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SAVINGS IN THE USE OF CHEMICALS IN DYEING ✓

(Stabilisation of sodium hydrosulphite through electrolysis)

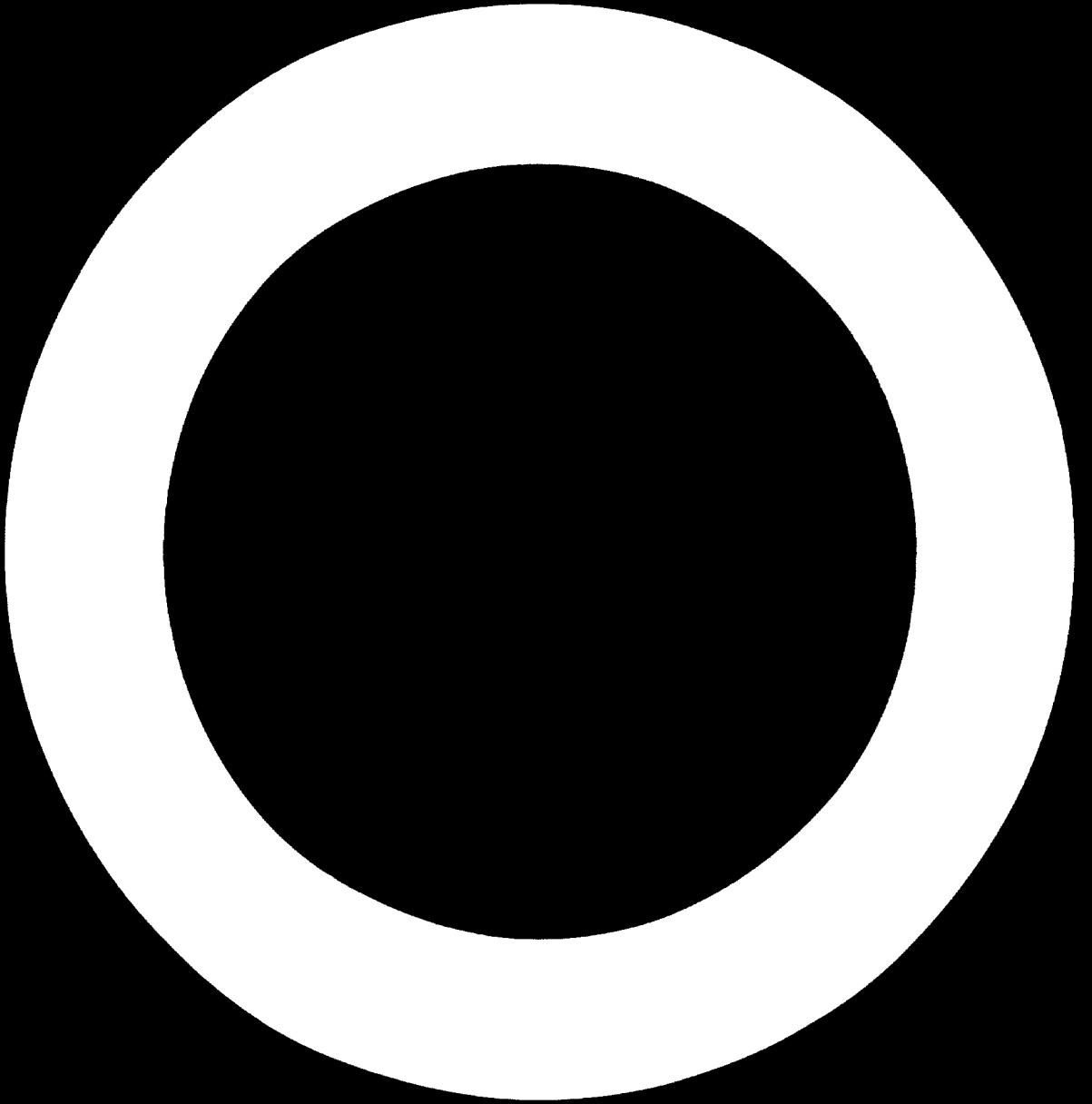
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I. INTRODUCTION

Dyeing of cellulosic textiles with vat dyestuffs is carried out on an extensive scale as the resultant dyeings show very good all round fastness properties. In order to avoid the oxidation of leuco vat dye during dyeing, large excess of sodium hydrosulphite is necessary, the excess amount being as much as 5 to 6 times the theoretical with some vat dyes. In addition to wastage, large excess of hydrosulphite can lead to overreduction, hydrolysis and crystallisation of vat dyes, specially at higher temperatures. The excessive electrolyte concentration developed in the dyebath due to use of large quantities of hydrosulphite at times results in rapid exhaustion and non-uniform dyeing.

II. METHODS FOR REDUCTION IN HYDROSULPHITE CONSUMPTION IN VAT DYEING

During the last few years, several attempts have been made to reduce the consumption of hydrosulphite in vat dyeing by adopting the following different approaches.

- A. Modification of the dyeing machine through use of submerged rollers or maintaining an atmosphere of nitrogen in the dye vessel.

A Japanese firm introduced an enclosed jig with submerged rollers where during the entire dyeing operation, the fabric roll remained below the level of dye liquor. This method of dyeing

did not find favour because in this case the liquor to material ratio increases considerably thereby making dyeing uneconomical. Under laboratory conditions, where nitrogen atmosphere is maintained, vat dyes remain in reduced form with only the stoichiometric quantity of hydrosulphite in the bath.

B. Increasing the red/ox potential of the system.

BASF has developed Rongal A which for continuous pad-steam process when used in combination with hydrosulphite offers the advantage of reduction in hydrosulphite consumption by 30% at proportions of hydrosulphite to Rongal A (3:2) [1]. This product is an activated sulphinic acid derivative and its solution in presence of caustic alkali develops red/ox potential higher than that of hydrosulphite. This sulphinic acid derivative does not have any stabilising effect on hydrosulphite whatsoever but both the reducing agents are supposed to react side by side with the dye and atmospheric oxygen.

