

# ACCELERATED OXIDATION OF COTTON CELLULOSE IN PRESENCE OF REDUCING SUBSTANCES—I

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## INTRODUCTION

NABAR, SCHOLEFIELD AND TURNER<sup>1, 3</sup> have studied in detail the oxidation of cotton cellulose by dilute solutions of sodium hypochlorite and have shown that the rate of its oxidation is very much increased if certain vat dyes in their reduced form are also present upon the fibre. They give data which indicate that the accelerated oxidation of cellulose is probably effected by a simpler and more consistent mechanism than is the slow oxidation of undyed cellulose studied by Clibbens and co-workers.<sup>2</sup> Unlike the slow oxidation, the mechanism of the accelerated oxidation does not appear to vary with the pH of the oxidising solution over a fairly wide range. Their results further showed that, for leuco-vat dyed cotton, the pH-oxygen uptake curve had a striking resemblance to a curve showing relation between pH and a value which was named "the corrected oxidation potential" of the hypochlorite solution. If the corrected oxidation potential is represented by  $E_{\text{corr}}$ ,  $E$  being the measured oxidation potential (referred to normal hydrogen electrode), developed when a bright clean platinum wire is immersed in a solution of sodium hypochlorite, the pH of which is  $X$ , then  $E_{\text{corr}} = E + 0.058 X$  (20° C.). To explain the above similarity, these authors suggested that  $E_{\text{corr}}$ , the corrected potential, may be considered to be either (A) the difference between the value representing the measured potential of sodium hypochlorite solution and a value representing the oxidation-reduction potential of cellulose or (B) the difference between the measured oxidation potential of the hypochlorite and the reduction potential of the reduced Cibacron Orange R present on the fibre. On this hypothesis,  $dE/dpH$  for both Cibacron Orange R and cellulose was shown by their results to be  $-0.058$  volts per pH at 20° C. over the pH range examined.<sup>1</sup> This value for  $dE/dpH$  is the same as that for the change in E.M.F. of the hydrogen electrode ( $H \rightarrow H^+ - e$ ) with pH at 20° C. It follows, therefore, from this hypothesis that at 30° C. the value of  $dE/dpH$  for Cibacron Orange R and for cellulose should change with temperature in the same manner in which it changes for the hydrogen electrode and that the corrected oxidation

potentials of hypochlorite at this temperature can be obtained by applying  $0.06 \times \text{pH}$  volts correction to the measured potential of hypochlorite.

The present work was undertaken in order to study the mechanism of the acceleration of the oxidation of cellulose in presence of reducing substances. Previous work referred to above <sup>1, 3</sup> on accelerated oxidation was carried out in Manchester at 20° C. The normal working temperatures in India, however, are nearer 30° C. It was more convenient, therefore, to arrange for the experiments to be carried out at 30° C. Sodium hypochlorite solutions are complex mixtures, a number of equilibria being operative over the whole pH range. In view of the complexity of these solutions, a similarity in their physico-chemical properties over a wide temperature variation may not be expected. Some of the earlier results, therefore, such as the measurement of oxidation potential of hypochlorite solutions and the oxidation of cotton cellulose in presence of leuco-vat dyes had to be repeated at 30° C. The present paper gives an account of the measurements of oxidation potential of sodium hypochlorite at 30° C. and shows how the corrected potential, if expressed as  $E_{\text{corr}} = E + 0.06 \times \text{pH}$  at 30° C. affects the relationship between the corrected oxidation potential-pH curve and the oxygen uptake-pH curve. If this "corrected oxidation potential" is considered as the measure of the oxidising intensity of sodium hypochlorite solutions, it is reasonable to expect that at 30° C. also, the shape of the curve relating pH to corrected oxidation potential should be similar to the shape of the curve relating pH to oxygen uptake at 30° C. as was obtained by Nabar, Scholefield and Turner<sup>1</sup> at 20° C. It is, however, interesting to find that the corrected oxidation potential-pH curve at 30° C. does not show any resemblance to the curve showing relation between oxygen consumption and pH at this temperature. It appears therefore that the method of applying correction to the measured values of oxidation potentials is not substantiated by results obtained by actual measurements.

