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ELECTRODE MONITORING OF DIAZOTISATION OF AROMATIC AMINES

S KRISHNAMURTHY, K S UDUPA, Y MAHADEVA IYER and H N VENKOBA RAO
Central Electrochemical Research Institute, Karaikudi-623 006

ABSTRACT

In the diazotisation process for the manufacture of azo dyes, normally starch iodide paper is used for detection of nitrous acid and terminate the process of addition of sodium nitrite at the end point. This is time consuming and leads to subjective errors with regard to the excess nitrous acid present resulting in shade variations from batch to batch of the azopigments produced. A sensitized metal electrode developed for this purpose along with the necessary potentiometric sensing circuit has been found to be quite effective. The results obtained using this electrode showed that control accuracies to 0.6 mM/l of nitrous acid could be achieved. On-off control units for flow control using this sensor have been found to be quite satisfactory for the purpose.

Key Words: Diazotisation, aromatic amine, on-off flow control unit

INTRODUCTION

The diazotisation is an important reaction in organic chemistry. The reaction involves the interaction of an aromatic amine, an inorganic acid and alkali nitrite in ice cold conditions. The detection of the completion of diazotisation reaction is the change in colour produced on placing a drop

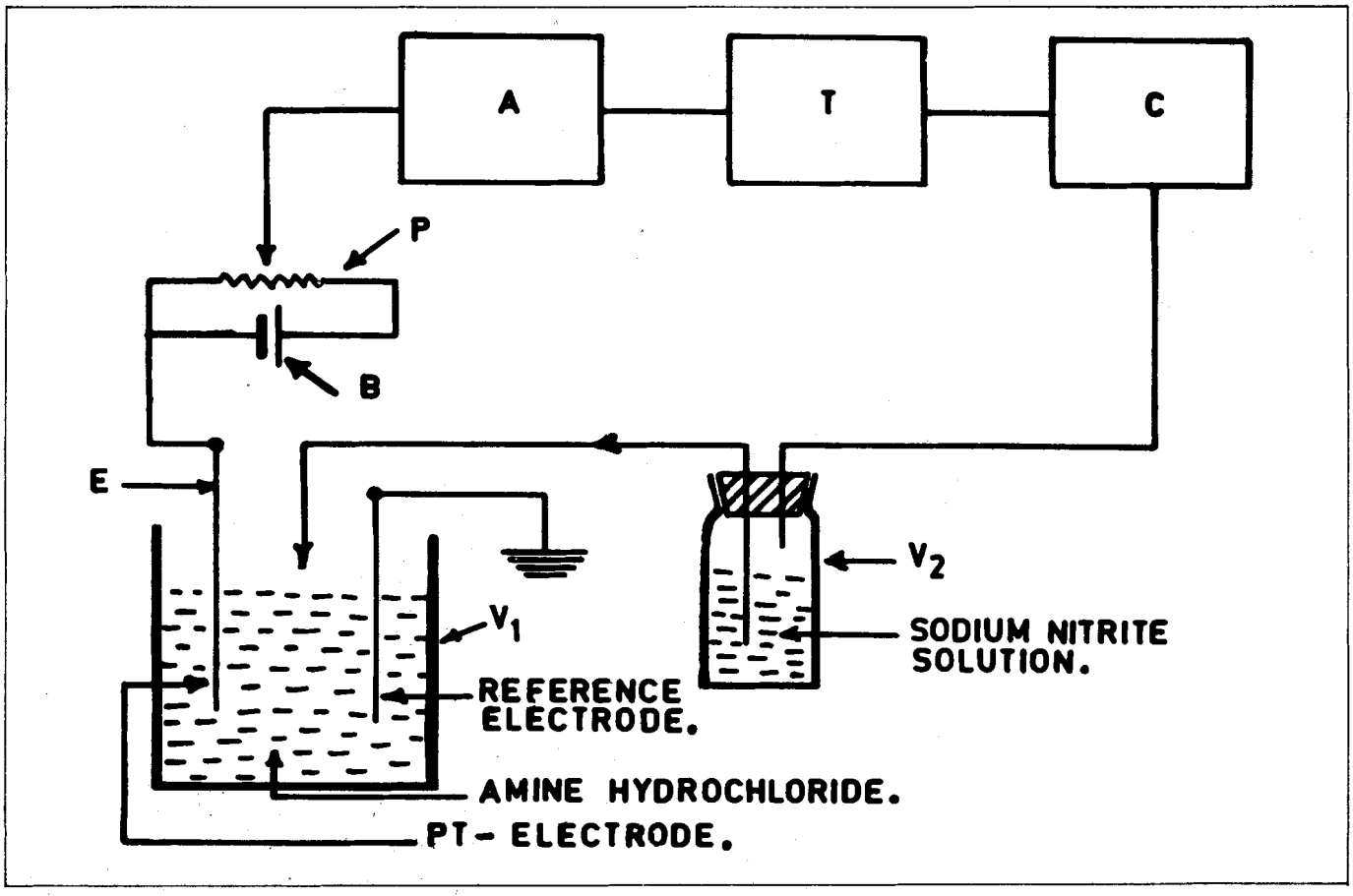

Fig.1 : 'On-off' control unit for diazotisation of aromatic amines

of solution on starch iodide paper. This is a tedious method and consumes lot of time and leads to subjective errors with regard to the excess of nitrous acid present. Several other methods have been investigated to find out the completion of the reaction. Potentiometric technique is one of the methods developed for this purpose [1,2,3]. It is found that a solution of nitrous acid in contact with a platinum electrode gives a definite potential. If an acid solution of aromatic amine is titrated against sodium nitrite, there is a jump in the potenital of the platinum indicator electrode and as the nitrous acid is consumed in the diazotisation reaction, the potential slowly falls to the original value. The rate of fall of potential depends on the rate of reaction between the amine and nitrous acid.

When a potentiometric technique for monitoring the diazotisation process is envisaged, the nitrous acid sensing indicator electrode should have the following characteristics: (i) the electrode potential (rest potential) should be stable throughout the process (ii) the electrode should be able to sense even small quantities of the nitrous acid repeatedly from experiment to experiment and (iii) it should be possible to use the electrode for as many experiments as possible in between the treatments. With the above requirements in view, work on the preparation of suitable indicator electrodes was carried out and the same has been reported. Along with the sensing electrode, necessary potentiometric sensing circuit for monitoring the concentration of nitrous acid during the process of diazotisation of aromatic amines was developed and the results of the same is described.

EXPERIMENTAL

(i) Platinum indicator electrode

A platinum wire 1 mm dia and 7 mm long fused to a glass tube is used as the indicator electrode. It is cleaned in hot chromic acid and flame treatment is given. Later the electrode has been seasoned by dipping in a solution of nitrous acid for one hour.

(ii) The "on-off" control unit