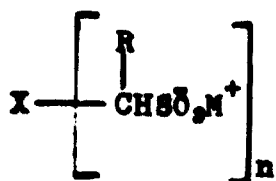
C. Partial substitution of hydrosulphite by cheaper reducing agents which have synergistic effect on the reduction characteristics of sodium hydrosulphite.

Numbers in the parentheses refer to the corresponding numbers in the reference list at the end of the paper.

When sodium sulphide is used along with hydrosulphite in vat dyeing, it has been found possible to reduce the consumption of hydrosulphite by about 30%, the extent depending on the dyeing technique used [2]. From the measurements of red/ox potentials and stability of alkaline solutions containing sodium hydrosulphite in combination with sodium sulphide, it has been concluded that the effectiveness of sodium sulphide is due to the synergistic effect produced.

D. Retardation of the decomposition of sodium hydrosulphite.

Etters [3] has described a hydrosulphite decomposition retarder of the general formula



where groups R and X determine, to a great extent, the stability of the complex formed with hydrosulphite and M is a monovalent cation. It has been claimed that reductions of the order of 20 - 40% in hydrosulphite consumption under specific conditions can be achieved by judicious use of the retarder.

D. Stabilisation of Reduced Vat Dyestuff.

Sodium borohydride, which is a potentially strong reducing agent, in combination with sodium hydrosulphite has been found to effect a reduction of 15 - 25% in hydrosulphite consumption [4,5]. Borohydride is supposed to act on some intermediate form of the vat dye, some state in between leuco form and oxidised form. This claim has been refuted by some workers [6,7] who have shown that although borohydride increases the negative potential of the dyebath, it fails to reduce vat dyes and also there is no improvement in the stability of the dyebath against oxidation.

E. Combination of leuco dye stabilisation and prevention of hydrosulphite oxidation.

Shah [8] from vat dyebath stability studies in presence of dextrin and sodium bisulphite has indicated the possibility of reducing consumption of hydrosulphite by 50% using a combination of these two compounds. Dextrin has been shown to increase the stability of leuco vat dye and sodium bisulphite to retard the rate of oxidation of excess hydrosulphite.

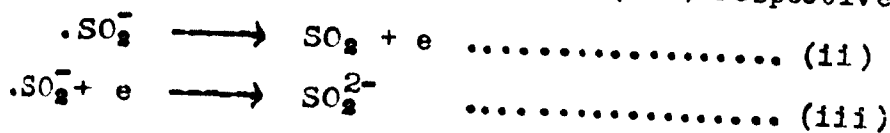
III. CATHODIC REDUCTION OF SODIUM HYDROSULPHITE

Furness[9] observed that all commercial hydrosulphites show a polarographic wave with a $E_{1/2}$ of -0.43 V and a slight kink between -0.5 and -0.6 V. When the polarogram was extended to more negative potential, a small cathodic wave was observed with a $E_{1/2}$ of -1.03 V. According to this investigator, the cathodic wave was due to the reduction of a species of hydrosulphite ion whose concentration at 25°C was much smaller than that of $\text{S}_2\text{O}_4^{2-}$ ion. An abnormally high temperature coefficient of 6% per $^{\circ}\text{C}$ for the limiting cathodic current was regarded as an indication of the effect of temperature on the hypothetical equilibrium between the two forms of sodium hydrosulphite.

Subsequently, Cernak [10] investigated exhaustively the polarographic behaviour of sodium hydrosulphite in neutral and alkaline media. At temperatures near 0°C , a single anodic wave controlled by diffusion was obtained. When the temperature was increased a new more negative anodic wave and a cathodic wave of equal heights were formed, and the ratio of the limiting current for the more negative anodic wave to the total limiting current increased from zero to unity with increasing temperature. This behaviour of sodium hydrosulphite has been explained by Cernak to be due to the decomposition of hydrosulphite according to the equation



to produce free radical ion $\cdot\text{SO}_3^-$. The free radical ions formed in reaction (i) could undergo electrochemical oxidation and reduction at the dropping mercury electrode as represented by reactions (ii) and (iii) respectively.



Electrode reaction (ii) gave rise to more negative anodic wave while reaction (iii) gave rise to the cathodic wave. The electrochemical reduction of the free radical ion $\cdot\text{SO}_3^-$ according to the reaction (iii) resulted in the formation of sulphoxylate ion SO_3^{2-} .

In order to examine critically the cathodic reduction of sodium hydrosulphite, in the present study, a controlled potential electrolysis cell (Figure I) was constructed, wherein the red/ox potential of hydrosulphite under different conditions viz. application of different cathodic potential, varying pH and temperature, etc. could be measured directly by a digital voltmeter.

It is observed that increasing cathodic potential increases rapidly the red/ox potential of alkaline hydrosulphite solution (Figure II), and this effect is more marked with increasing pH of the solution and increasing temperature (Figures III and IV). These results indicate that by appropriate cathodic reduction under suitable conditions, it is possible to generate from sodium hydrosulphite a powerful reducing species with red/ox potential higher than that of hydrosulphite

itself. The rate of decomposition of this species in air at 30°C is found to be higher than that of hydrosulphite (Figure V), and this rate is accelerated when temperature is increased from 30 to 60°C.