#### EXPERIMENTAL METHODS

Sodium hypochlorite used in these investigations was prepared according to the method of M. Musprat and E. S. Smith.<sup>4</sup> The stock solution contained 2 to 2.5 N free alkali, 150–160 gms. per litre of active chlorine and was practically free from chlorate and carbonate.

*Determination of the concentration of available chlorine.*—This was done by acidifying an aliquot portion of the diluted hypochlorite solution, adding excess of potassium iodide and titrating with standard sodium thiosulphate solution. The concentration of active chlorine in buffered sodium hypochlorite solutions used for measuring the oxidation potential was adjusted

as near as possible to 3 gms. available chlorine per litre. The pH of the buffered sodium hypochlorite solutions was determined by using Morton type glass electrode system and a valve potentiometer supplied by Cambridge Scientific Instrument Company, Ltd., England.

*Determination of oxidation potentials.*—The apparatus and procedure for the determination of oxidation potential of hypochlorite solutions was the same as that described by Nabar, Scholefield and Turner.<sup>1</sup> The method is based on the one used by Remington and Trimble.<sup>5</sup> Platinum electrodes cleaned with strict adherence to detail described by them, were placed in buffered sodium hypochlorite solutions and the potential developed was measured by combining them with a saturated calomel half-cell. The E.M.F. of the resultant cell was measured on the valve potentiometer referred to above. Close agreement between individual electrodes was obtained. All measurements were carried out at  $30 \pm 0.1^\circ \text{C}$ .

*Buffer systems.*—The pH range examined has been covered by the following buffer systems:—

- (a) Mixtures<sup>6</sup> of N/5 potassium di-hydrogen phosphate with N/5 disodium hydrogen phosphate for pH values between 5 and 8.
- (b) Mixtures<sup>7</sup> of sodium borate and N/10 hydrochloric acid for pH values between 8 and 9.15.

*Cotton.*—Fully bleached 18's yarn manufactured from Indian cotton was used for oxygen consumption experiments. The grey yarn was subjected to standard bleaching treatment ensuring more or less complete removal of impurities from the cellulose. After thorough washing, drying and conditioning, the cotton had the following properties:—

Cuprammonium fluidity <sup>8</sup> (0.5% solution)	..	..	3.7
Copper number <sup>8</sup> (Heyes' method)	..	..	.015
Milliequivalents <sup>10</sup> of $-\text{COOH}$ per 100 gms. of cellulose			0.5

*Method of dyeing.*—Cibanone Orange R was pasted with a small quantity of monopol soap and dispersed in two litres of cold water. Calculated quantities of caustic soda and hydrosulphite were added while stirring the mixture. It was then gradually heated to  $60^\circ \text{C}$ . and then allowed to vat at this temperature for 30 minutes. 100 gms. of cotton yarn was wetted out with water containing little alkali and hydrosulphite. It was squeezed and then worked in the dye solution for  $\frac{1}{4}$ th of an hour. The cotton, as far as possible, was kept immersed below the surface of the liquor during the dyeing. It was then removed from the dye-bath and excess liquor evenly wrung out. The dyeing was then kept immersed in cold running water till

the oxidation of the dyeing was complete. This took about 2 hours. It was squeezed, allowed to dry and conditioned in dark and stored away from dust and light.

