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

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INTRODUCTION

IN the previous communication,[1] an account of the measurements of oxidation potentials of dilute sodium hypochlorite solutions and of the estimation of oxygen consumption from such solutions when cotton dyed with reduced Cibanone Orange R was treated with them, was given. It was shown that the curves relating "corrected oxidation potential" to pH and oxygen consumption to pH, were similar in shape at 20° C., but at 30° C. the shapes of the curves showing this relationships were not at all comparable. It was suggested that the method of applying correction to the measured oxidation potential at 20° C. was either not applicable to similar measurements at 30° C. or that the oxidation potentials were not at all indicative of the intensity of oxidation.

Nabar and Turner[2] made earlier similar observations by replacing the accelerating system leuco vat dye→vat dye by ferrous hydroxide→ ferric hydroxide. They showed that at 20° C. the oxidation of cellulose in the presence of ferrous hydroxide resembled in principle, the oxidation of cellulose accelerated by leuco Cibanone Orange R, but the pH for maximum oxygen transfer and for maximum cuprammonium fluidity of the oxidised cotton in presence of ferrous hydroxide was shifted approximately by one pH unit to the acid side from the region of maximum activity in presence of reduced Cibanone Orange R.[3] Apart from these differences, however, the reaction accelerated by ferrous hydroxide appeared to be similar to that accelerated by a reduced vat dye. Their results further indicated a fairly consistent mode of oxygen transfer to cellulose over the whole pH range a fact which was strongly demonstrated by earlier results with leuco Cibanone Orange R.[3] It is of great interest to point out that only the pH for maximum oxygen transfer to cellulose from sodium hypochlorite solution is influenced by the reduced substance deposited on the fibre, but the mechanism of oxidation of cellulose remained unaltered. These results further indicated that the method of correcting the measured oxidation potentials to explain the shape of the pH-oxygen uptake curve, is not applicable to all accelerated oxidation systems even at 20° C.; otherwise the difference in the pH for maximum oxygen transfer in presence of the above two reducing substances would not have occurred.

From the foregoing it may be concluded that the rate of oxygen transfer to cellulose during hypochlorite treatment is primarily conditioned by the physico-chemical behaviour of the reducing substance present on the cellulose substrate. The present investigation was undertaken to see how far the behaviour of reducing substances of varied chemical structure, substantiated the above conclusion. From a study of the behaviour of twelve leuco vat dyes belonging to widely differing chemical structure, it is shown that the shape of the curve relating pH to oxygen uptake is not at all comparable with the pH-corrected oxidation potential curve. Further, the pH for maximum oxygen transfer is entirely determined by the particular reducing substance present on the cellulose.

These results fully substantiate the suggestion[1] that the corrected oxidation potentials obtained by applying ·06 × pH volts (30° C.) as correction to the measured value of the potential is not indicative of the oxidising intensity of hypochlorite solutions.

Experimental Methods

Cotton.—Grey yarn (18's) manufactured from Indian cotton was carefully purified by subjecting it to a standard bleaching treatment. In the fully bleached condition, the cellulose possessed the following chemical properties: Cuprammonium fluidity[4] (0·5% solution) = 3·7; copper number[5] = 0·015; milliequivalents of —COOH per 100 g. cellulose[6] = 0·5.

About 50 g. of the purified yarn was dyed with each of the vat dyes as described in the earlier communication.[3] The dyed yarn was conditioned. For each hypochlorite treatment 10 ± 0·1 g. of the conditioned yarn was used. It was reduced using 2% cold sodium hydrosulphite solution and after repeated washing with oxygen-free distilled water to remove sodium hydrosulphite, the reduced dyeing was treated with sodium hypochlorite solution adjusted to a definite hydrogen-ion concentration and strength of available chlorine. The details of the reduction, the hypochlorite treatment and the determination of the oxygen consumed are similar to those used by Nabar, Scholefield and Turner.[3]