The potential of the indicator electrode is sensed by FET input operational amplifier (A) after being compensated by means of a series opposition source. The reference electrode is saturated calomel electrode (Fig. 1). Hence any change in the potential even of the order of 0.5 to 0.6mV is amplified by the amplifier (A) which is operated in the non-inverting mode. This amplified signal is applied to the base of the transistor (T) whose collector lead being the relay; which in turn switches "on/off" the flow system. When the diazotisation is complete, the added nitrite (nitrous acid) will not be consumed and hence the sensor assumes a higher potential to inhibit the addition of further sodium nitrite from vessel V_2 into the system. All the aromatic amines used for diazotisation, hydrochloric acid and sodium nitrite were of AR quality. In cases where the diazotisation reaction is slow, small quantity of sodium bromide (AR) is added to the system to increase the rate of reaction.

RESULTS AND DISCUSSION

Diazotisation is a quantitative reaction which takes place at temperatures between 0-10°C. The diazonium salts formed during the reaction have poor stability especially in the presence of excess of nitrous acid. Therefore it is necessary that the nitrous acid present in the system should be as low as possible. Two equivalents of mineral acid is needed for smooth reaction but an excess of half an equivalent is normally added to maintain sufficient hydrogen ion concentration. At low hydrogen ion concentration, the diazonium salt formed reacts with the free base to give diazomino compound. In the cases of very weak amines such as o-chloro-p-nitroaniline, p-nitroaniline etc. it is necessary to initially convert these amines to its hydrochloride salt by dissolving in hot hydrochloric acid. These amine hydrochlorides are taken for carrying out the diazotisation reaction after carrying out proper dilution to the required hydrogen ion concentration.

The indicator electrode prepared after the series of treatments were found to have a wide rest potential range (say 10 to 400 mV). This could be due to the nature and the history of the electrode concerned. But the potential was found to stabilize around a value and remain at the same value. The flow of nitrite was set by creating a small potential difference between the set values and the rest potential. Once the solution is added, the rise in potential of the order of 1mV maintained by means of a digital multimeter enabled stopping of the flow. The flow got automatically stopped when the potential difference crossed 0.5mV. In the initial stages of the experiment, on time was larger than the off time. As the end point is reached, the on time to off time ratio decreased in such a way that the off time becomes much larger compared to the on time. It was observed that the flow could be controlled even to one drop accuracy corresponding to 0.6 mM/l of sodium nitrite. The control accuracy ensures uniform pigment shade from batch to batch which was produced in the subsequent coupling stage. When starch iodide paper is used for the purpose, it has been reported by manufacturers that the shade varied very much from batch to batch in addition to the time consumed in controlling the diazotisation reaction. Though in practice an attempt is being made to destroy the excess of nitrous acid by means of addition of urea, it has not been a complete success. In contrast to this, the present method of detection ensures a minium amount of nitrous acid during the process of diazotisation at the end of the reaction.

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