

ELECTROLYTIC PREPARATION OF AZO-DYES—II

A. Effect on Dye Yield of Duration of Electrolysis

THE mechanism of the formation of azo-dyes at the anode in an electrolytic cell was discussed in an earlier communication.¹ It was observed that hydroxyl ion discharge at the anode is likely to interfere with the discharge of nitrite ions, so that the chances of the amine getting diazotised with 100% current efficiency were remote. If this were true, a good deal of nitrite would be left unreacted at the end of a run during which only the theoretical quantity of current had been passed. A higher yield of the dye should therefore be obtained if the current were passed for more than the theoretical period of time. This was found to be so. The electrolysis was carried out under the same conditions as before, but the current was passed for thrice the time theoretically required, at a current density of 5 amps./dm.² The yield of dye was found to be better, and there was no deterioration either in the colour of the dye or in the shade produced by it on silk. Yield of dye: 2.4 gm. or 43% of the theoretical.

It is interesting to mention at this point that Brockman and Griffin² report a similar observation in connection with the electrolytic preparation of another dye, Orange II. On investigation, qualitative agreement with their observation was noticed, but as with Roccein, it was not possible to secure the same yield of dye that they claim.

A mixture of sulphanilic acid (2.5 g.), β -naphthol (1.8 g.), sodium hydroxide (0.8 g.), and sodium nitrite (1.0 g. in 150 cc. of water), were electrolysed for the theoretical length of time. The current density employed was 5 amps./dm.² After the electrolysis, the dye was precipitated as the barium salt by the addition of barium chloride solution, filtered, washed and dried. Yield of dye: (Ba salt) 1.55 g. or 31% of the theoretical.

Brockman and Griffin claim to have obtained this dye in 46.8% yield, and better still, i.e., 67.7% when twice the theoretical amount of current had been passed.

This claim could not be verified. On passing the current for three times the theoretical length of time, other conditions remaining the same, the yield of dye improved but amounted only to 2.77 gm. of the barium salt, or 55.4% of the theoretical yield.

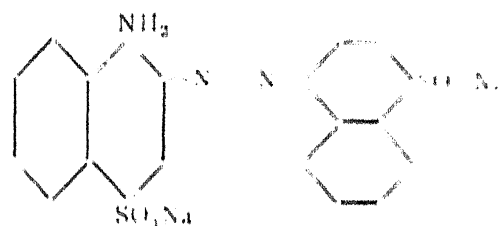
The dye had a good red colour, and the colour on silk was quite pleasing and compared very

favourably with the shade produced by Orange II prepared in the usual way.

B. Preparation of Congo Red

The study of diazo-dyes has a twofold interest. In the first place, this group of dyes, headed by Congo Red, forms the commercially well-known group of dyestuff: known as the direct cotton dyes, on account of their ability to produce good, fast shades on cotton fabric without the aid of mordants. Secondly, it is generally not so easy to prepare these dyes as it is to prepare mono-azo dyes. For one thing, tetrazotisation (i.e. diazotisation of both the amino groups) of the benzidine base is difficult, and then, the velocity of the coupling is slowed down to a very great extent when one of the two diazotised groups has coupled.

Brockman and Griffin (*loc. cit.*) who have studied the formation of Congo Red in the electrolytic cell, report an additional complication. After electrolyzing the proper components in the manner already described at a platinum anode, they state that instead of the anticipated Congo Red, a dye of the structure:



was formed through the partial diazotisation of the sodium naphthionate and coupling with unreacted naphthionate; Congo Red being obtained only in minute amounts. They therefore contradict the claim made by Loh³ that Congo Red could be got by electrolytic methods.

This problem was considered worth study, since the practical value of a good method of getting direct cotton dyes by electrolytic methods already outlined cannot be underestimated.

Since the most important aspect of the problem is the tetrazotisation of benzidine, a coupling component that is unlikely to interfere with this step in the formation of the dye had to be used. The closest analogue to sodium naphthionate is the sodium salt of Neville-Winther's acid (1,4-naphthol sulphonic acid). There is no risk of interference from the coupling component to the tetrazotisation of benzidine, if this acid were used, since there are no amino groups in it.