*Reduction of the dyeing.*—10 grams of the dyed yarn was treated with a cold 2% sodium hydrosulphite solution for 3 minutes, since it was observed that the reduction of the dyestuff takes place within the first half a minute after coming in contact with the hydrosulphite solution, as seen by a change in colour. The dyeing was then removed from the hydrosulphite bath, the excess solution wrung out rapidly and the reduced dyeing immersed at once in cold distilled water from which air had been expelled by previous boiling. It was kept stirred below the surface of water for one minute and then transferred to another such bath. This was repeated five times. Finally, the yarn was squeezed between fingers to remove the excess water and at once transferred to a hypochlorite solution suitably buffered and kept ready in a stoppered flask.

The repeated washings of the reduced dyeing described above were sufficient to remove any impurities carried from the reduction bath by the cotton.

*Hypochlorite treatment of the reduced dyeings and the determination of the oxygen consumed.*—The method is similar to the one used by Nabar, Scholefield and Turner.<sup>1</sup> 10 gms. of the reduced vat dyeing prepared by the procedure described above was used for oxidation experiments. It was found by experiment that this weight of cotton approximately displaced 10 c.c. of water. It is impossible to get the reduced and washed dyeings in dry condition and hence it is necessary that the reduced dyeings are transferred to the hypochlorite solution in a wet state. The cotton therefore carries with it an indeterminate weight of water and dilutes the hypochlorite. To allow for this dilution, the following procedure was adopted.

A flat bottomed flask was graduated to hold 560 c.c. (550 c.c. for the liquor and 10 c.c. for cotton). In this flask, 500 c.c. of the buffered sodium hypochlorite solution were placed. After the introduction of the wet dyeing, the volume was made up to 560 c.c. with cold distilled water. This diluted the original 500 c.c. of the hypochlorite solution to 550 c.c. Side by side from the stock solution, a further 227.3 c.c. of the solution was taken and diluted to 250 c.c. with distilled water to correspond with the solution used in oxidising the dyeing. This was used as a control experiment. After hypochlorite treatment (10 minutes), the liquor which remained was analysed for the concentration of available chlorine and its final pH determined. At the same time, pH and the concentration of available chlorine in the

control experiment was found out. From the difference in the concentrations of available chlorine in the control experiment and the solution after treatment, the net amount of oxygen used during the treatment can be calculated. The pH of the control solution and of the one after the treatment was more or less the same.

The reduction and oxidation experiments of the dyeing were carried out in a dimly lit room. The hypochlorite solution used for the oxidation experiments was always set at about 3 gms. available chlorine per litre. The time of treatment was exactly 10 minutes. During the treatment, the dyeing was stirred regularly below the surface of the liquor to ensure uniform contact. The concentration of available chlorine was determined by using 5 c.c. of the solution at a time, adding 3 c.c. of 10% potassium iodide and acidifying with acetic acid. The liberated iodine was titrated with N/50 sodium thiosulphate solution using starch as indicator.

The oxidised cotton was washed thoroughly free of chlorine.

*Determination of cuprammonium fluidity.*—The cuprammonium fluidity of the various oxidised samples was determined by the standard B.C.I.R.A.<sup>8</sup> method. Owing to the high level of degradation of most of the samples, the fluidity was determined in 1% solution. The final values are for cotton, for 1% solution and are corrected for loss of kinetic energy due to the rapid flow of the issuing solutions.

### EXPERIMENTAL RESULTS

The experimental results are described in Tables I to III. The measurements of oxidation potentials and the values of the “corrected oxidation potentials” are shown in Table I. The relation between measured oxidation potentials and pH is shown in Fig. 1 and the relation between corrected

TABLE I. *Oxidation potentials of sodium hypochlorite solutions at 30° C.*

pH of hypochlorite solution	Oxidation potentials (millivolts)	Corrected oxidation potentials (millivolts) (Correction = 80 × pH mv.)
9.13	979	1527
8.36	1052	1554
7.92	1090	1565
7.48	1128	1577
7.04	1158	1580
6.50	1200	1590
5.98	1233	1593
5.60	1261	1597
4.95	1303	1600

