ACCELERATED OXIDATION OF COTTON CELLULOSE IN PRESENCE OF REDUCING SUBSTANCES—PART III

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Introduction

Mhatre, Nabar and Vyas[1] have investigated the accelerated oxidation of cellulose by hypochlorite solutions in presence of a number of reducing substances such as leuco compounds of vat dyes belonging to different chemical structure and also ferrous hydroxide and have arrived at the following conclusions:

(1) The rate of oxygen transfer, the amount of oxygen transferred and the pH for maximum oxygen uptake by the cellulose substrate depend on the particular reducing substance present on the fibre during the oxidation.

(2) With at least twelve leuco vat dyes examined in detail, there exists no similarity between the pH-corrected oxidation potential[2] curve and the curves showing relation between pH and oxygen uptake and pH and cuprammonium fluidity.

(3) At 30° C., the corrected oxidation potential as obtained by applying a correction of $0 \cdot 06 \times$ pH to the measured value of the potential, is not a measure of the oxidising intensity of hypochlorite solutions.

(4) Although for each of the dyes examined, the similarity in shape of curves relating pH to (*a*) oxygen consumed, (*b*) cuprammonium fluidity, (*c*) copper number and (*d*) carboxylic acid content does not materially alter, each accelerator is found to have a specific influence on the degree of oxidation. Further the oxidation accelerated by leuco compounds of vat dyes such as Cibanone Orange R, Cibanone Yellow R, Caledon Yellow GN, etc., shows a maximum intensity of oxidation at about pH $7 \cdot 3$. By replacing the accelerating system by leuco Ciba Blue 2 B or ferrous hydroxide, the pH for maximum oxidation is shifted to $6 \cdot 3$ while with leuco compounds of Caledon Jade Green XS, Caledon Green BS and Indanthren Dark Blue BO the pH for maximum oxidation is at about $5 \cdot 4$.

From the foregoing it is clear that the reducing substance present on cellulose maintains its identity as seen by the shift in the pH at which maximum chemical attack takes place and that it is some intrinsic physico-chemical property of the reducing substance present on cellulose during the oxidation that is responsible for this acceleration.

In an attempt to explain the accelerated oxidation of cotton cellulose by hypochlorite in presence of reduced Cibanone Orange R, Nabar, Scholefield and Turner[2] suggested that an estimate of the intensity of oxidation may be given either by (a) the difference between a value representing the measured potential of sodium hypochlorite solution and a value representing the oxidation-reduction potential of the cellulose substrate or (b) the difference between the measured oxidation potential of the hypochlorite solution and the oxidation-reduction potential of the reduced Cibanone Orange R present on the fibre. The first suggestion has been critically examined in the earlier communication of this series,[3] and it has been shown that it does not stand to experimental investigation. The present paper deals with an account of the investigation concerning the second suggestion made by the above authors.[2]

Electrical measurements on the system leuco vat dye ⇌ vat dye are not easy to carry out owing to the extremely low solubility of these compounds in aqueous medium. This is further complicated by pH of the medium which directly influences the dissociation of the weakly acidic dissociable groups of the leuco compounds.

In the present investigation, experimental difficulties have been considerable and in spite of the accumulation of considerable data, it has not yet been possible to put forward a full theoretical explanation of the significance of the results. Nevertheless they give a clear indication of the part played by the reducing substances in bringing about an accelerated oxidation of cellulose by hypochlorite solutions.

Two dyes, Cibanone Orange R and Ciba Blue 2 B, were selected for the experimental investigation. These were dyed according to usual dyeing practice on loose cotton and yarn, previously purified. The redox potentials of the two vat dyes while upon the fibre were then measured by a new method developed after a considerable experimentation.[4, 5]

It is shown that there is a very close similarity between the curve showing the relationship of pH to the difference in the oxidation potential of the hypochlorite and the reduction potential of the leuco vat dye and the curve showing the relation between the pH of the oxidising medium and the

oxygen consumed by the leuco vat dyed cotton. This observation is further supported by the straight line relationship existing between the oxygen consumption and the difference in the oxidation potentials of the hypochlorite and the reduction potentials for both the dyes.

EXPERIMENTAL METHODS

Cotton.—Cotton in the form of yarn and loose cotton was used. It was purified according to the method employed for the preparation of standard cellulose.[6]

Method of dyeing.—Two per cent. dyeings of Cibanone Orange R and Ciba Blue 2 B were prepared. The dyestuff was carefully vatted and the dyeing was carried out at 60° C. in a dark room for ¾ of an hour. After the dyeing was complete the oxidation was allowed to take place slowly in cold running water. The full details of the method are given elsewhere.[2]

Reduction of the dyeing and the determination of oxygen consumption.—

Ten grams of the dyed yarn was treated with 2% cold solution of sodium hydrosulphite, the leuco-vat dyed yarn thus obtained was washed thoroughly with oxygen free cold distilled water and then treated with a suitably buffered sodium hypochlorite solution. This was carried out strictly adhering to details described by Nabar, Scholefield and Turner.[2]

Determination of the reduction potential of vat dyes.—The method used is similar to the one used by Mhatre and Nabar[4] for the determination of the reduction potential of ferrous hydroxide. The electrode consists of a stout platinum wire sealed in a bulb blown at the end of a glass tube 3 mm. diameter. The electrodes were properly cleaned, adhering to details described by Mhatre and Nabar.[4]