Application of ferrous hydroxide to yarn and determination of oxygen consumed by ferrous hydroxide deposited cotton when treated with sodium hypochlorite solutions.—The production of cotton uniformly impregnated with the desired hydroxide and of approximately constant iron content was carried out as follows: Skeins of cotton (5 g.; 54 in. circumference) were cut through at one point. A tight tie-band was placed at each cut end, as near to the end as possible. The whole was weighed, placed in a 600 ml. beaker and covered with 400 ml. of a solution of ferrous ammonium sulphate containing 195 g. A. R. $FeSO_4.(NH_4)_2SO_4.6H_2O$ and 5 ml. of 5-N-sulphuric acid in 1 1. of boiled-out water. After uniform agitation the cotton was allowed to stand for 4 min. under the surface of the solution. It was then opened out and passed in the rope-like form at a fixed uniform speed through a pad mangle with rubber-rollers. By fixing a mark on the screw adjusting the roller pressure, and bringing the screw always to the same position, each batch of cotton was submitted to approximately the same pressure during padding, and it was found that the expression of liquid varied very little from one batch of cotton to another. After one padding, the cotton was again immersed in the iron solution, after it had been brought up to its original volume by adding fresh stock solution. The padding operation was repeated and the yarn transferred to 500 ml. of N-sodium carbonate solution prepared with cold, boiled out distilled water. It was stirred continuously under the surface for 1 min. and allowed to stand for a further 2 min. Stirring in this way is essential to ensure uniform distribution of the precipitate on the fibre. After precipitation of the hydroxide, the yarn was removed from the alkali solution, squeezed rapidly and washed under the surface of a large volume of cold, boiled out distilled water. The washing treatment was repeated 5 times, and the yarn then squeezed rapidly and uniformly and transferred at once to the appropriate buffered hypochlorite solution. The ferrous hydroxide precipitated in this way was pale and rather dull green.

The yarn thus obtained was immediately transferred to a suitably buffered sodium hypochlorite solution and the loss of available oxygen was determined after 10 min. treatment. The details of the procedure are similar to those described by Nabar and Turner.[2]

Determination of cuprammonium fluidity.—The curpammonium fluidity of the various oxidised samples was determined by the method of Clibbens and Geake.[4] Owing to the high level of degradation of most of the samples, the fluidity was determined in 1% solution.

Determination of copper number.—The copper number has been determined by Hayes' micro-method.[5] Due to the high level of degradation, half the weight of sample, normally recommended, has been taken. Another noteworthy feature is that N/25 potassium permanganate solution is replaced by N/25 ceric sulphate using *o*-ferrous phenanthroline complex as internal indicator.

Determination of carboxyl content.—The determination has been carried out by Neale and Stringfellow's alkali titration method,[6] One gram of the cation-free material is suspended in a mixture of 25 ml. of carbonate free 0·02 N caustic soda, 25 ml. of 5% solution of sodium chloride and 25 ml. of carbon dioxide-free distilled water. At the end of one hour the excess of alkali is back titrated with 0·02 N hydrochloric acid using Bromo-Cresol purple as indicator.

Estimation of iron on the fibre.—About 1 g. of the cotton was slowly ignited in a platinum crucible and heated for three hours. At the end it was cooled and digested with concentrated hydrochloric acid. The solution was then transferred to a conical flask and the crucible washed with 2 N hydrochloric acid. The contents of the flask were then diluted with dilute hydrochloric acid, 10 ml. of concentrated hydrochloric acid added and heated to boiling. Stannous chloride solution (3%) was then added drop by drop till all the iron was reduced. To the cold solution, 10 ml. of mercuric chloride and a drop of ortho-ferrous phenanthroline was added and the solution titrated against N/50 ceric sulphate.