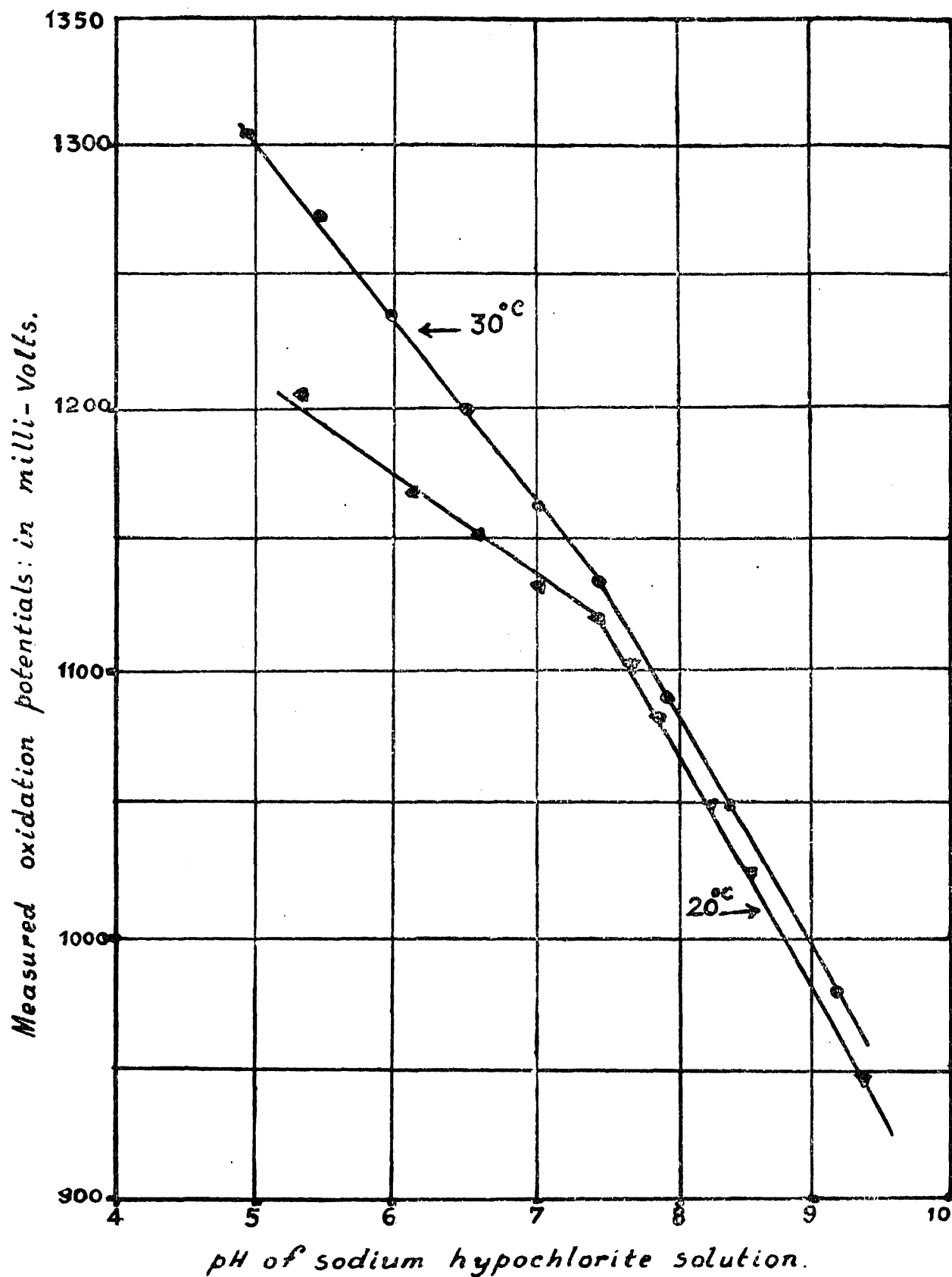


FIG. 1. Relation between measured oxidation potential and pH of dilute solutions of sodium hypochlorite.

oxidation potentials and pH of the hypochlorite solutions is shown in Fig. 2.