Loose cotton dyed with the vat dyestuff was wrapped tightly round the platinum wire. Clean mercury was then filled in the glass tube. Three such electrodes were fixed in a rubber stopper and placed in boiling distilled water so as to remove all the occluded air from the dyed cotton. This also serves to bring about an initial wetting out of the cotton. The electrodes were then immersed in a 2% solution of sodium hydrosulphite to bring about the reduction of the vat dye. The reduced dyeings on the electrode were then immersed at once in cold air-free distilled water. The electrodes were moved backwards and forwards below the surface of water for one minute and then transferred to another such bath. This was repeated three times and then immediately immersed in a buffer solution which was boiled sufficiently and cooled to 30° C., while purified hydrogen was vigorously bubbled in.
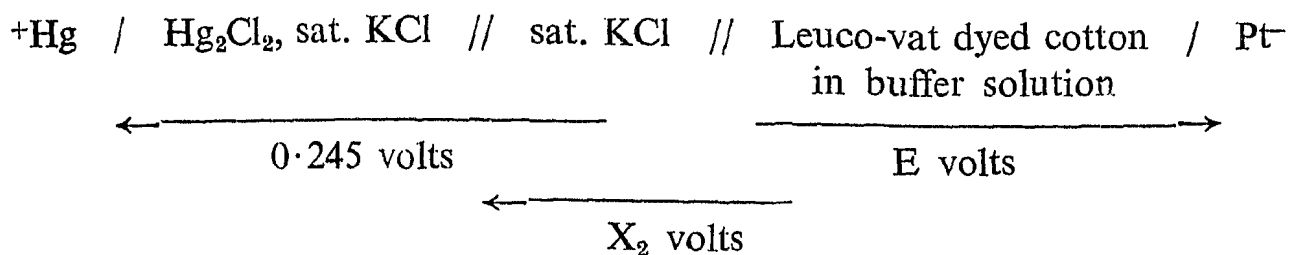
The apparatus used is shown in the diagram.
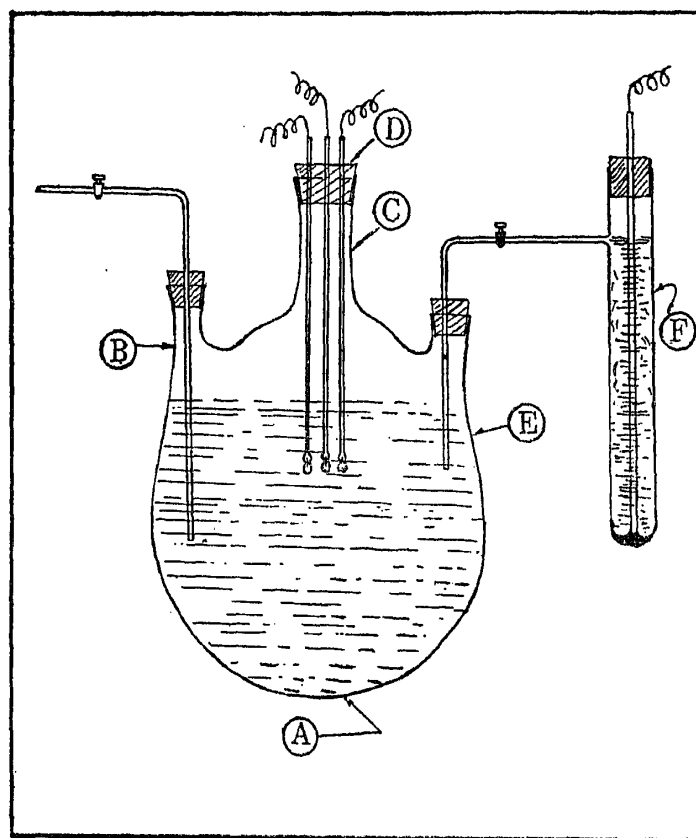
Diagram

A is a three-necked flask in which the boiled out buffer solution is kept. Through the neck *B*, the hydrogen gas is bubbled in, while the buffer is being cooled. In the neck *C*, the stopper *D*, carrying the electrodes, is fixed. The neck *E* carries a saturated calomel half cell *F*. The end of the side tube of the electrode vessel was sealed by an agar agar jelly in order to prevent rapid diffusion of potassium chloride solution into the buffer. After the buffer had been cooled to nearly 30° C., the whole apparatus was kept in a thermostat adjusted to 30° C. $\pm$ 0·1. The bubbling of purified hydrogen gas was continued for about 15 minutes more in order to allow the buffer to attain a temperature of 30° C. $\pm$ 0·1. The bubbling was then stopped and the neck *B* was tightly stoppered with a rubber bung.

The two electrodes, *i.e.*, the platinum electrode and the calomel electrode *F* thus formed a cell and the potential of the cell was then measured using Cambridge Scientific Instrument Company's valve potentiometer. The measurements of E.M.F. were made at an interval of about 5 minutes, until a stable value was reached. For this, the experiment had to be continued for a period of over three hours. The readings were plotted against time

and the horizontal portion of the curve was taken to represent the potential of the leuco-vat dye at that pH value.

Three electrodes were used for each pH value and the average of these was taken. Sometimes an electrode behaved erratically and so was discarded. The value was accepted only when it was reproduced. For each pH value, the whole experiment was independently repeated twice or thrice using new platinum electrodes and it was found that the values were reproducible with good accuracy. The actual measurement consists in determining the e.m.f. of the following cell:—

+Hg / Hg_2Cl_2, sat. KCl // sat. KCl // Leuco-vat dyed cotton / Pt⁻ in buffer solution

$$\xleftarrow{\hspace{4cm}} \qquad \xrightarrow{\hspace{5cm}}$$

0·245 volts E volts

$$\xleftarrow{\hspace{3cm}}$$

X_2 volts

$E = X_2 - 0.245$, where E is the reduction potential.

Two typical curves for Ciba Blue 2 B showing the behaviour of the electrodes in acid pH and alkaline pH are shown in Figs. 1 and 2 respectively.
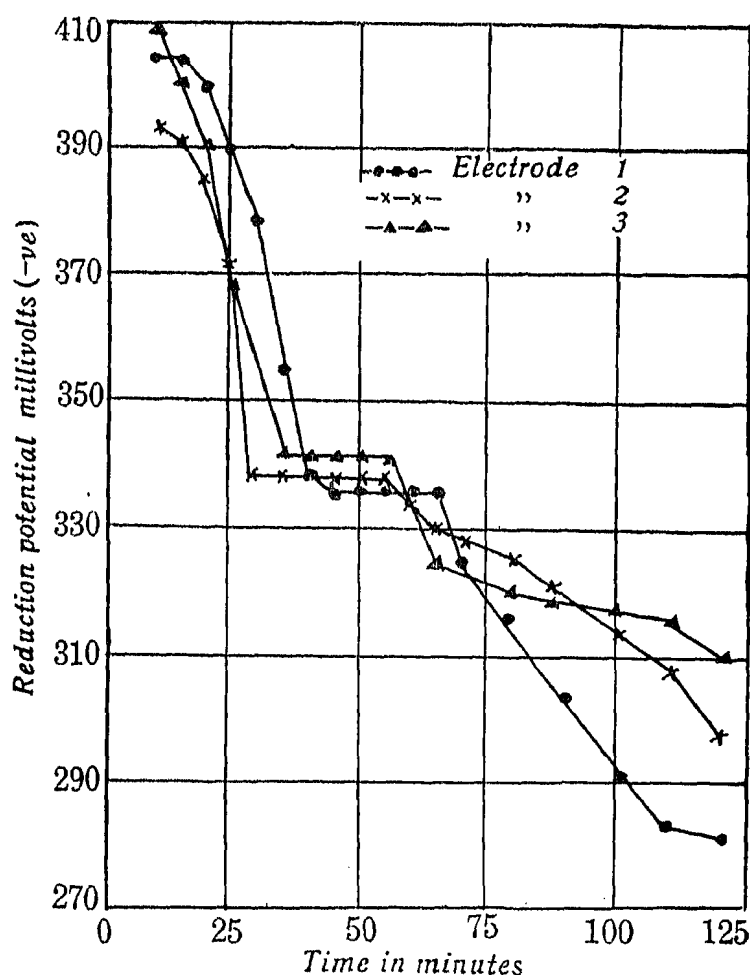