Subsequently, experiments were carried out wherein an electric current was applied to alkaline sodium hydrosulphite solution under different experimental conditions and total quantity of reducing compounds formed in the solution was determined. It is observed that when an electric current is applied to an alkaline hydrosulphite solution, the stability of the solution increases and the rate of overall decomposition is less than that observed without the application of the current (Figure VI). The stabilisation has been found to be more marked up to a duration of about 120 min. but beyond this stage, decomposition of the reducing solution appears to follow the same rate as that of hydrosulphite in absence of applied current. Stabilisation is better effected at higher concentrations of hydrosulphite and at temperatures of 30°C as compared with 60°C. Potentiometric titration of the alkaline sodium hydrosulphite in absence and after application of electric current was carried out with potassium ferricyanide as oxidising agent. It is observed that whereas in case of hydrosulphite solution in absence of current, there is only one inflexion point corresponding to -780 mV, when current is passed through the solution, two inflexion points corresponding to

-1157 and -770 mV are observed (Figure VII) indicating that a different reducing species with a red/ox potential much higher than that of hydrosulphite is generated when an electric current is applied to the hydrosulphite solution. Furthermore, the quantity of the oxidising agent, $K_3Fe(CN)_6$, required for titration is more when electric current is passed through the solution.

IV. DEVELOPMENT OF A PROCESS FOR REDUCTION IN HYDROSULPHITE CONSUMPTION IN VAT DYEING.

In order to find whether the generation of a more powerful reducing species than hydrosulphite through cathodic reduction could be made use for effecting reduction in hydrosulphite consumption in vat dyeing, electrode systems were designed both for continuous dyeing as well as jig dyeing (Figures VIII and IX) and appropriate DC current was passed through the alkaline hydrosulphite solution. It is observed that substantial reduction in the quantity of hydrosulphite required could be effected by application of the current as compared with that required in conventional vat dyeing. Reduction effected is dependent on the method of application of the vat dye (Table 1).

In the design of the electrodes two factors appear to play important role for optimum reduction in hydrosulphite consumption. Firstly, a large surface of cathode is desirable to produce increased quantity of the reducing species with high red/ox potential, and

secondly the material of construction of the cathode is equally important. When the reaction is cathodic reduction occurring at fairly negative cathodic potentials, it becomes necessary to use cathodic materials with a high overvoltage for hydrogen evolution so that the desired cathodic reaction takes place selectively without loss in current efficiency due to hydrogen evolution. In the present process, high nickel stainless steel mesh has been used as cathode material, as this metal lies midway in the overvoltage series in the alkaline range. This material has been found to be satisfactory and is being currently in use in all units installed for continuous dyeing. However, laboratory studies suggest that cathode materials having very high overvoltage have very high conversion efficiency of hydrosulphite to sulphoxylate. In fact, no conversion was observed when platinum or iron, which are very low in the overvoltage series, was used as cathode material. The highest conversion efficiency was obtained with the highest overvoltage materials mercury > lead > zinc. It was also observed that metals which are very efficient as cathode materials are also very efficient as catalyst for the oxidation of hydrosulphite by atmospheric oxygen under open circuit conditions. For the present electrochemical process, excessive cost of platinum, iridium and palladium precludes their use as anode materials though chemical attack on these anodes is negligible. Stainless steel

strips as anode have proved satisfactory in the present process, and although some oxidation and wear of the anode does take place, the replacement costs are small. If sodium chloride is present in the alkaline hydrosulphite solution, graphite rods can be used as anode. However, in this case, chlorine gets liberated at the anode. To prevent the oxygen liberated at the anode from oxidising hydrosulphite in the bath, porous PVC filter tube, closed at the bottom with a porous PVC disc, has been used as a diaphragm (Figure VIII). In case of jig dyeing, the jig vessel itself has been made a cathode to make available as much surface as possible for cathodic reduction and stainless steel mesh anode is kept just below the surface of the liquor to facilitate the escape of liberated oxygen into the atmosphere (Figure IX).

The process has till now been introduced in 26 textile mills in India. 7 continuous dyeing ranges, 70 jigs and 1 molten metal dyeing unit have been fitted with appropriate electrode systems, and substantial reduction in hydrosulphite consumption has been achieved during the last two years during which the process has been in full commercial use in the textile industry in India.

In conclusion, cathodic reduction of sodium hydrosulphite by use of appropriate electrode systems and conditions of electrolysis offers a method for substantial reduction in hydrosulphite consumption in vat

dyeing. The process is simple to operate, capital cost of electrode system is much less as compared with the savings in the use of hydrosulphite achieved, and the cost of consumption of electricity is quite low. In addition to reduction in hydrosulphite consumption and consequently lower cost of dyeing vat dyes, the process is advantageous from the point of view of reduction in stream pollution to a certain extent as it involves electrolysis which results only in the formation of non-toxic gases, hydrogen and oxygen.

Table 1. Possible reduction in sodium hydrosulphite consumption for different application techniques

Method	Reduction, % of normal
Leuco vat dyeing	15 - 20
Continuous dyeing (wet-on-wet)	25 - 30
Continuous dyeing (pad-dry-development)	30 - 35
Pad-jig dyeing (wet-on-wet)	25 - 30
Pad-jig dyeing (pad-dry-development)	30 - 35
Molten metal dyeing	35 - 40

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Legend for Figures:

- Figure I. Controlled potential electrolysis cell
 (perpendicular section).
- Figure II. Variation in red/ox potential with applied
 cathodic potential.
- Figure III. Variation in red/ox potential at different
 pH under constant cathodic potential.
- Figure IV. Variation in red/ox potential at different
 temperatures.
- Figure V. Decomposition of $\text{Na}_2\text{S}_2\text{O}_4$ and reducing species
 in air at 30°C.
- Figure VI. Stabilisation of $\text{Na}_2\text{S}_2\text{O}_4$ at different
 temperatures through electrolysis.
- Figure VII. Red/ox titration of $\text{Na}_2\text{S}_2\text{O}_4$ solution before
 and after electrolysis.
- Figure VIII. Electrode assembly for continuous dyeing.
- Figure IX. Electrode assembly for jig dyeing.