EXPERIMENTAL RESULTS

A synopsis of experimental results is given in Tables I to III. From a study of twelve vat dyes of widely differing chemical structure, it is found

TABLE I. *Oxidation of cellulose in presence of leuco compounds of vat dyes (30°C.) for ten minutes*

pH of hypo-chlorite solution	Cibanone Orange R		Cibanone Yellow R		Indathrene Yellow FFRK		Indanthrene Yellow G		Ciba Green G	Cibanone Yellow GC	Caledon Gold Orange G
	(A)	(B)	(A)	(B)	(A)	(B)	(A)	(B)	(A)	(A)	(A)
5·0	10·0	13·3	..	..	9·0	12·9	13·8	18·0	15·8	..	..
5·1	..	..	8·2	9·8	..	..	..	..	..	11·1	8·0
5·5	..	..	..	..	..	..	..	..	..	13·3	..
5·8	..	..	..	..	..	..	15·8	23·6	..	..	..
6·0	16·0	23·7	..	..	11·2	15·8	16·7	29·4	..	..	10·5
6·1	16·9	25·9	12·2	15·8	..	..	..	..	19·9	15·7	..
6·5	..	..	14·8	22·5	11·4	16·7	..	..	..	18·4	13·0
7·	..	..	..	..	..	..	18·0	28·0	21·8	21·1	14·3
7·1	..	..	..	..	13·7	19·9	..	..	..	..	..
7·3	20·7	30·9	15·8	23·4	..	..	..	..	..	19·0	13·6
8·1	17·2	26·4	..	..	8·7	10·5	12·1	16·0	..	..	..
8·2	..	..	11·6	18·0	..	..	..	..	17·4	15·5	7·7
8·5	12·3	19·0	..	..	..	..	..	..	..	..	..
8·6	..	..	..	..	..	..	9·8	12·4	..	..	..
8·7	..	..	..	..	..	..	..	..	..	9·0	..
9·0	..	..	..	..	..	..	..	..	14·0	..	..
9·1	8·6	14·1	6·0	10·2	5·9	6·6	6·7	8·0	..	..	..
9·3	=	..	..	..	..	..	..	..	..	8·5	5·0

A = Milliatoms of oxygen consumed per 100 *g.* of reduced dyeing.
B = Cuprammonium fluidity of the treated dyeings (1% solution).

TABLE II. *Oxidation of cellulose in presence of leuco compounds of vat dyes (30° C.) for ten minutes*

pH of hypochlorite solution	Ciba Blue 2B		Ind. Dark Blue BO	Cal. Green BS	Cal. Jade Green XS
	A	B	A	A	A
4·5	..	..	28·7	22·5	12·0
4·6	22 8	24·5	30·0	..	..
5·1	..	..	..	..	14·0
5·4	27·8	27·5	33·6	25·2	15·8
5·8	31·8	31·0	..	..	..
6·0	..	..	..	21·6	..
6·1	..	..	22·2	..	12·0
6·3	34·4	34·5	..	..	..
6·5	..	..	..	15·1	10·8
6·7	..	..	12·7	..	..
7·0	..	..	11·5	13·2	..
7·3	28·4	21·6	..	..	..
7·6	..	..	..	..	8·0
8·0	24·8	13·1	..	..	..
8·2	..	..	7·9	10·6	7·4
9·0	20·6	11·0	7·0	..	..
9·2	..	..	..	9·6	7·4

A = Milliatoms of oxygen consumed per 100 grams dyeing.
B = Cuprammonium fluidity of the treated dyeing (1% solution).

TABLE III. *Oxidation of cotton impregnated with ferrous hydroxide* (30°*C.*) *for ten min.*

pH of hypochlorite solution	Per cent. of Fe on the fibre	Milli-atoms of oxygen per 100 g. of cotton	Cuprammonium fluidity (1% solution)	Increase in copper number	Increase in -COOH m.e. per 100 g. of Cotton
5·4	1·18	31·1	28·2	8·2	5·0
6·8	1·14	33·1	29·5	3·3	5·2
6·3	1·22	39·0	32·3	9·6	6·2
6·7	1·13	33·1	30·1	8·5	5·2
7·0	1·15	22·0	25·3	5·7	3·6
7·4	1·22	16·1	21·2	4·3	2·5
8·0	1·23	5·7	10·0	0·8	1·3
9·1	1·21	2·2	1·3	0·1	0·7
10·0	1·21	1·14	0·9	0·04	0·5

that they fall into three categories with respect to their influence on the rate of oxygen transfer to cellulose. In Table I are given results obtained with seven dyes which may be said to show a normal behaviour, comparable with the known properties of hypochlorite solutions during bleaching practice, The maximum oxygen transfer to cellulose takes place in this case at about pH 7·3. These results are shown in Fig. 1.