FIG. 1. Relation between time of measurement and reduction potentials of Ciba Blue 2 B at pH 6·15

FIG. 2. Relation between time of measurement and the reduction potential
of Ciba Blue 2 B at pH 8·36

It was found that on alkaline side, the values go on increasing with time, reach a stable value and then fall slowly; while on acid side the values fall continuously from the beginning, reach a stable value and then again fall rapidly.

It is found that the ease of measurement and the stability of the equilibrium on alkaline side is much greater than that on the acid side. To ensure that the potential developed when the leuco-vat dyed cotton is in contact with the platinum wire, is due to the presence of the leuco-vat dye only, blanks were carried out with the following systems:

(1) Hg^+ / Hg_2Cl_2, Sat. KCl // Sat. KCl   //   air-free   / Pt^-
                              solution   buffer
                                            solution

(2) Hg^+ / Hg_2Cl_2, Sat. KCl // Sat. KCl   //   loose dyed cotton / Pt^-
                              solution   in air-free
                                            buffer solution

Experiments were done exactly under the same conditions as those when determining the reduction potential of the vat dye and it was found that in neither case, stable and reproducible potential could be established.

Calibration of the glass electrode.—The glass electrode is not reliable for the determination of pH values higher than 9·5 and was hence calibrated for pH values between 9 and 12 with buffers of known pH.

EXPERIMENTAL RESULTS

The experimental results are described in Tables I to VI. The measured values of the reduction potentials for Cibanone Orange R and Ciba Blue 2 B are given in Tables I and II respectively and the relation between the reduction potentials and pH for the two dyes is graphically shown in Figs. 3 and 4 respectively.

Examination of these curves shows a resemblance to a neutralization curve of polybasic weak acid group by group. Further it is seen that the number of inflexions in the curve for any particular dye are definite. In the case of Cibanone Orange R, these are four, while in case of Ciba Blue 2 B these are only two.

TABLE I

Relation between pH and reduction potential of Cibanone Orange R

(Each value of redox potential is a mean of three independent measurements)

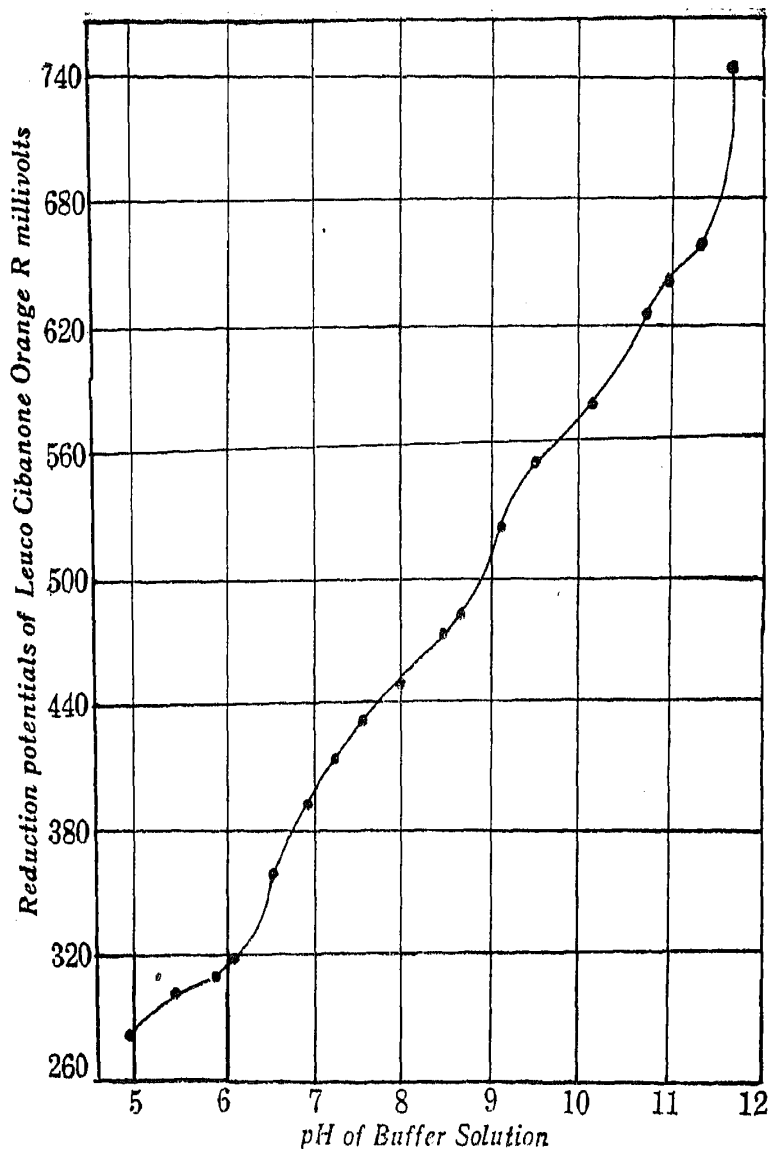| pH of the buffer solution	Measured potentials (millivolts)			Mean
	Expt. 1	Expt. 2	Expt. 3	
11·75	744·3	744·6	··	744·4
11·40	662·5	667·0	660·7	660·7
11·00	645·5	644·0	··	644·7
10·80	627·7	629·0	··	628·2
10·15	582·0	585·5	582·0	583·6
9·58	558·5	558·5	··	558·5
9·15	527·5	524·5	523·5	525·7
8·68	481·0	482·5	··	481·7
8·02	448·5	451·0	··	449·7
7·55	433·5	435·5	··	434·5
7·25	417·0	414·5	··	415·5
6·95	389·5	385·5	388·5	387·7
6·55	359·5	358·9	··	359·2
6·06	317·5	321·5	··	318·7
5·92	310·5	309·0	··	319·7
5·38	300·0	299·7	303·5	302·0
4·95	281·0	276·5	281·5	279·3