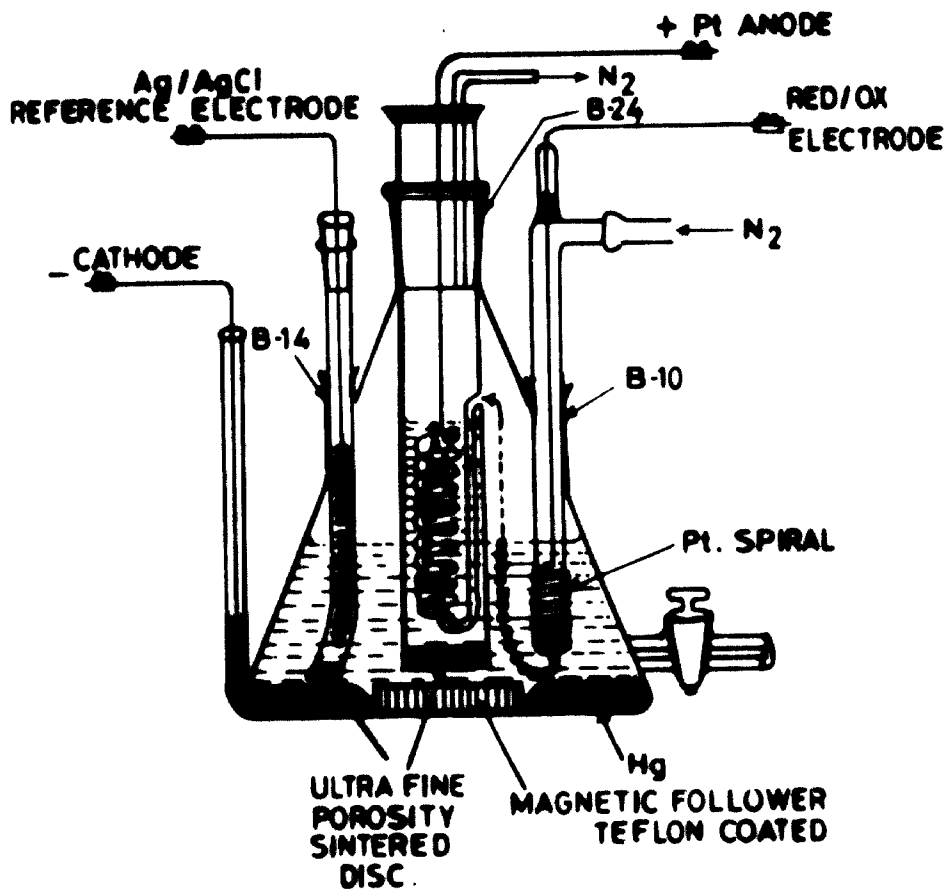


FIG. 1.

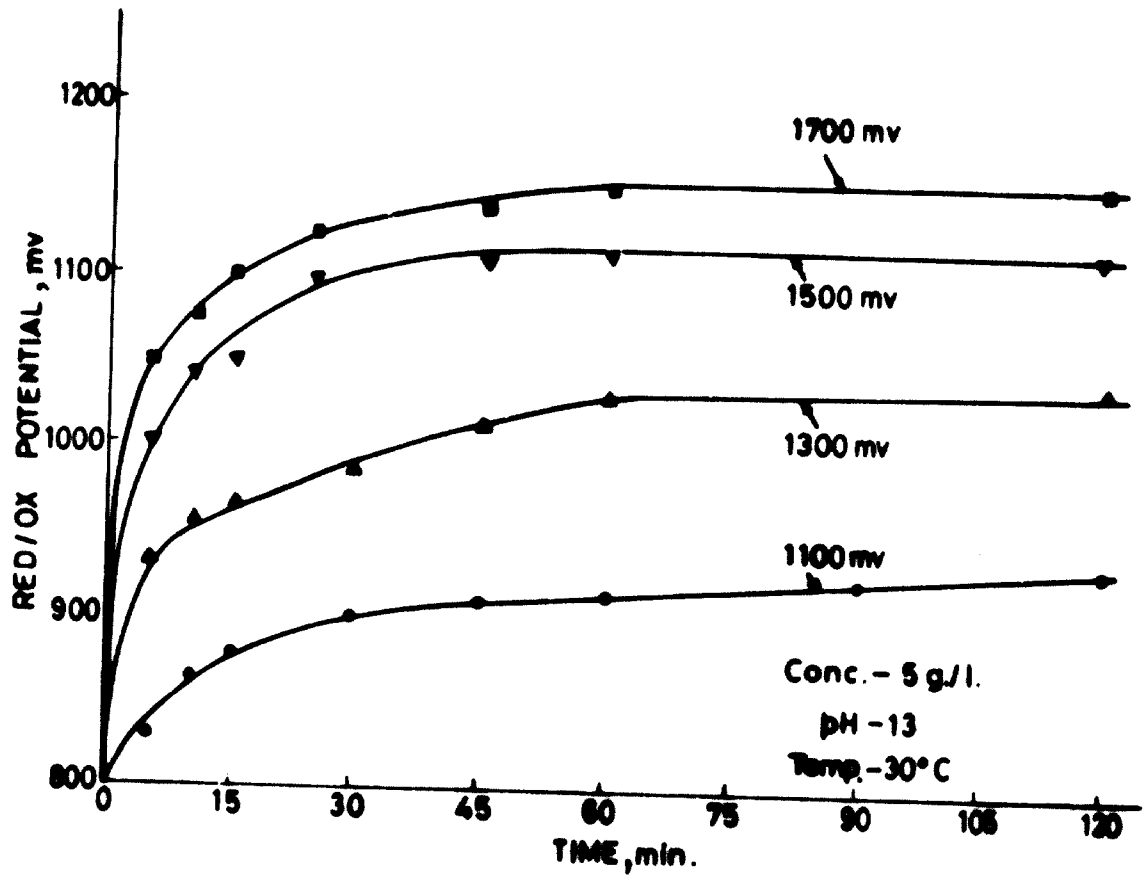


FIG. 2.