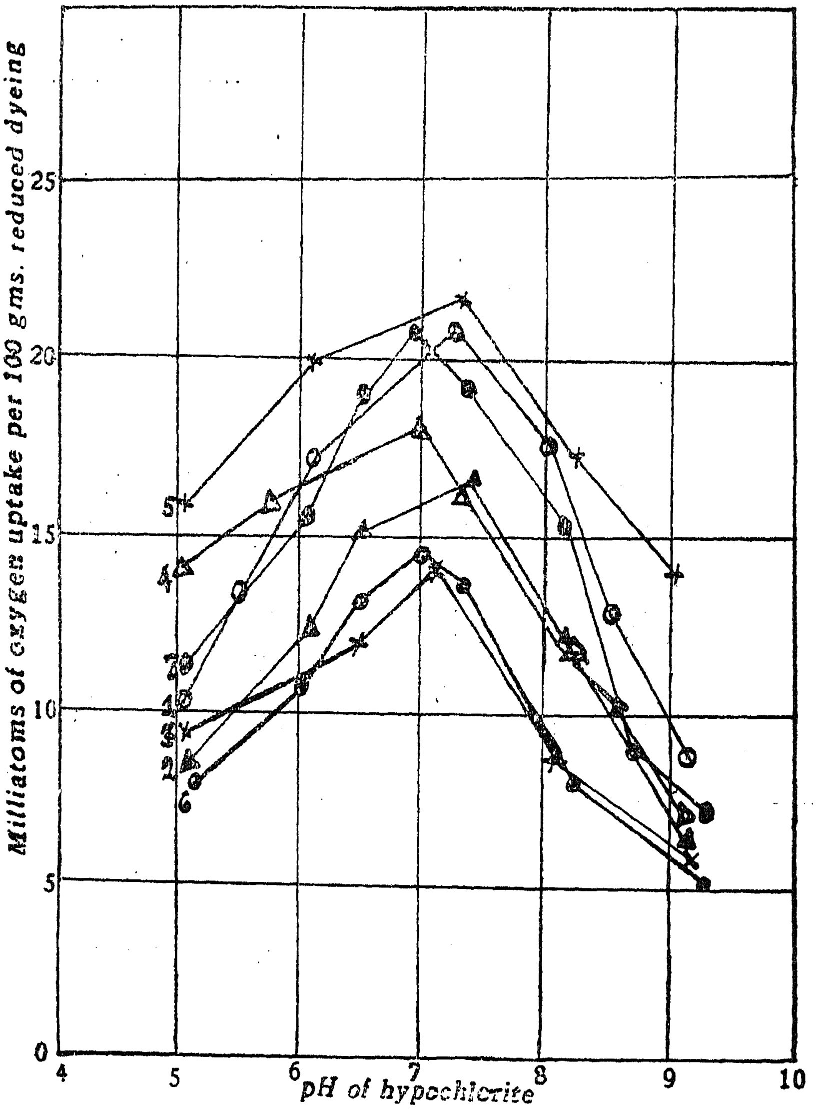

FIG. 1. Relation between pH and oxygen uptake by reduced dyeings of (1) Cibanone Orange R; (2) Cibanone Yellow R; (3) Indanthrene Yellow FFRK; (4) Indanthrene Yellow G; (5) Ciba Green G; (6) Caledon Gold Orange G; and (7) Cibanone Yellow GC, when treated with dilute sodium hypochlorite solutions for 10 mins.

It is seen that the general shape of the curves for the various dyes is similar to one another, only the intensity of oxidation is different.

In Table II results obtained with leuco Ciba Blue 2B, Indanthrene Dark Blue BO, Caledon Green BS and Caledon Jade Green XS are given. The maximum oxygen uptake with Ciba Blue 2B occurs at about pH 6·3, but with the other three dyes the same takes place at about pH 5·4. The relation between pH and oxygen uptake for these four dyes is shown in Fig. 2.