EXPERIMENTAL

The cell employed for the electrolysis has been already described.¹ Neville-Winther's acid

(2.8 g.), benzidine (1.15 g.), sodium hydroxide (0.5 g.), and sodium nitrite (0.9 g. in 150 c.c. of water), were electrolysed at a current density of 5 amps./dm.² The anolyte did not develop any colour, even when the temperature was raised to 65°-70° C. A purple colour developed, however, when the run was repeated after adding twice the amount of sodium hydroxide (1.0 gm.). After the current was passed for the theoretical time, the anolyte was cooled and filtered in order to remove the unreacted benzidine. The filtrate was saturated with sodium chloride, and the dye separated as a flocculent precipitate. This was filtered at the pump, redissolved in a small quantity of water (50 c.c.) and salted out carefully, with good stirring, till the separation of the dye appeared to be complete. This procedure was followed in order to remove a small proportion of the sodium salt of Nevile-Winther's acid which was also precipitated in the first stage. The precipitated dye was then filtered at the pump, sucked as dry as possible, dried in the air-oven and weighed.

Yield: 1.10 gm. or 25.7% of the theoretical. This dye gave a lilac shade on cotton dyed from a slightly alkaline bath.

It was felt that Congo Red could be obtained by employing the same conditions. The interfering reaction of sodium naphthionate could not of course be entirely suppressed; but some Congo Red was likely to be formed at the same time. This expectation was realised. The experiment was carried out with sodium naphthionate (3.06 g.), benzidine, (1.15 g.), sodium nitrite (0.87 g.), and sodium hydroxide (1.00 g. in 150 c.c. of water). The conditions of electrolysis were the same as those already described for the previous preparation. The temperature was 60°-65° C. At the end of the run, the red coloured anolyte was cooled and filtered. The filtrate was boiled with 5 gm. of freshly ignited magnesium oxide for 20 minutes, cooled and filtered. The filtrate had a dark red colour, and on evaporation gave a reddish black powder which was very hygroscopic. This powder dissolved in water to give a red solution, which on treatment with dilute sulphuric acid turned purple, and a precipitate slowly formed. Filter-paper dipped in this solution turned red in colour, which became purple when touched with a drop of dilute sulphuric acid. This colour was entirely different from that given by Congo Red test paper. Evidently this powder was the dye reported by Brockman and Griffin, namely, 1-amino-1', 2-azo naphthalene disulphonic acid-4,4',

The residue was a chalky red powder. This was boiled with a small quantity of strong sodium carbonate solution in order to bring into solution any Congo Red that might be present as the magnesium compound. The reaction appeared to be very slow and only partial. The sodium carbonate solution was therefore removed and the residue transferred to a small beaker and treated with sufficient hydrochloric acid to neutralise the magnesium oxide completely. A very dark blue, almost black precipitate immediately formed. This was rapidly filtered at the pump, transferred to a beaker again and treated with a slight excess of sodium carbonate solution. A red coloured solution was obtained from which a dark red precipitate was formed on saturating with sodium chloride. This was filtered, sucked as dry as possible and then dried in the air-oven. A dark red powder which dissolved readily in water to give a brownish red solution was got. Filter-paper dipped in this solution had a bright red colour and turned blue when touched with a drop of dilute sulphuric acid. Cotton dyed from a slightly alkaline bath with this dye had a bright red colour, while silk and wool took on a brownish red shade. Yield of dye: 0.6 gm. or 14% of the theoretical. This dye is Congo Red, more or less pure.

This figure provides an interesting contrast to the yield when Nevile-Winther's acid was employed as the coupling component, and enables a rough idea to be gained of the extent to which the diazotisation of sodium naphthionate proceeds side by side with the tetrazotisation of benzidine.

It was not possible to improve the yield of dye by altering the conditions. An increase in the amount of alkali merely reduced the yield and no dye at all was formed in an excessively alkaline anolyte. Factors such as current density and temperature had no influence on the course of the reaction.

This method of preparing benzidine dyes is therefore restricted to such types where the coupling component has no diazotisable amino groups.

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1. Sitaraman, M. V., and Raman, V. V., *Curr. Sci.*, 1948, 17, 234. 2. Brockman and Griffin, *Trans. Amer. Electrochem. Soc.*, 1939, 75, 216. 3. Löb, *Z. Elektrochem.*, 1904, 10, 237.