FIG. 3. Relation between pH and the reduction potential of Cibanone Orange *R*

TABLE II

Relation between pH and reduction potential of Ciba Blue 2 B

pH of the buffer solution	Measured potentials (millivolts)			Mean
	Ext. 1	Expt. 2	Expt. 3	
11·75	734·0	737·0	..	735·5
11·20	657·5	659·9	..	658·2
10·68	612·0	611·5	..	611·7
10·00	561·5	562·5	564·5	563·0
9·55	547·5	545·5	..	546·8
9·15	522·0	522·5	..	522·3
8·36	485·0	487·5	490·0	488·7
7·65	423·5	422·5	..	423·2
7·02	390·5	392·5	..	391·5
6·72	378·0	378·5	..	378·3
6·34	362·5	365·5	364·0	364·5
6·15	339·0	336·5	..	338·0
5·83	309·5	302·0	..	305·6
5·30	286·0	286·0	..	286·0
4·85	272·5	265·5	..	267·3
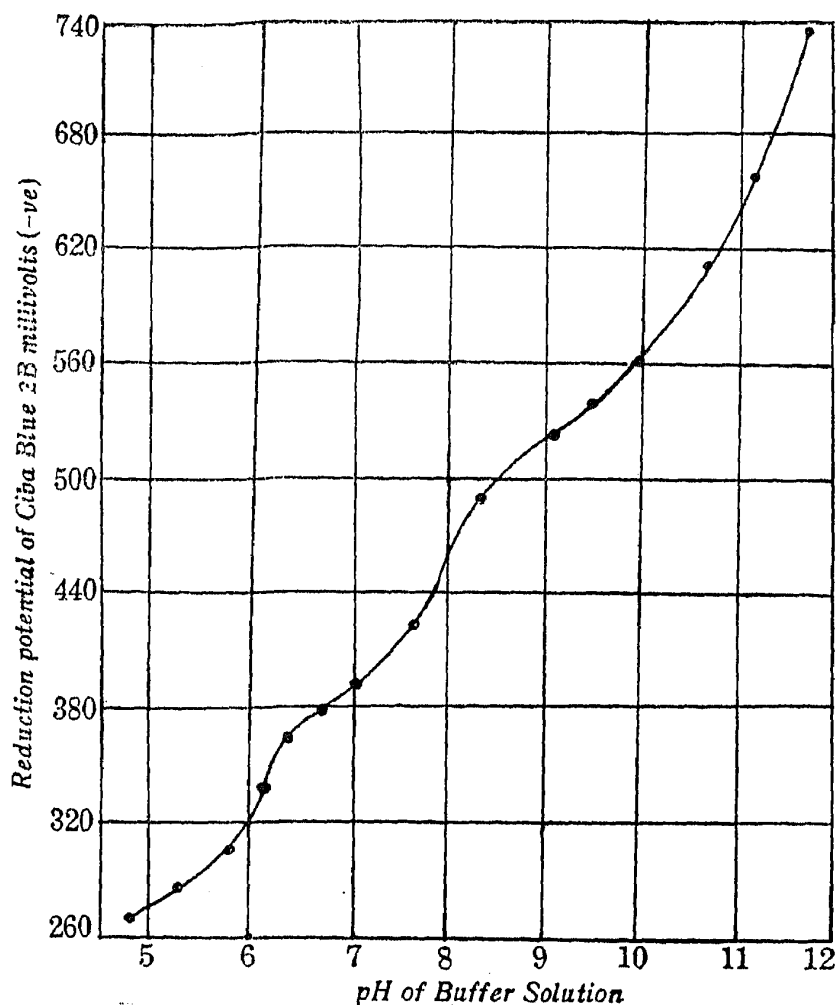
FIG. 4. Relation between pH and the reduction potential of Ciba Blue 2 B

Tables III and IV give the relation between pH and the difference in the oxidation potential of sodium hypochlorite and the reduction potential of the vat dyestuff. The values of the oxidation potentials of sodium hypochlorite are reproduced from Part I of the present communication[3]; the reduction potentials of Cibanone Orange R and Ciba Blue 2 B are taken from Tables I and II respectively. From the two sets of figures the differences are calculated. The relation between this difference and pH is shown graphically in Figs. 5 and 6. It is seen that Cibanone Orange R shows a maximum at pH 7·25 while Ciba Blue 2 B shows it at pH 6·34.
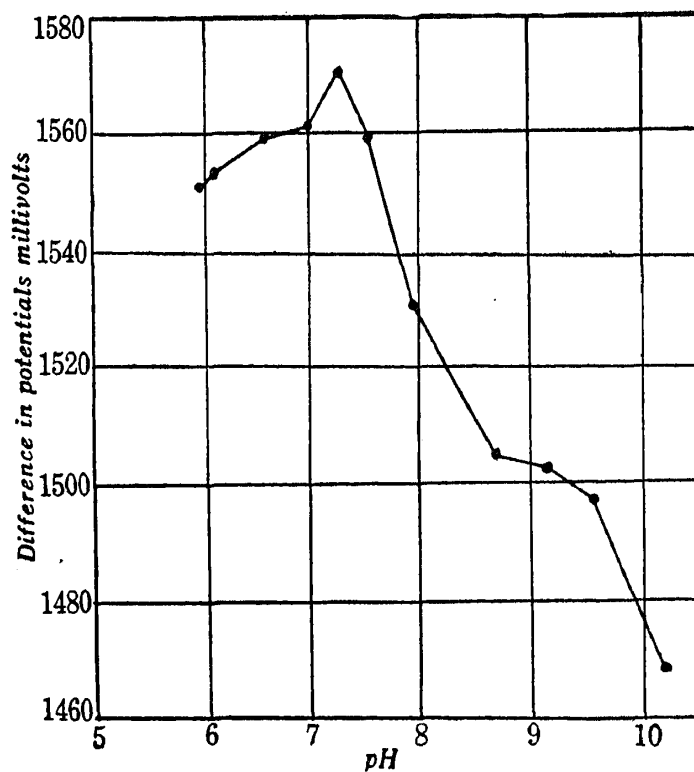
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TABLE III

Relation between pH and the difference in oxidation potential of hypochlorite and reduction potential of Cibanone Orange R

pH	Oxidation potentials (millivolts)* (+) A	Reduction potential of Cibanone Orange R (millivolts) (−)B	Difference in millivolts A−(−B)=A+B
10·15	885	583·6	1468·6
9·58	939	558·4	1497·4
9·15	977	525·7	1502·7
8·68	1023	481·7	1504·7
8·02	1081	449·5	1430·5
7·55	1126	433·4	1559·4
7·25	1155	415·7	1570·7
6·95	1173	387·7	1560·7
6·55	1200	359·2	1559·2
6·06	1234	318·7	1552·7
5·92	1241	310·0	1551·0
5·38	1277	302·0	1579·0
4·95	1305	279·3	1584·3

* Reproduced from the paper by Joshi, Mhatre and Nabar, *This Journal*, 1949, **29**, 277.