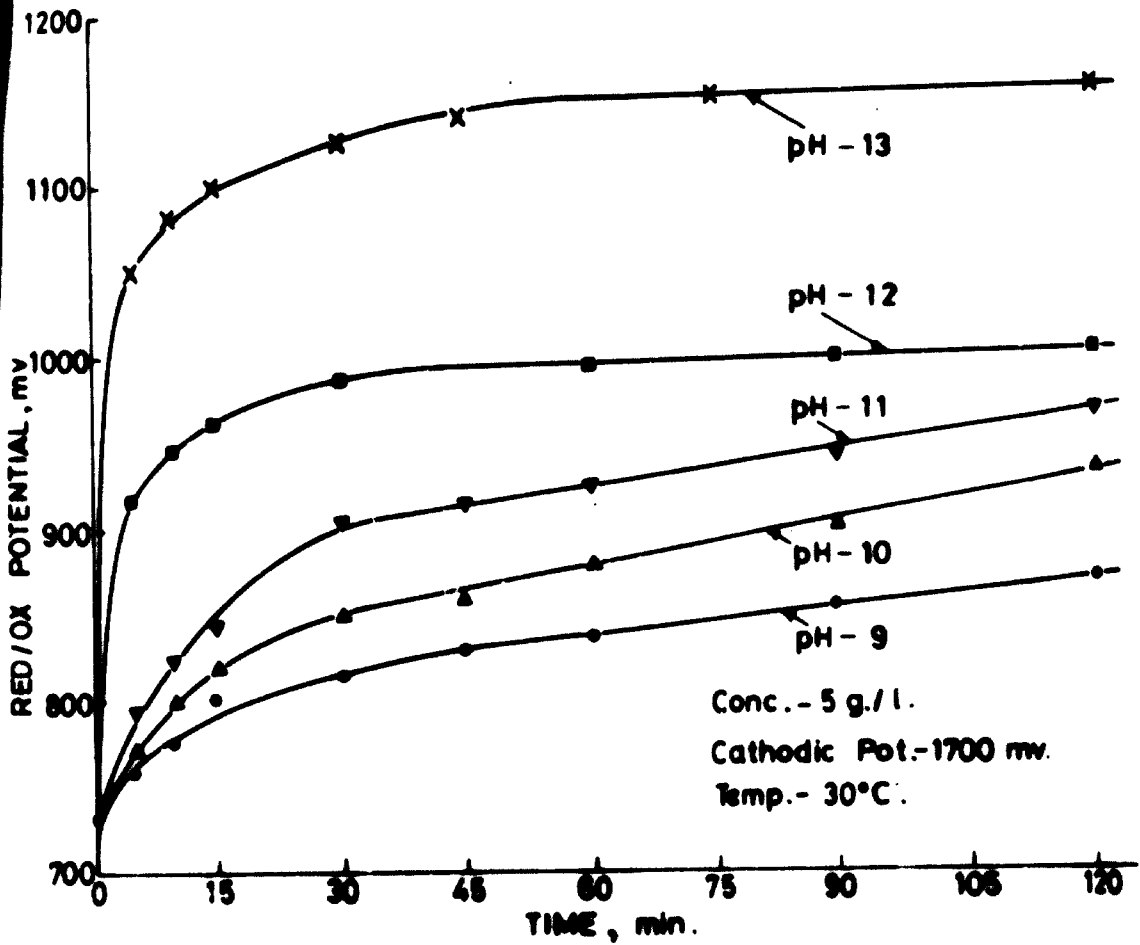


FIG. 3.

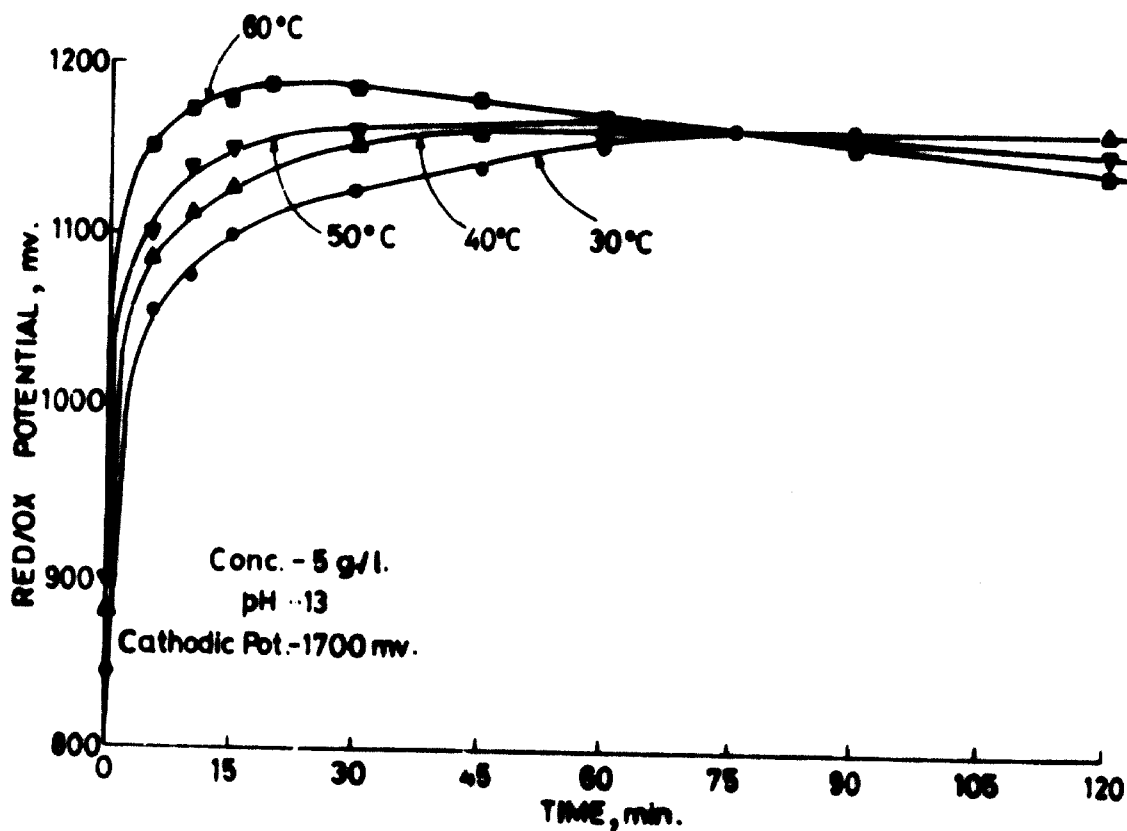


FIG. 4.

