

AMPEROMETRY FOR MONITORING OF AZOPIGMENT PRODUCTION
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ABSTRACT

In the final stage of production of azopigments, the diazotised amine is added to an appropriate coupling agent under optimum pH conditions. Here the concentration of the diazonium compound added has to be closely monitored in order to ensure uniform pigment quality from batch to batch. In the present study, conditions have been optimised for close control and monitoring of flow of diazonium salt solution during the coupling reaction. The on-off controller developed based on this could provide close control to an accuracy of polarographic sensitivity for amperometric detection.

Key Words: Amperometry, diazocoupling, on-off flow control unit

INTRODUCTION

During the process for the production of azopigments, the diazonium salt solution is added to a coupling agent under optimum pH conditions. It has been reported that for the production of pure brilliant azo

dyes of uniform size and shade, a close control of the coupling reaction is important. Variation in the behaviour of the colouring properties between batches of the same dye or pigment has been found to depend on the concentration of diazonium chloride component during the reaction. Therefore monitoring the concentration of diazo component during the coupling

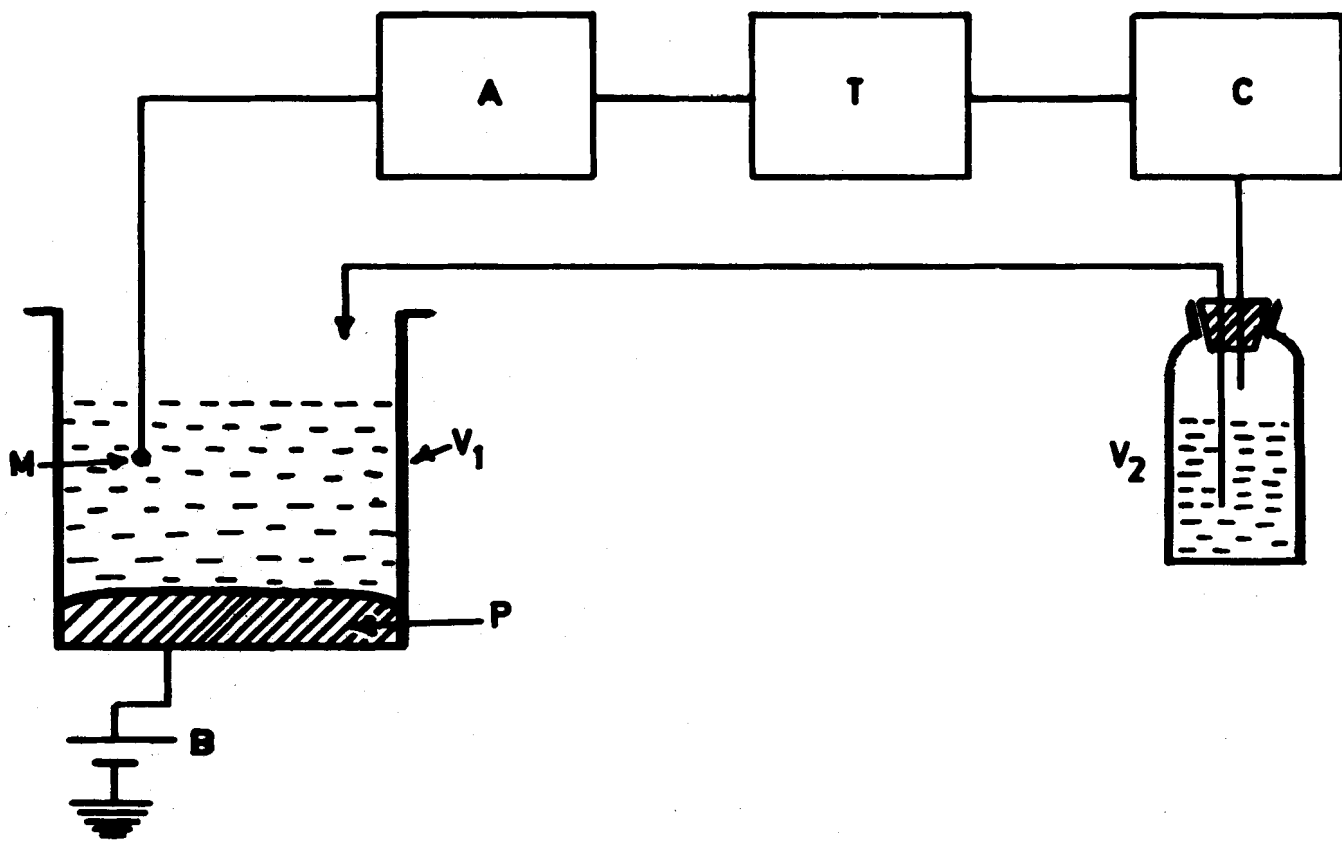


Fig.1: Circuit for monitoring the diazotisation reaction

reaction is very important. The present method of detecting the diazonium chloride present in the system is by placing a drop of the test solution on a filter paper and place the drop of the coupling component by the side of the first drop. If a diazonium salt is present a coloured line will appear at the boundary 1. However, this is not a completely satisfactory method since it is time consuming and is subjective.

The diazo compounds are polarographically reducible and the same can be sensed by amperometric techniques and thereby the addition of the diazo component monitored. The polarographic reduction of the diazo group is found to take place in two main steps, the first at 0.0 to -0.3V vs SCE and the second at much more negative potentials 2-4. The reduction of the diazotised aromatic amine at a dropping mercury electrode (DME) is a highly irreversible process, and the total diffusion current corresponds to 4 electron reduction. The reduction is not observed above pH 8-10 if the product of the coupling reaction being azo-dyes or azo-pigments. They will be insoluble in the medium and do not contribute to the diffusion current. In this paper the polarographic behaviour of diazonium chloride derived from o-chloro, p-nitro aniline (OCPNA) and the optimum conditions of the amperometric determination of the same have been investigated. Necessary circuit for sensing the diffusion current and monitoring the concentration of the diazonium chloride has been developed and the results are discussed.

