186°, required 67.8 per cent. of sodium hydroxide for neutralisation, when strongly heated yielded an anhydride melting at 118—119°, and had all the properties of succinic acid.

The mother liquors by evaporation gave a small amount of syrupy residue, in which some gluten and a little succinic acid appeared to be present. No well-defined third compound could be isolated from it.

The small amounts of brown substance obtained during the fractionations described above, when added to the main bulk (A) increased its weight to 3.90 grams, or 5.2 per cent. of the 'seeth water' residue. By directly treating the latter with dilute hydrochloric acid, a somewhat larger quantity, equivalent to 5.58 per cent., was obtained, which on analysis gave N=7.3 per cent.

'Mahl Table' 'Seeth Water' Residue.

This material when examined by the methods previously described yielded much more brown matter than the sample (a). Thus, whereas fractionation gave 12.03 per cent., the yield by the direct neutralisation method was 12.54 per cent. An analysis of the latter preparation gave N=6.87 per cent., and that this was a mixture was indicated by the isolation from it of a more readily soluble fraction, in which but 4.57 per cent. of nitrogen was present.

In the ordinary process of manufacture of natural indigo, the indigo precipitate before filtration is boiled in the so-called 'mahl boiler,' and that a purification here occurs is evident, in that brown matter originally carried down with the dye is removed by solution in the hot 'seeth water.' That samples (a) and (b) correspond fairly closely with one another is certain from the analytical results and from the fact that they represent respectively operations occurring in the same factory on July 17th and July 23rd, 1913.

The indigotin present was approximately 0.10 per cent. (0.0732 gram from 75 grams of the residue), a loss more trivial than in the former instance, the volume of liquid here dealt with being comparatively small, whereas succinic acid (1.63 grams, or 2.18 per cent.) and an indigo gluten fraction of considerable amount were also isolated.

Sample (c).

This product, of which only 25 grams were available, yielded 11·18 per cent. of brown matter containing N=7·77 per cent., the indigotin present being estimated 0·082 per cent. No record of its origin was available, but as a close resemblance exists between the analytical results found with both this and sample (*b*), it is reasonable to presume that it was obtained by the evaporation of 'mahl table' 'seeth water.'

The following table illustrates the main results above recorded :

	<i>a.</i>	<i>b.</i>	<i>c.</i>
	Per cent.	Per cent.	Per cent.
Nitrogen	2·25	2·77	2·72
Ash	27·23	25·90	26·87
Volatile acids...	23·80	21·04	—
Succinic acid ...	2·21	2·18	—
Brown matter..	5·58	12·03	11·18
Indigotin.....	0·18	0·10	0·082

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