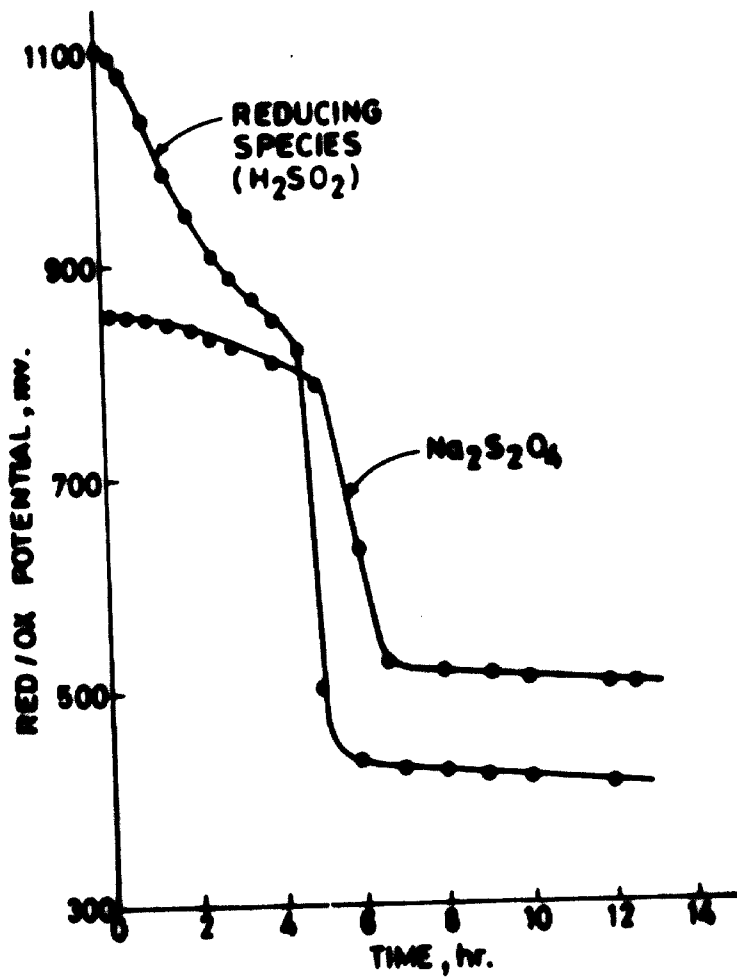


FIG. 5.

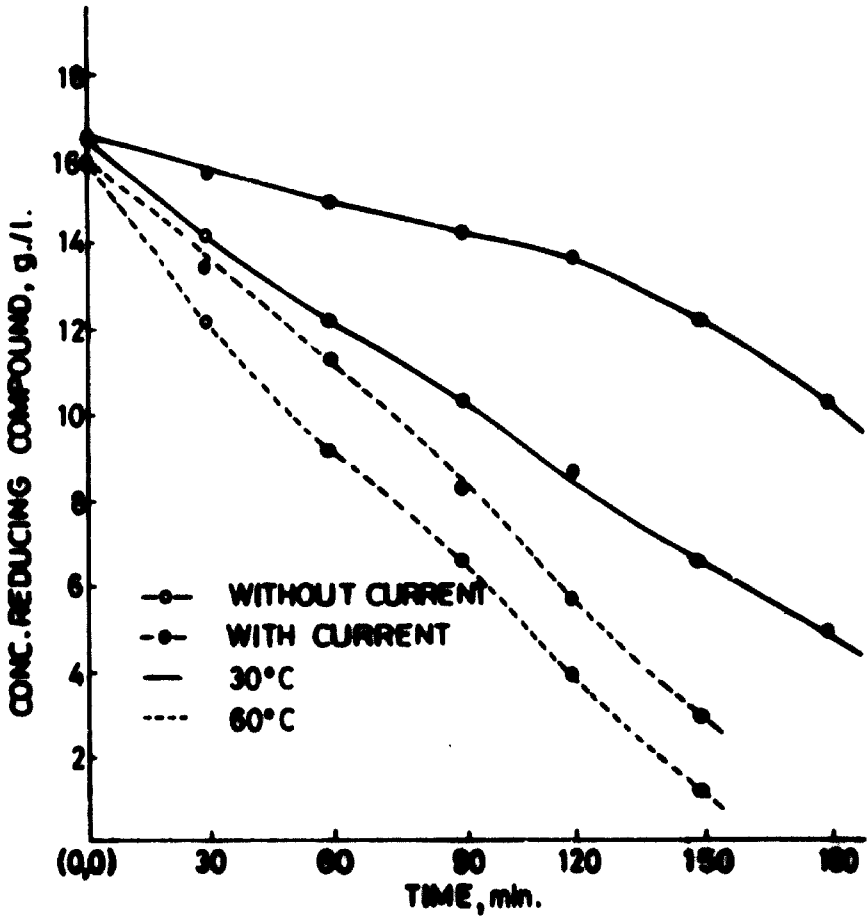


FIG. 6.