EXPERIMENTAL

OCPNA was converted into its hydrochloride by dissolving in hot concentrated HCl and the same was later diazotized after dilution to required concentration. A coupling solution of β -naphthol in a buffered solution of pH 4.4 was used for polarographic study. Purified N_2 gas was used for deoxygenation and to maintain inert atmosphere. The DME was used as a working electrode and mercury pool served as reference electrode. The drop time is 4 sec/drop.

The monitoring of the diazo concentration was carried out using the circuit as shown in Figure 1. It consists of polarographic cell V_1 in which M is the dropping mercury electrode and P is the mercury pool reference electrode. Source B is used to fix the potential of the DME with reference to pool electrode. Current amplifier A amplifies the polarographic current giving an output voltage proportional to the current. The output current operates relay T and compressor C to force o-chloro p-nitro diazonium chloride solution from reservoir V_2 to V_1 which contains β -naphthol in a buffered medium.

The polarographic behaviour of o-chloro p-nitro diazonium chloride was studied at different pH viz. 1.6, 4.4 and 8. From the studies it was concluded that pH 4.4 was the best for the diazonium chloride. A typical polarogram is shown in figure 2. It is seen that there is a wave at potential of -350mV vs Hg pool. In order to use the polarographic technique for the determination of diazonium salt it is necessary that there is a linear relationship between the diffusion current and the concentration of diazo compound at the half wave potential. Such behaviour was found to hold good in the present case and is shown in the figure 3. This property of linear variation of diffusion current with concentration of diazonium chloride was used in the amperometric determination of the same during the coupling reaction with β -naphthol. It is necessary to take a solution of sufficient buffer capacity; since the OCPNA is a weak base and is diazotised under fairly high acidic condition.

RESULTS AND DISCUSSION

To start with, the concentration of o-chloro p-nitro diazonium chloride is zero in vessel V_1 and hence the relay energises the compressor to force the diazonium chloride solution from V_2 to V_1 . When the concentration

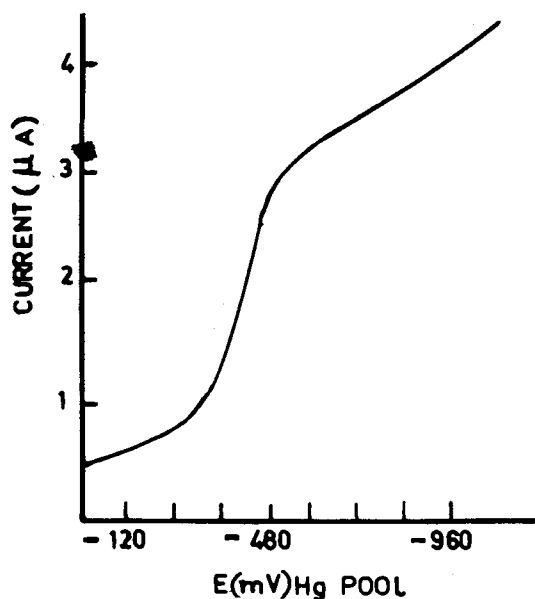


Fig.2 : Polarogramme of o-chloro-p-nitrodiazonium chloride at pH 4.4

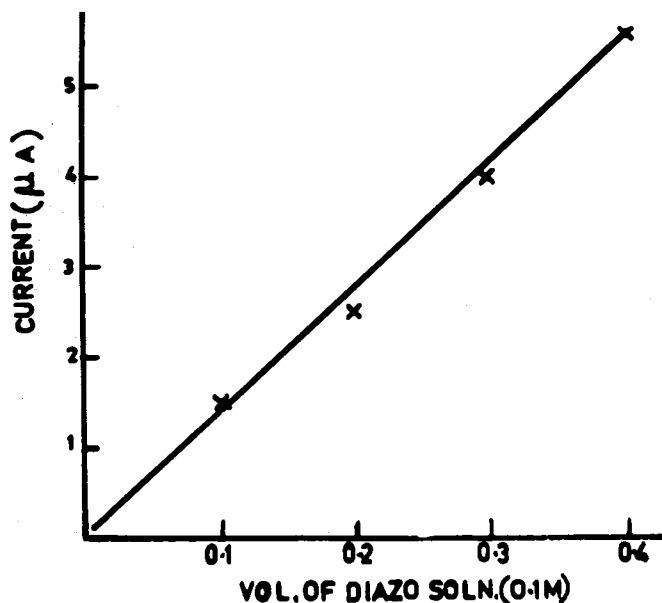


Fig.3 : Plot of diffusion current vs concentration for diazonium chloride

of diazonium chloride exceeds 10^{-3} M, the polarographic current at a potential of -350mV with respect to Hg pool actuates the relay to switch off the flow.

In a typical run the DME is maintained at -350mV with respect to Hg pool electrode. β -naphthol contained in a buffer of pH 4.4 is taken in vessel V_1 and deaerated and the quiescent current adjusted to 1 micro amp. which enables the amplifier to energise the relay which in turn switches on the compressor C to force diazonium salt solution from vessel V_2 to V_1 . When this concentration is such that the quiescent current exceeds 1 micro amp. the transistor relay switches off the flow.

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