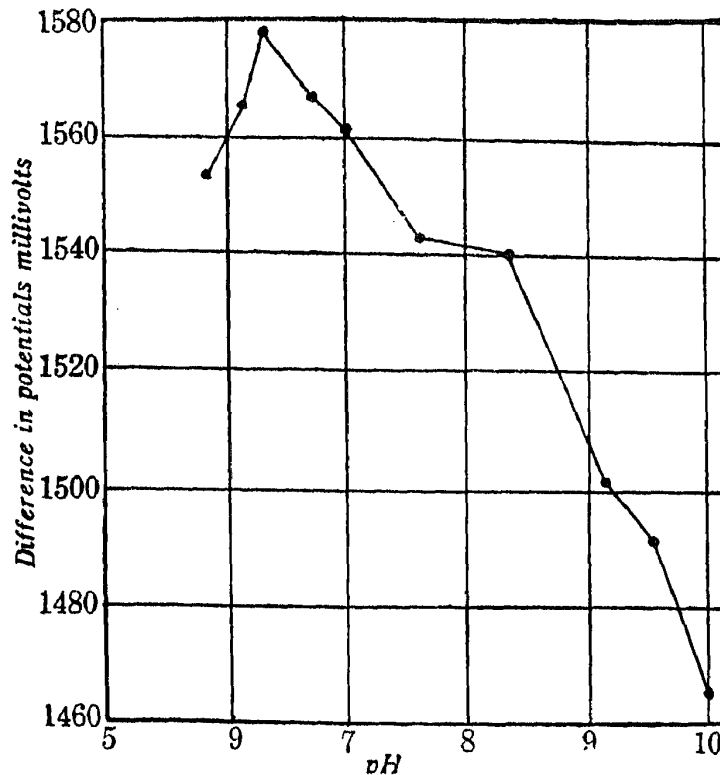FIG. 5. Relation between pH and difference in the oxidation potential of hypochlorite and reduction potential of Cibanone Orange *R*

TABLE IV

*Relation between pH and the difference in the oxidation
potential of sodium hypochlorite and the reduction
potential of Ciba Blue 2 B*

pH	Oxidation potential of hypochlorite (millivolts)* (+) A	Reduction potential of Ciba Blue 2B (millivolts) (−) B	Difference between potentials (millivolts) A−(−B)=A+B
10·00	900	563·0	1463·0
9·55	942	546·8	1488·8
9·15	977	522·3	1499·3
8·36	1050	488·7	1538·7
7·65	1112	423·2	1541·2
7·02	1168	392·3	1560·3
6·72	1188	378·3	1566·3
6·34	1214	364·5	1578·5
6·14	1227	338·0	1565·0
5·83	1248	305·6	1553·6
5·30	1282	287·5	1569·5
4·85	1311	267·3	1578·3

* Reproduced as indicated in Table III.

FIG. 6. Relation between pH and difference in the oxidation potential of hypochlorite
and reduction potential of Ciba Blue 2 B

The values of oxygen consumption by leuco-Cibanone Orange **R** and leuco-Ciba Blue 2 B dyed cotton at 30° C. are shown in Tables V and VI respectively and the relation between pH and oxygen consumption is graphically shown in Figs. 7 and 8.

TABLE V

Relation between pH and oxygen consumption (Temp. 30° C.)

(Cibanone Orange R)

pH of buffered sodium hypochlorite solution	Milliatoms of oxygen consumed by 100 g. of dyed cellulose
9·08	7·90
8·90	8·08
7·98	11·02
7·30	20·73
6·91	19·82
6·06	16·91
5·81	12·75
5·32	11·27
4·99	9·02
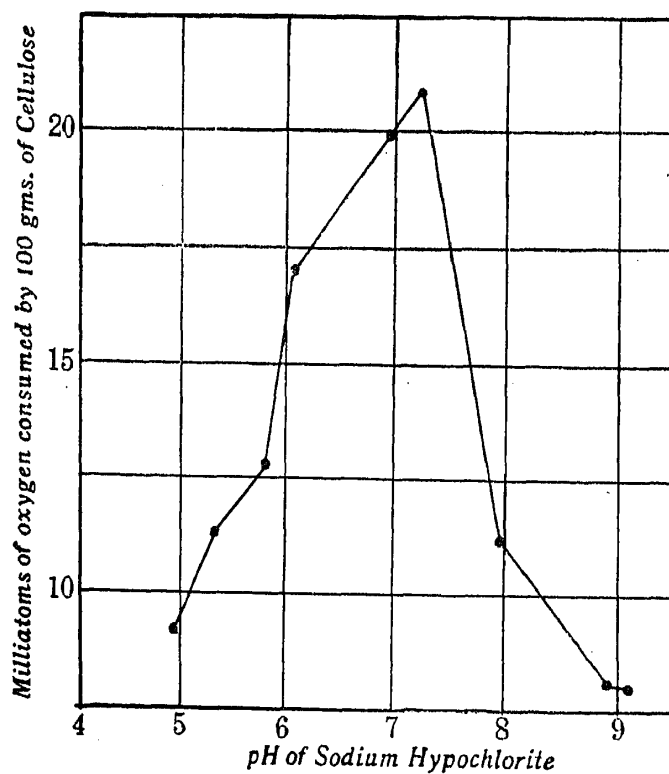
FIG. 7. Relation between pH of sodium hypochlorite solution and oxygen consumed by Cibanone Orange *R*, dyed cotton