The results obtained when cotton impregnated with ferrous hydroxide was treated with hypochlorite solutions at 30° C. are given in Table III and

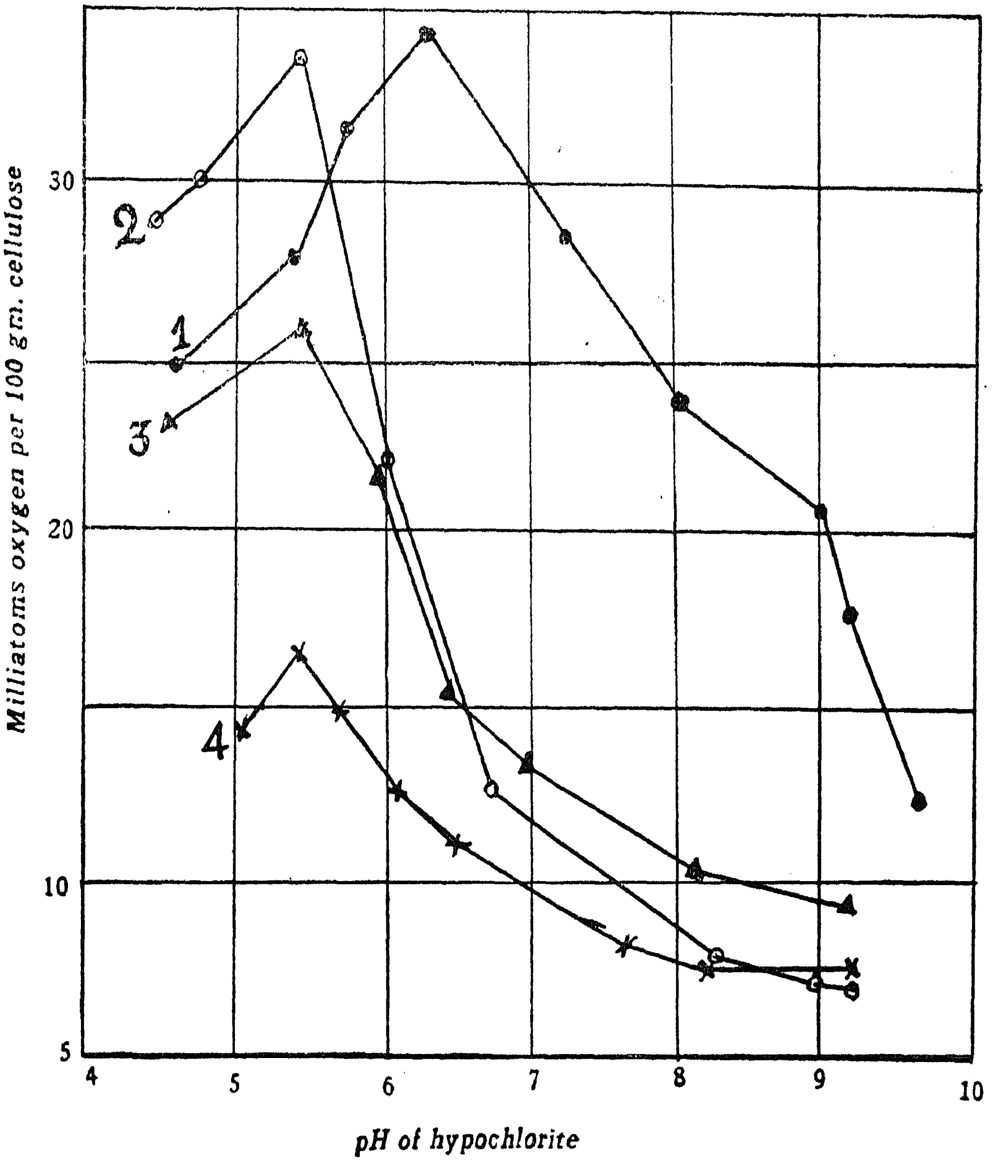

FIG. 2. Relation between pH and oxygen uptake by reduced dyeings of (1) Ciba Blue 2B; (2) Indanthrene Dark Blue BO; (3) Caledon Green BS; and (4) Caledon Jade Green XS when treated with dilute sodium hypochlorite solutions for 10 mins.