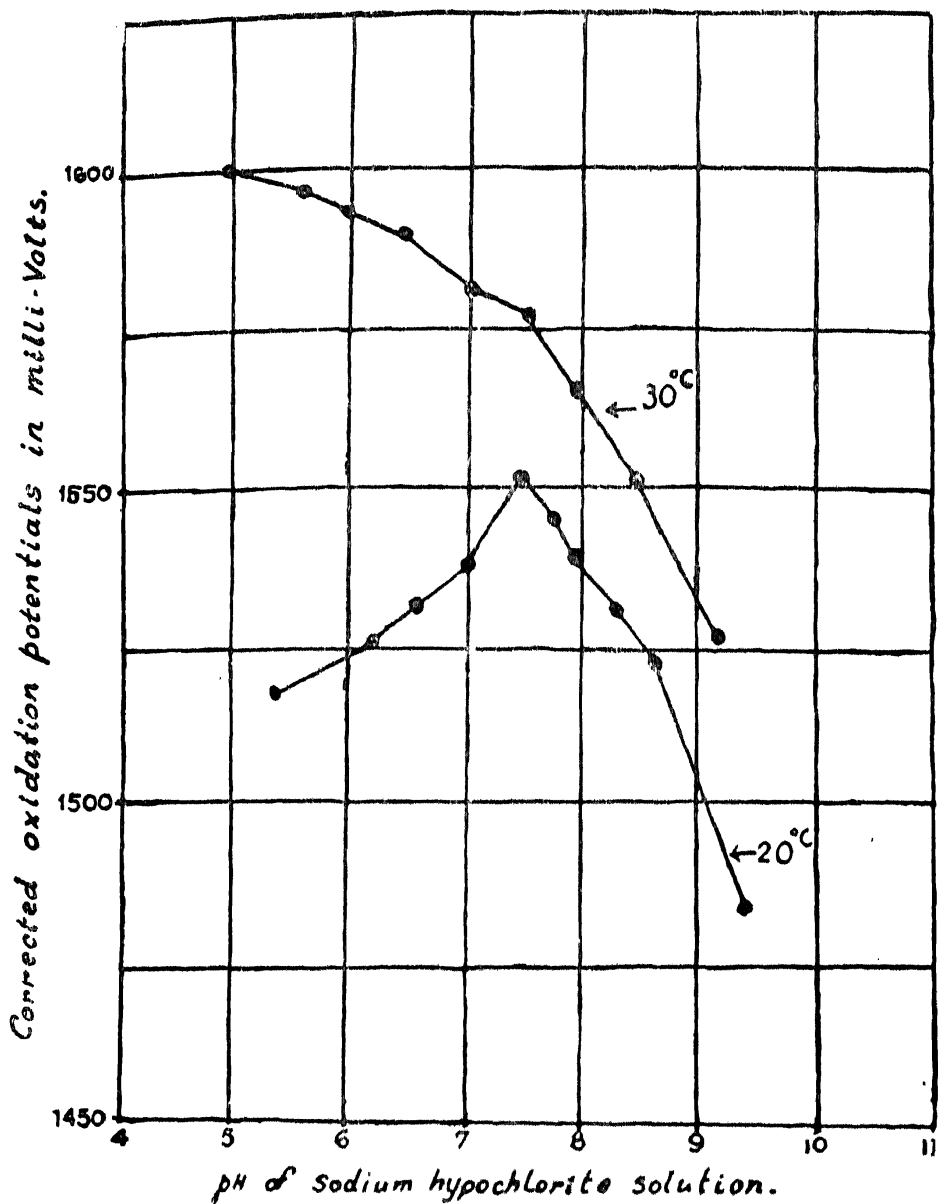


FIG. 2. Relation between 'corrected oxidation potential' and pH of dilute solutions of sodium hypochlorite.