TABLE VI

Relation between pH and oxygen consumption (Temp. 30° *C.)*

(Ciba Blue 2 B)

pH of buffer sodium hypochlorite solution	Milliatoms of oxygen consumed by 100 g. of dyed cellulose
9·056	14·06
8·10	22·28
7·48	23·83
6·99	27·63
6·13	34·21
5·98	29·02
5·40	27·54
4·60	24·70
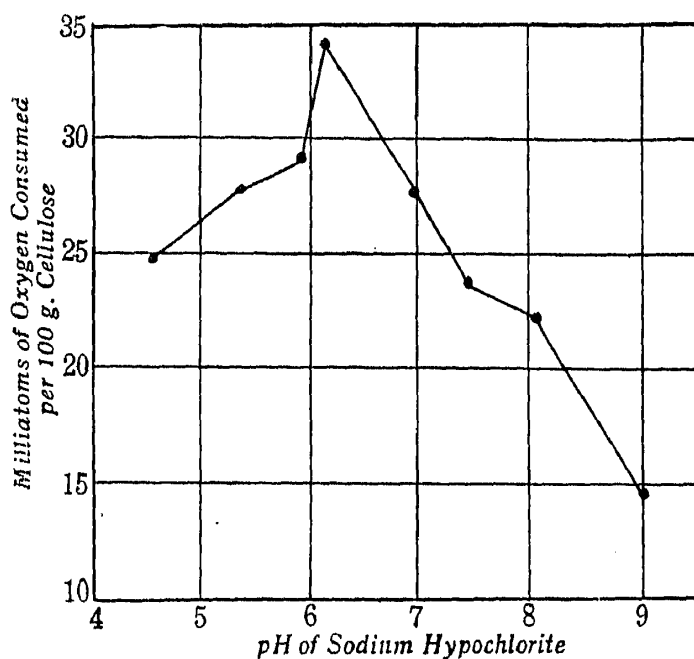
FIG. 8. Relation between pH of sodium hypochlorite solution and oxygen consumed by Ciba Blue 2 B dyed cotton.

It is interesting to find that for Cibanone Orange R, the maximum oxygen consumption takes place at pH 7·3, which is the same as in Fig. 5; and in case of Ciba Blue 2 B, it is at pH 6·34 which is also the maximum point in Fig. 6.

In Fig. 9 is shown the relation between the oxygen consumption and the difference between the potentials for both the dyes. There exists a straight line relationship between the two quantities which indicates that the rate of oxygen transfer is directly proportional to the difference in the potential values,
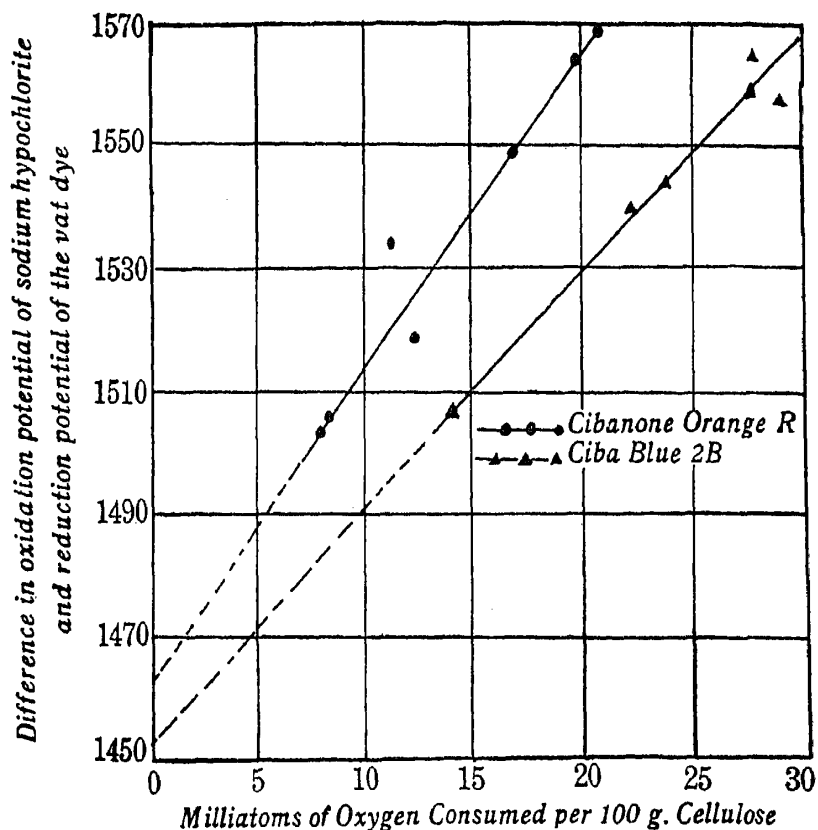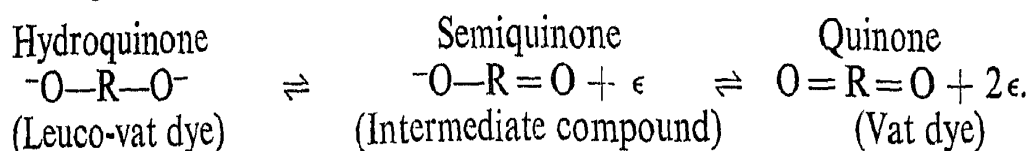
FIG. 9

It is extremely interesting to note that both the straight lines when produced backwards cut the potential axis at about 1,455–1,466 millivolts, indicating that for this difference theoretically no acceleration of the oxidation should occur. Nabar, Scholefield and Turner[2] have also made similar observations.

DISCUSSION

The results described in the foregoing have to be discussed so as to bring out clearly: (A) the significance of the electrometric measurements for the system Pt/leuco-vat dyed cotton in air-free buffer solution and (B) the mechanism of acceleration of the oxiadtion.

(A) *The significance of the electrometric measurements for the system Pt/ leuco-vat dyed cotton in air-free buffer solution.*—In considering the theoretical aspects of the potential measurements of the system, Pt/leuco-vat dye-cellulose complex (in air-free buffer solution of known pH value), a number of equilibria, set up as a result of (a) the molecular structure of the dye, (b) the ease with which it can be reduced and oxidised, and (c) the influence of hydrogen-ion concentration on (i) the equilibrium:—Quinone $\leftrightarrows$ Hydroquinone and (ii) the dissociation of the hydroxyl groups of the leuco compound, will have to be considered.