shown in Fig. 3. In this case the maximum oxygen transfer takes place at about pH 6·3. For ready reference similar curve at 20° C. reproduced from the paper by Nabar and Turner[2] is also shown in the same figure. The shape of the curves at 20°C. and 30°C. is similar. In the same figure curves relating pH to (*a*) cuprammonium fluidity, (*b*) copper number and (*c*) carboxylic acid content for the ferrous hydroxide oxycellulose samples at 30°C. are shown. The shape of these three curves is similar to the shape of the pH oxygen curves at 20° C. and 30° C. This indicates that the mechanism of oxidation is the same at both the temperatures.

In Fig. 4 the curves relating pH to corrected oxidation potentials both at 20° and 30° C. are reproduced from the earlier communication,[1] for ready

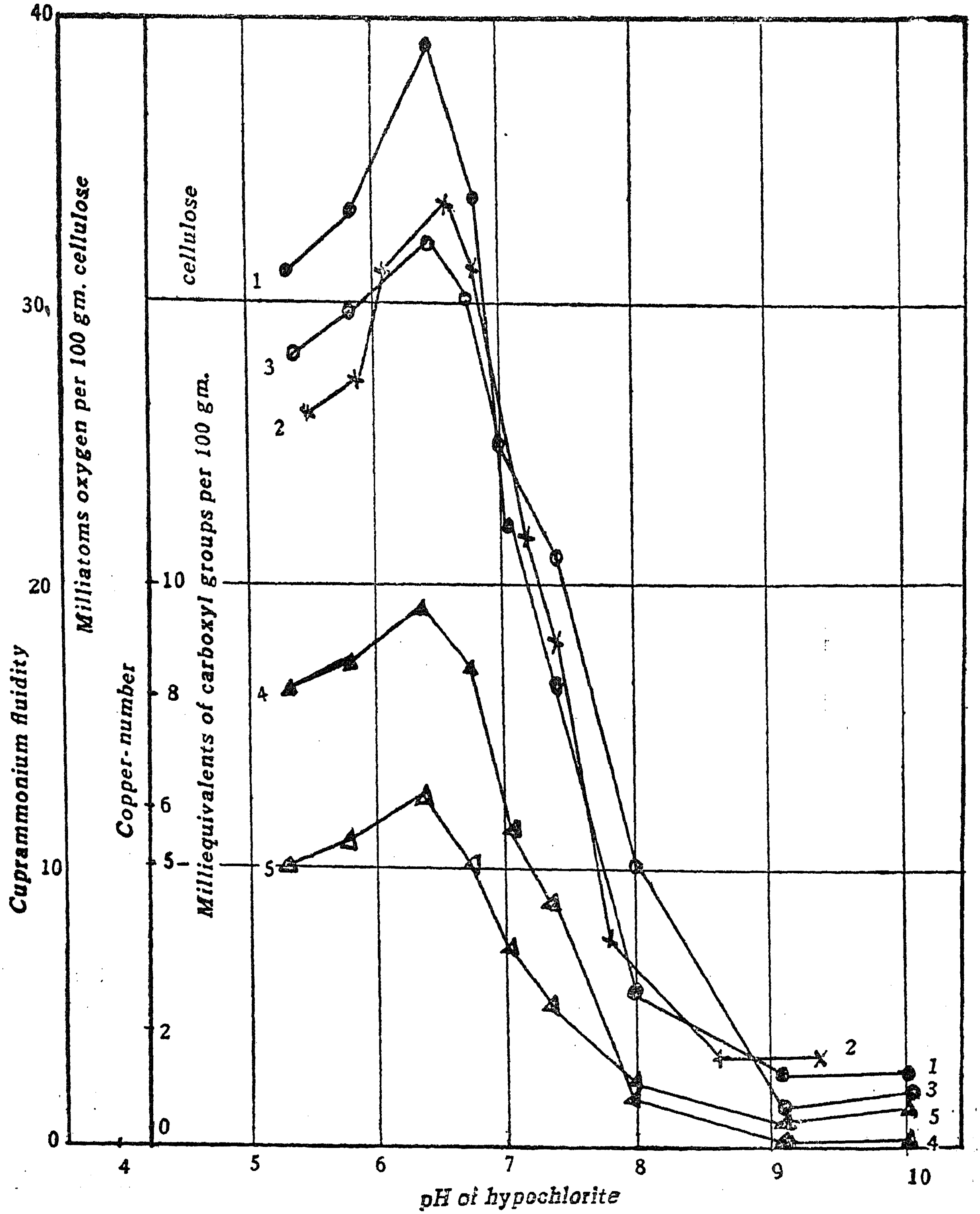

FIG. 3. Relation between pH and (1) Oxygen uptake (30° C.); (2) Oxygen uptake (20° C.) (3) Cuprammonium fluidity (30° C.); (4) Copper number (30° C.); (5) Carboxylic acid content (30° C.) for ferrous hydroxide impregnated cotton when treated with dilute sodium hypochlorite solutions for 10 mins.

reference. It is interesting to point out that the curves shown in Fig. 1 resemble in shape the curve relating pH to corrected oxidation potential at 20° C. but none of the curves in Figs. 1 to 3 show any resemblance to a similar curve (Fig. 4) at 30° C.