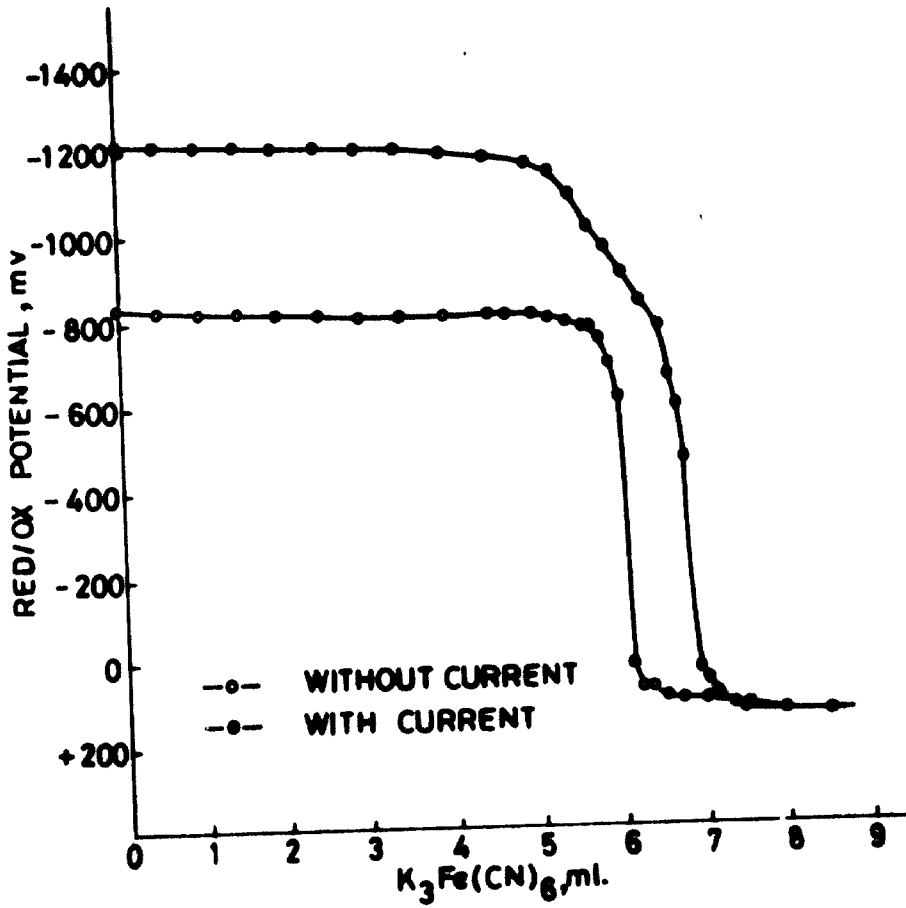


FIG. 7.

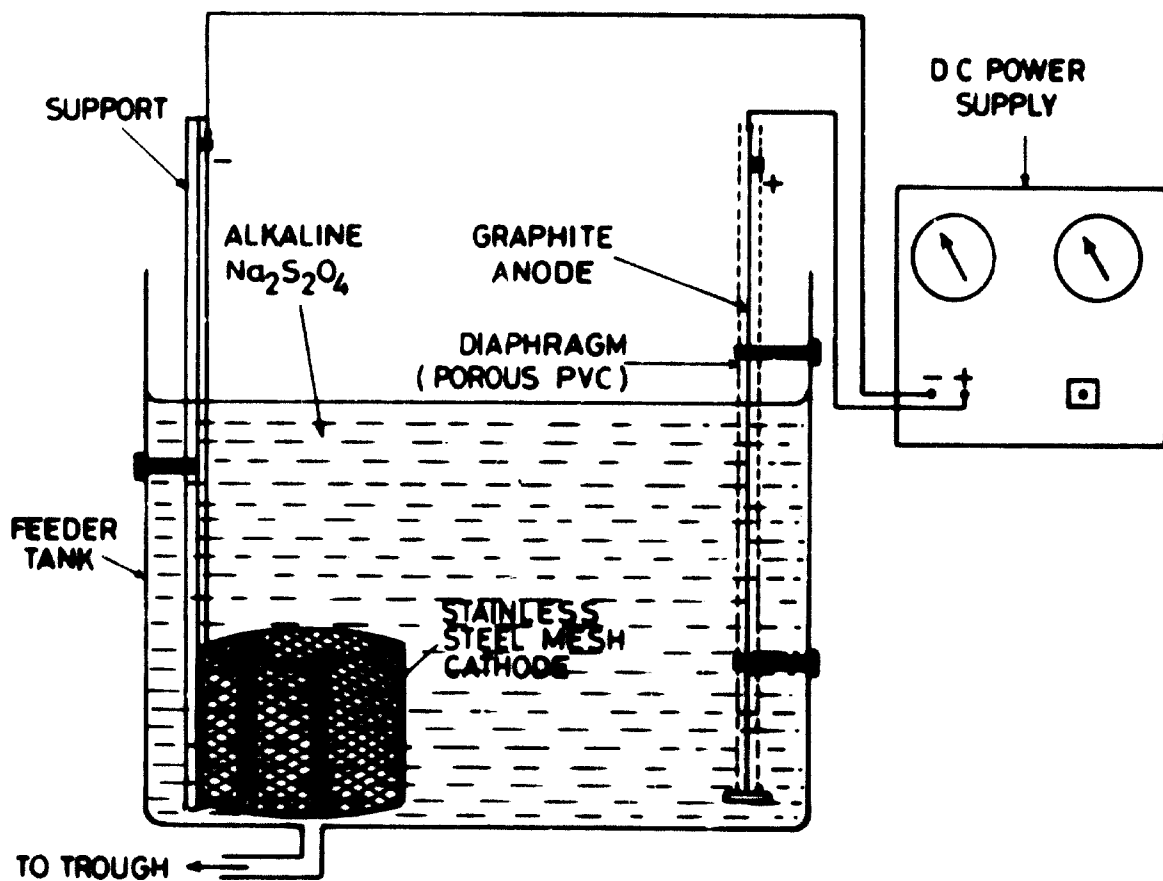


FIG. 8.