The values of oxygen consumption by leuco-Cibanone Orange R dyed cotton at 30° C. are shown in Table II. The relation between oxygen consumption and pH is shown in Fig. 3. For the sake of comparison similar curve at 20° C. reproduced from the paper by Nabar, Scholefield and Turner<sup>1</sup> is shown in the same figure. It is seen that the general shape of the two curves is very similar, both showing maximum oxygen consumption at about pH 7.3. It is interesting to note that the curve at 20° C. stands higher than the one at 30° C., the reasons for which, at present, are not quite clear.

TABLE II. *Relation between pH of hypochlorite solutions and oxygen consumption by Cibanone Orange R dyed cotton. Temp. 30° C.*

pH of the hypochlorite solution	Milliatoms of Oxygen consumed per 100 gm. of dyed cellulose
9.28	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

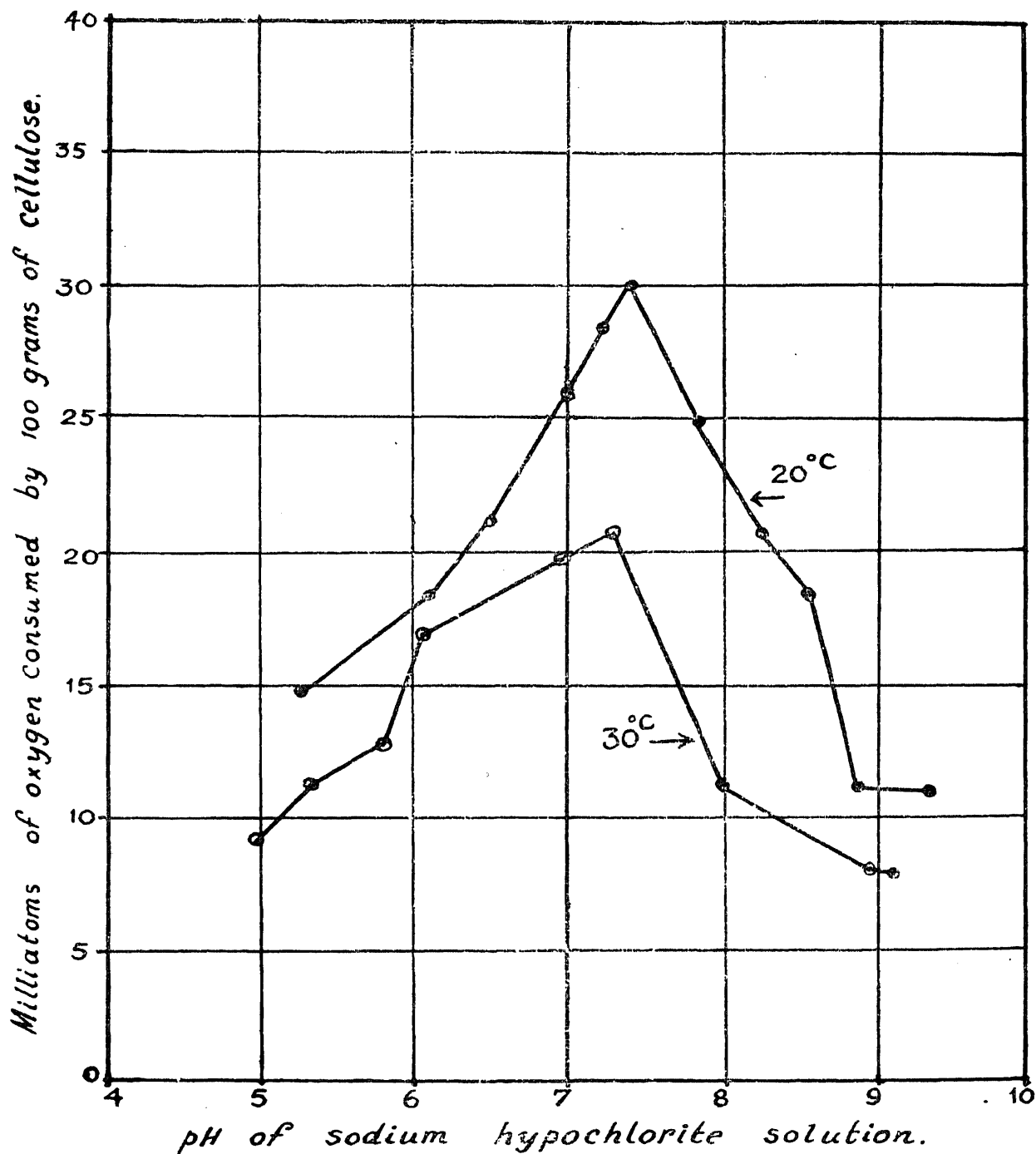


FIG. 3. Relation between the oxygen consumed by leuco-Cibanone Orange R dyed cotton and pH of the sodium hypochlorite solution.



TABLE III. Relation between cuprammonium fluidity of the treated dyeings and the pH of sodium hypochlorite solutions. Temp. 30° C.

Fluidity of original dyeing (1% soln) = 1.15

pH of hypochlorite solution	Cuprammonium fluidity (1% solution)
4.99	13.3
5.68	23.67
6.08	25.87
7.30	30.35
8.07	26.37
8.54	22.62
9.06	18.56