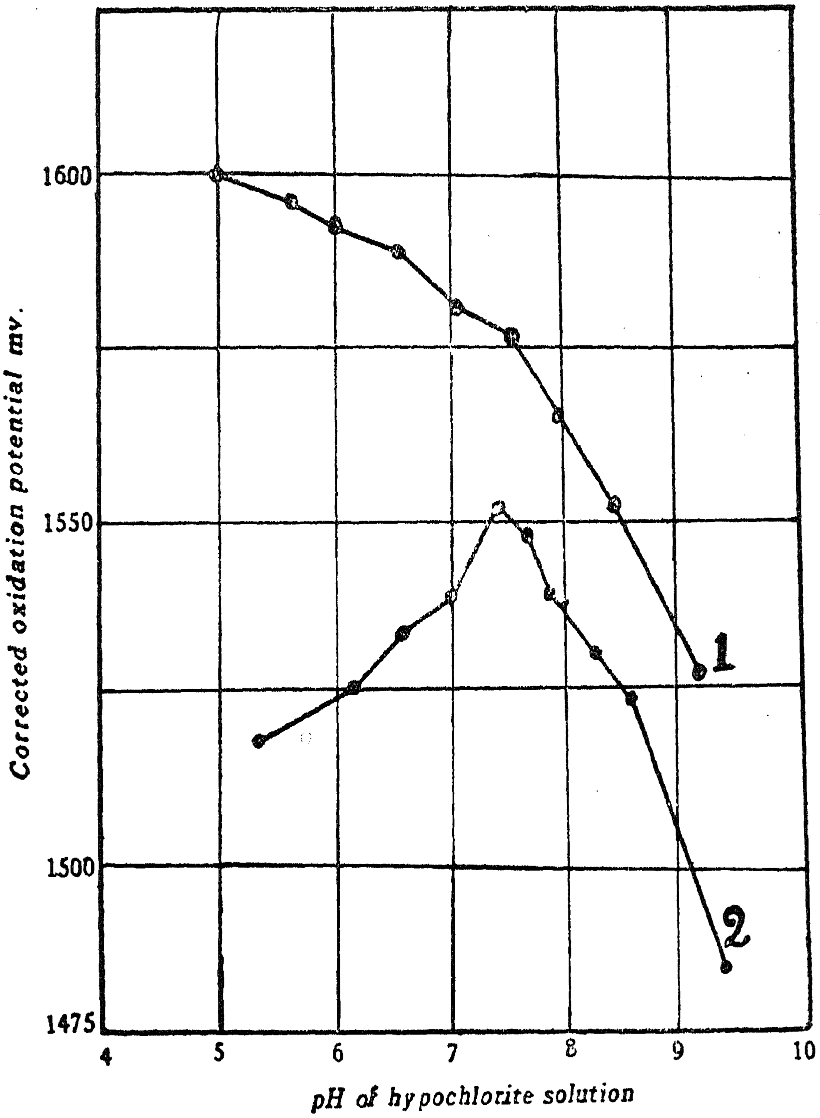

FIG. 4. Relation between pH and corrected oxidation potentials of sodium hypochlorite solutions at (1) 30° C. and (2) 20° C.

DISCUSSION

The curves in Figs. 1, 2 and 3 bring out the influence of reducing substances on the rate of oxygen transfer to cellulose from hypochlorite solutions in a striking manner. Although for each of the various dyes examined the similarity in shape of the 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 its own influence on the degree of oxidation. Further, the oxidation, accelerated by leuco compounds of Cibanone Orange R, Cibanone Yellow R, Caledon Yellow GN, etc. shown in Fig. 1 shows a maximum intensity of oxidation between pH 7 and 7·3. By replacing the above accelerating systems by leuco Ciba Blue 2B, the maximum oxygen consumption is shifted to pH 6·3, while leuco compounds of Indanthrene Dark Blue BO, Caledon Green

BS and Caledon Jade Green XS cause the pH for maximum oxygen transfer to be shifted to 5·4. In presence of the inorganic accelerating system ferrous hydroxide → ferric hydroxide, the maximum oxygen transfer takes place at about pH 6·3. It is thus clear that the reducing substance present on the cellulose, maintains its identity. This is seen from the following *viz.*, the shift in the pH at which maximum oxygen transfer and maximum chemical attack on the cellulose substrate takes place. It appears that some intrinsic physico-chemical property of the reducing substance present on cellulose during the oxidation, is responsible for this behaviour.

Comparing these results with those for the corrected oxidation potentials in Fig. 4, it is found that the curve at 30° C. shows no resemblance to any of the curves relating pH to oxygen transfer in Figs. 1, 2 and 3. Hence no linear relationship between the corrected oxidation potentials and oxygen transfer may be expected. Nabar, Scholefield and Turner[3] obtained a linear relationship between these two quantities for leuco Cibanone Orange R at 20° C. But as will be seen from the results described earlier, this does not seem to be possible for leuco Cibanone Orange R at 30° C. or for ferrous hydroxide even at 20°C.