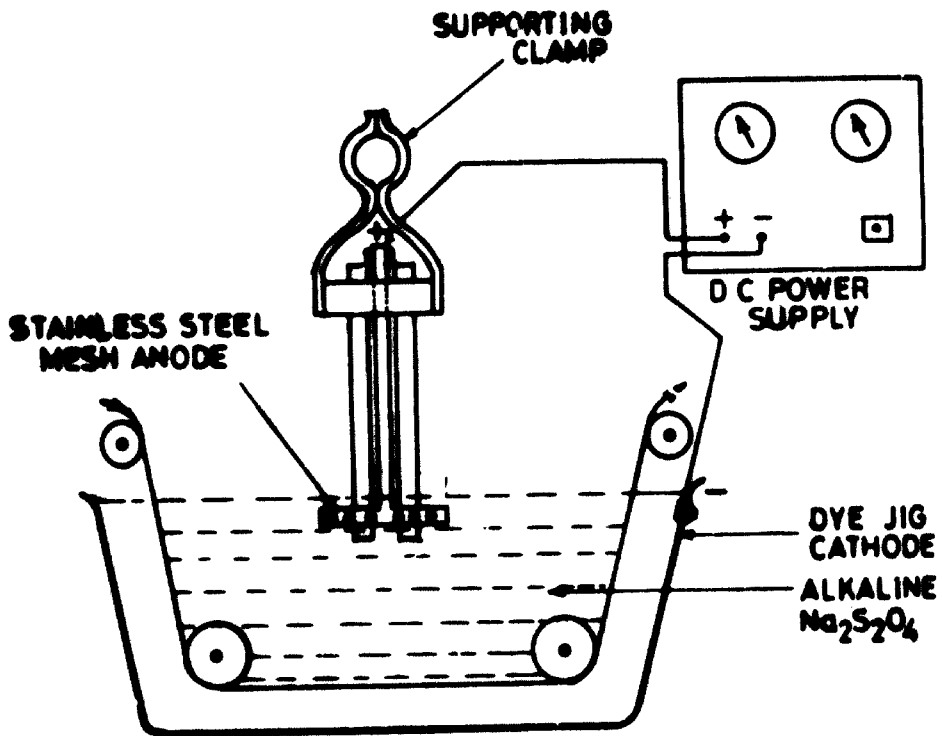
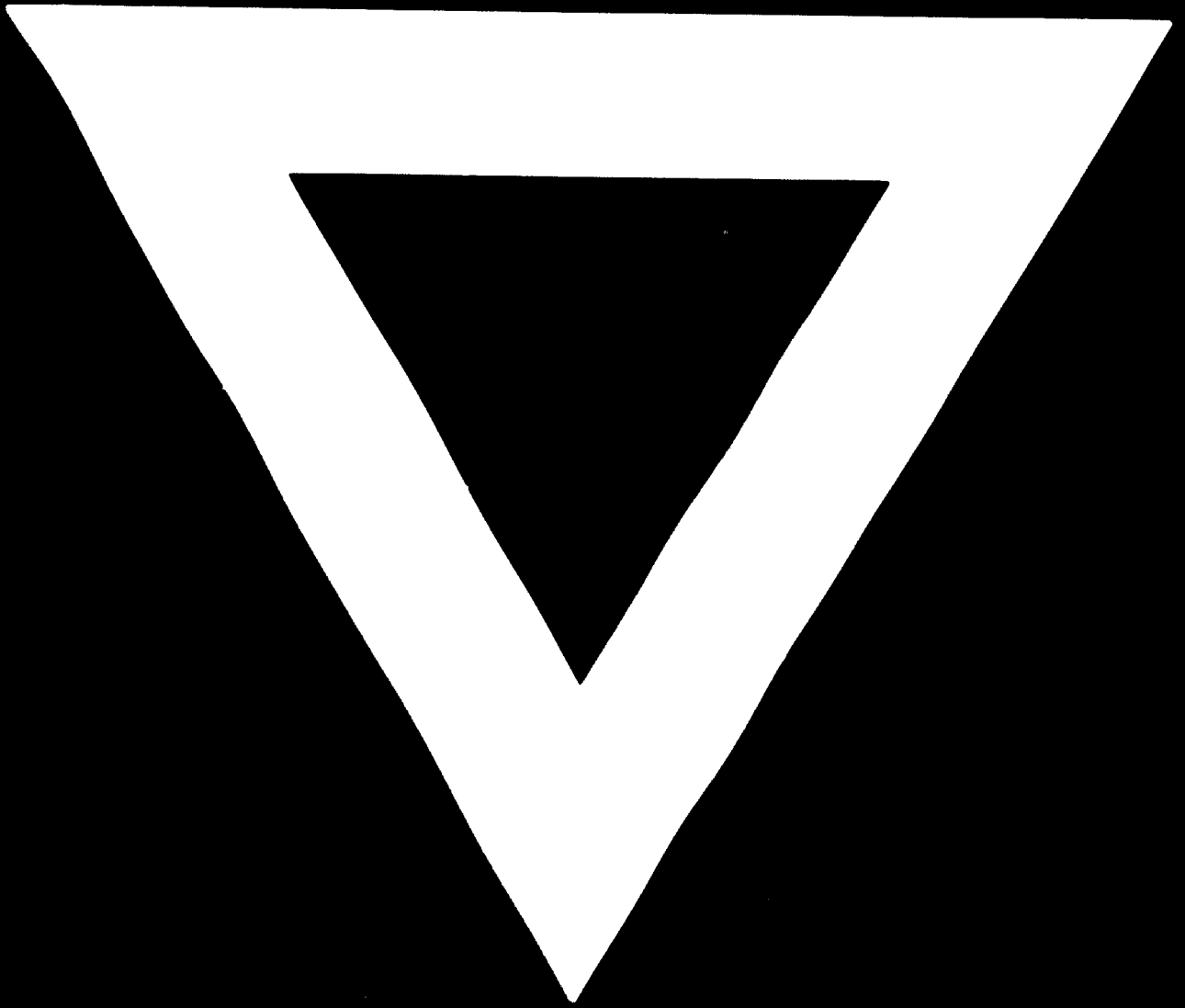


FIG. 9.





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