During the change, leuco-vat dye →vat dye, evidence[1,7,8] of the formation of an intermediate compound known as semiquinone is available. The stages undergone during the oxidation may be represented as

Hydroquinone   Semiquinone   Quinone

$^-O—R—O^- \quad \rightleftharpoons \quad ^-O—R=O + \epsilon \quad \rightleftharpoons \quad O=R=O + 2\epsilon.$

(Leuco-vat dye)   (Intermediate compound)   (Vat dye)

There is also ample evidence[7,8,9,10] to indictae that vat dyes and their leuco-compounds when present together behave identically with many other typical reversible oxidation-reduction systems. If all the forms in which a vat dye can exist are considered as dissolved in the buffer solution and if an indifferent electrode such as platinum is placed in this solution, due to the interchange of electrons, the electrode will acquire a definite charge. The general equation relating to the composition of such a reversible system to the potential set up may be expressed as follows:—

$$E = E_0 + \frac{RT}{nF} \ln \frac{[\text{oxidant}]}{[\text{reductant}]}.$$

Apart from the straightforward equilibrium mentioned, *viz.*,
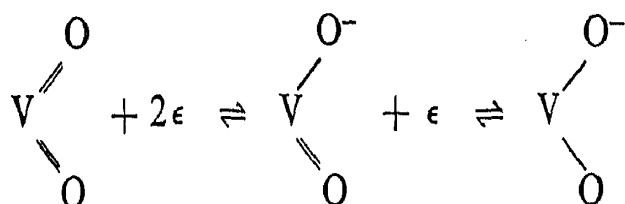
which may be operative in a definite manner at a fixed hydrogen-ion concentration, when one considers it in solutions of different hydrogen-ion concentrations, the system becomes more complicated and under these circumstances, the number of equilibria to be encountered which may influence the actual value of the potential set up at the platinum electrode, may be represented by the following scheme:
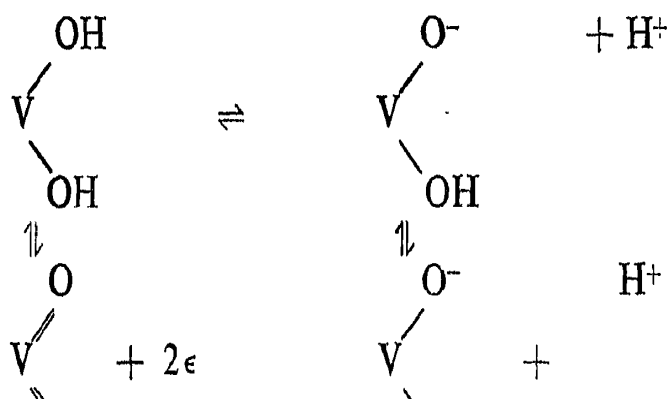
Hence the curve relating pH to the reduction potential may not be as simple as to be represented by the equation referred to above. To add to this difficulty, one has to encounter the extremely small solubility of the vat dyes and their leuco-compounds in aqueous medium so that the system, though electrochemically sound, is poorly poised and hence takes a considerably long time to come to a steady value.

Examination of the curves shown in Figs. 1 and 2 giving relation between the reduction potential and the time of measurement, shows that there is a region which is definitely constant. For alkaline buffers, the potentials slowly rise with time, come to a steady value which remains constant for several minutes and then show a steady fall. On the acid side, however, the potential values show a drop in the beginning, then reach a stable value remaining constant for several minutes and then show a steady fall. Throughout the measurements, these stable values of the potentials have been accepted as the measure of the potential set up at the platinum electrode due to the combined influence of the various equilibria already mentioned.
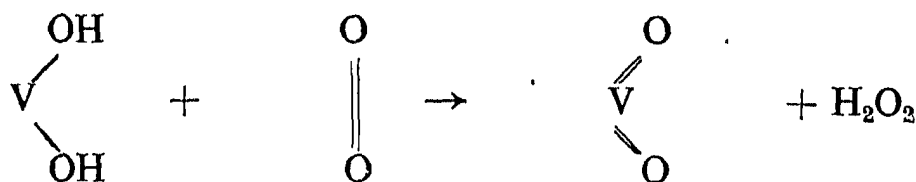
It is interesting to inquire why the potential values on the acid side first decrease, come to a steady value and fall again, while those on the alkaline side first increase, reach a stable value and then drop. Several factors may be responsible for this behaviour. Firstly, the leuco-dyed cotton, which has been wrapped round the platinum wire, is washed with distilled water, the pH of which is near about the neutral point. When such an electrode in contact with air-free distilled water is placed in an acid buffer, some time is necessary for the acid buffer to diffuse into the cotton and the water into the buffer solution so that an equilibrium buffer mixture is formed. Since the reduction potentials become more and more negative with increasing pH, it is expected that the electrode potential in presence of air-free distilled water (which is approximately neutral in pH) will be higher than what it would be if the electrode were in contact with the acid buffer itself. The slow diffusion of the buffer into the cotton and the consequent displacement of water, causes a fall in the potential until an equilibrium is reached when the potential remains steady. The fall which occurs after the potential has remained steady for several minutes may be due to the slow diffusion of oxygen into the electrode vessel upsetting the equilibrium set up at the electrode. Oxygen might be introduced through tiny leakages in the various connections made to the electrode vessel or through the calomel half cell. On the alkaline side, however, the potentials first rise, indicating that the outside buffer which is of a higher pH value slowly displaces the water until an equilibrium buffer mixture is formed when a stable value is

attained. This is followed by a steady fall, the reasons for which appear to be the same as those advanced above.

The electrometric measurements as described in the foregoing are distinct from those made by Geake and Appleton[8] for vat dyestuffs. They measured the potentials of several vat ⇌ leuco-vat dye systems in presence of aqueous alkaline solutions mixed with pyridine, so that the potentials measured were due to the true equilibrium of the leuco-vat ⇌ vat-dye system.

Examination of the curve in Fig. 3 giving relation between pH and the reduction potential of Cibanone Orange R reveals that there are four distinct inflexions or steps indicating the possibility of the presence of four weakly dissociating acid groups in the molecule. In a leuco-vat dye, these are represented by hydroxyl groups formed during the change Quinone ⇌ Hydroquinone. Similar curve (Fig. 4) for Ciba Blue 2 B shows a definite presence of two inflexions or steps. From the chemical constitution of Ciba Blue 2 B, it is easily seen that it contains two carbonyl groups capable of being reduced to the hydroxyl stage, so that the two inflexions on the pH-reduction potential curve (Fig. 4) confirm the presence of two weakly dissociable acid groups. If this hypothesis is correct, then from what has been said above, Cibanone Orange R, the constitution of which is unknown, may contain four reducible carbonyl groups. This agrees very well with the results obtained by Atherton and Turner[11] on the basis of the reoxidation of leuco-Cibanone Orange R by air and the simultaneous formation of hydrogen peroxide. From the amounts of hydrogen peroxide formed during the reoxidation of leuco-Cibanone Orange R, the above authors on the basis of the reaction

$$\begin{array}{c}\text{OH}\\ \diagup\\ \text{V}\\ \diagdown\\ \text{OH}\end{array} \quad + \quad \begin{array}{c}\text{O}\\ \|\\ \|\\ \text{O}\end{array} \quad \longrightarrow \quad \begin{array}{c}\text{O}\\ \diagup\\ \text{V}\\ \diagdown\\ \text{O}\end{array} \quad + \text{H}_2\text{O}_2$$

predict the presence of four reducible positions in the dye molecule.