It must be pointed out here that the system leuco vat dye → vat dye is not as simple as it appears at first sight. This is further complicated by the influence of the hydrogen-ion concentration of the oxidising system as it profoundly affects the dissociation of the weakly acidic dissociable groups of the leuco compounds. Since the influence of the reduced vat dye on the oxidation is so considerable, it may be reasonably assumed that the physico-chemical properties of the leuco compound will influence the course of oxidation and also the rate of oxygen transfer to the cellulose substrate on which they are deposited. Electrical measurements on the system leuco vat dye → vat dye are extremely difficult to carry out owing to the very low solubility of these compounds in aqueous medium. Attempts are being made in this laboratory to study this aspect of the investigation.

SUMMARY

1. The relation between pH of sodium hypochlorite solutions and the amount of oxygen consumed at 30° C. by cotton in presence of ferrous hydroxide and a number of vat dyes belonging to different chemical structural groups, is determined.

2. It is found that the reduced substances do not show uniform behaviour. The rate of oxygen uptake, the amount of oxygen transferred and the pH of maximum oxygen uptake by the cellulose substrate, are dependent

on the individual reducing substance present on the fibre during the hypochlorite treatment.

3. At 30° C., there exists no similarity between the pH-corrected oxidation potentials curve and the curve showing relation between pH and oxygen uptake or fluidity.

4. The corrected oxidation potentials as obtained by applying a correction of $0{\cdot}06 \times$ pH volts to the measured value of the potentials is not a measure of the oxidising intensity of hypochlorite solutions.

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