Another interesting feature of the results is the fact that each hydroxyl group dissociates independently of the other and it appears from the distinct steps in the curves (Figs. 3, 4) that unless dissociation of one hydroxyl group is complete, the next hydroxyl group is not affected at all, so that the various hydroxyl groups follow one another until the dye molecule is fully dissociated. It can also be said that the various hydroxyl groups differ with respect to their ionisation constant, since they are progressively dissociating one after the other with increasing pH. It is difficult to state which

of the hydroxyl groups first start functioning. All the same it is clear that each inflexion indicates complete dissociation of one hydroxyl group. This behaviour is quite common with polybasic organic acids.

Hence, apart from the possibility of the actual determination of the reduction potentials of vat dyes from the point of view of their tendering activity, this method might be of use in determining the number of chemically reducible groupings in a vat dyestuff of unknown constitution.

(b) *Mechanism of accelaration of the oxidation.*—The most outstanding feature of the results described earlier is the close similarity in the shape of the curve showing relation between pH and oxygen consumption and that of the curve showing relationship of pH to difference between the oxidation potential of sodium hypochlorite solution and reduction potential of vat dyes [Cibanone Orange R (Figs. 7 and 5) and Ciba Blue 2 B (Figs. 8 and 6)].

The pH-oxygen consumption curve (Fig. 7) for Cibanone Orange R shows a maximum at pH 7·3 which is also the maximum point in the curve (Fig. 5) showing the relation between pH and the difference between the oxidation potential of sodium hypochlorite and the reduction potential of Cibanone Orange R. The same similarity as shown in case of Cibanone Orange R exists in the curves in Figs. 8 and 6 for Ciba Blue 2 B also, but is not so complete due to the fact that Ciba Blue 2 B itself is susceptible to attack by sodium hypochlorite.[12] Ciba Blue 2 B undergoes destruction by the action of the hypochlorite solution and the decomposition products thus formed are known to accelerate the decomposition of sodium hypochlorite.[12] In spite of this, however, the maximum points in both the curves coincide at about pH 6·3.

One point of great interest that must be mentioned here is the straight line relationship obtained between the oxygen uptake and the difference between the oxidation potential of hypochlorite and the reduction potential of the vat dyestuff (Fig. 9). This shows that the extent of chemical attack is directly proportional to the difference in the oxidation potential of the hypochlorite and the reduction potential of the vat dye; hence the latter can be considered as the measure of the oxidising intensity.

If the mechanism of oxygen transfer to cellulose in case of both the dyes is the same, one would expect the two straight lines to coincide with one another or at least to be parallel to one another. It is, however, seen that the oxygen loss per millivolt in case of Ciba Blue 2 B is greater than that for Cibanone Orange R. This greater rate of oxygen transfer, as has already been pointed out, must be due to the self-oxidation of Ciba Blue 2 B.[12] The

actual amount of oxygen which is utilized in this reaction is not easy to be determined.

If the straight lines, in Fig. 9 are extended backwards so as to cut the e.m.f. axis, it is found that for Cibanone Orange R the line crosses the axis at an e.m.f. value of about 1,462 millivolts; while the same for Ciba Blue 2 B crosses at about 1,454 millivolts, indicating that for differences in the oxidation potential of hypochlorite and the reduction potential of the reducing substances, below these values, there should be no appreciable acceleration. Even allowing for the very complex system under examination and the experimental error that is likely to occur, it is interesting to find the two values of the potentials in case of both the dyes to be very near to one another. It is equally interesting to recall similar observation recorded by Nabar, Scholefield and Turner,[2] who suggested from similar argument, that at 20° C. for Cibanone Orange R, below 1,483 millivolts, for corrected oxidation potential, no acceleration should take place.

From what has been said above, it may be concluded that the accelerated oxidation is conditioned by the reduction potential of the vat dye present on the fibre. This may not be as simple as it appears since as has already been mentioned in the first part of the discussion, the system is extremely complicated due to the various equilibria operating simultaneously.

It must be pointed out that, while considering the influence of reduced vat dyes in accelerating the rate of cellulose oxidation by hypochlorite solutions, Nabar, Scholefield and Turner[2] suggested that the measure of the tendency of hypochlorite to attack cellulose may not be its oxidation potential alone but the difference between the value of this potential and the reduction potential of the reduced vat dyestuff present on the fibre. The results described in the foregoing substantiate the suggestion.

It is extremely interesting to mention the results obtained by Mhatre and Nabar[4] for $Fe^{\cdot\cdot} \leftrightarrows Fe^{\cdot\cdot\cdot}$ system on cotton. They showed similar behaviour to exist when $Fe(OH)_2$ deposited on cotton is oxidized to the ferric stage by sodium hypochlorite. The coincidence of the pH value (pH 6·3) for maximum oxygen consumption with that where maximum point is obtained in the curve showing the relation of pH to the difference between the oxidation potential of hypochlorite and the reduction potential of ferrous hydroxide is equally strongly demonstrated by their results.

From what has been said in the foregoing, it is clearly seen that the three reducing substances, namely, leuco-Cibanone Orange R, leuco-Ciba Blue 2 B and Ferrous Hydroxide, when deposited on cotton, influence the

course of oxygen transfer in such a manner that the pH for maximum rate of oxygen transfer to cellulose is not the same in all the three cases. For leuco-Cibanone Orange R, this happens to be at about pH 7·3, while for ferrous hydroxide it is approximately at pH 6·3, which is also the point of maximum oxygen consumption for leuco-Ciba Blue 2 B.

From the various observations recorded above, it is easily seen that the pH for maximum oxygen transfer is different for different reducing substances and that the course of oxygen transfer is determined by the combined effect of the hypochlorite and the reducing substance.

All these observations lead one to think that in presence of substances such as those mentioned above, the hypochlorite looses its identity as far as the rate of oxygen transfer to cellulose is concerned and is solely guided by certain physico-chemical properties of the substances present. As has been demonstrated at least in the three cases, e.g., those of the systems $Fe^{..} \leftrightarrows Fe^{...}$, leuco-Cibanone Orange $R \leftrightarrows$ Cibanone Orange R and leuco-Ciba Blue $2 B \leftrightarrows$ Ciba Blue 2 B, the reduction potentials as measured by the method described, play an important part in determining the course of oxidation and also the point of maximum oxygen consumption.

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