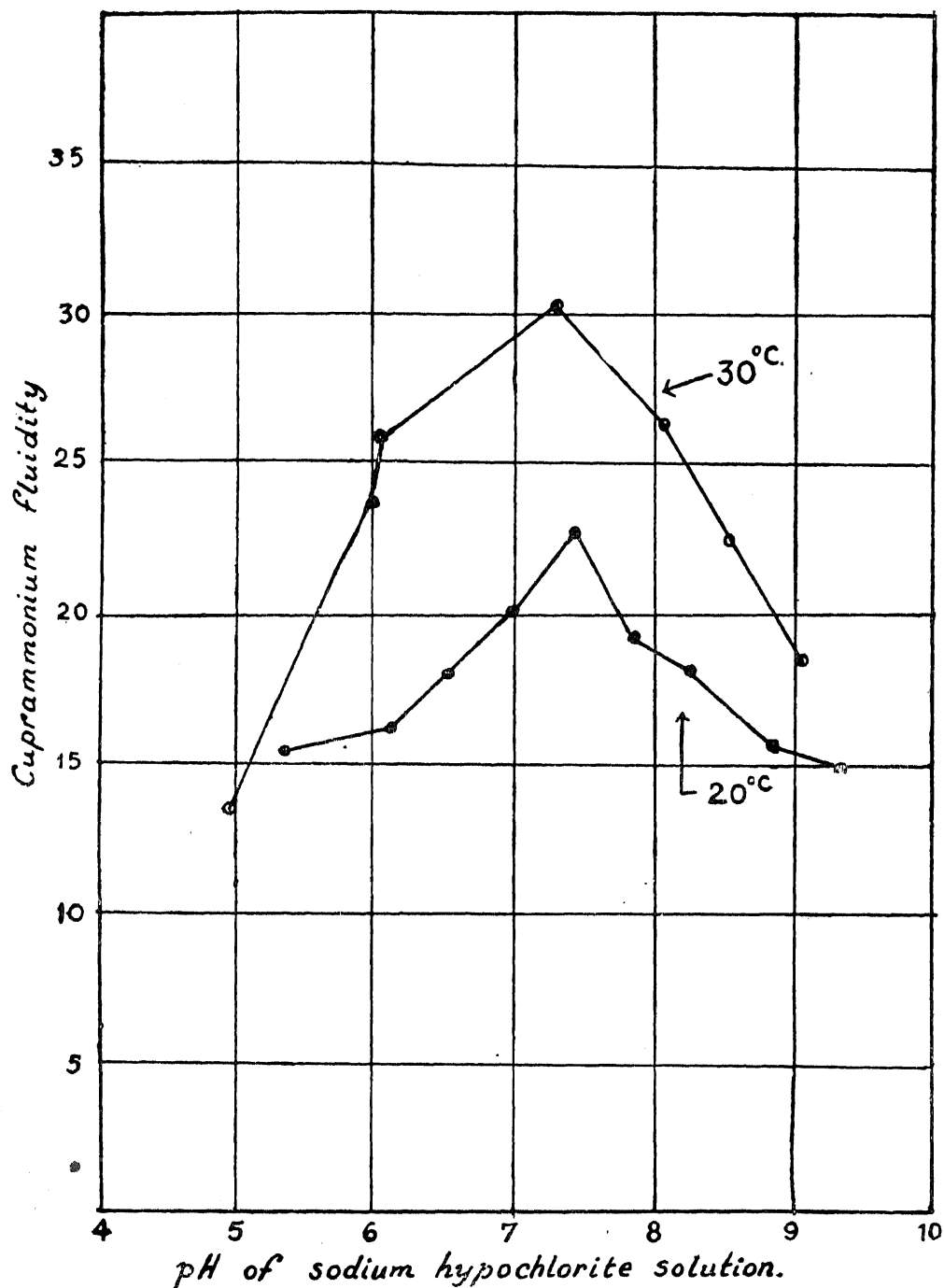


FIG. 4. Relation between the cuprammonium fluidity of the treated cotton and the pH of the sodium hypochlorite solution.

The values of cuprammonium fluidity of the treated dyeings are given in Table III. The relation between the cuprammonium fluidity and pH is shown in Fig. 4. Similar curve at 20° C. from the above paper<sup>1</sup> is also shown in the same figure for comparison. It will be seen that, what has been said about the oxygen consumption-pH curves above, is also equally true for the cuprammonium fluidity-pH curves. The maximum degradation of the cellulose occurs at that pH at which maximum oxygen consumption also takes place.

#### DISCUSSION

An examination of the curves in Fig. 1 reveals that the values of the oxidation potentials of sodium hypochlorite solution at 30° C. are higher than those at 20° C., the differences being more marked on the acid side of neutrality. This may be expected, since it is known that hypochlorites are more active at higher temperatures. A careful study of the curves further reveals that from pH values of approximately 7 and above, the two curves practically possess the same slope, but below pH 7 the slopes become different. It is found that for this portion of the curve at 30° C., the slope is nearly twice that at 20° C.

Still more interesting is the effect of temperature on the corrected oxidation potentials. From Fig. 2, it is seen that the corrected potentials at 20° C., when related to pH, show a maximum value between pH 7 and 8. A similar curve at 30° C. does not, however, show any maximum at all. Nabar, Scholefield and Turner<sup>1</sup> have shown a striking resemblance between the shape of the curve relating pH to corrected oxidation potential and a curve relating pH to oxygen uptake by leuco-vat dyed cotton at 20° C. This is clearly seen from Figs. 2 and 3. If the intensity of oxidation of sodium hypochlorite solution is represented by corrected oxidation potential, obtained by applying a correction of 0.058 pH volts at 20° C. or  $0.06 \times \text{pH}$  volts at 30° C. to the measured potential, then, as in the curves in Fig. 2, a similarity in the shape between pH-oxygen uptake curves and the pH-cuprammonium fluidity curves at 20° C. and 30° C. respectively, in presence of leuco-Cibanone Orange R, may not be expected. The curves showing the relationship of pH with the oxygen uptake by leuco-Cibanone Orange R dyed cotton at 30° C. (Fig. 3) as well as that of pH with the cuprammonium fluidity of the treated cotton (Fig. 4), however, show a complete resemblance in shape to those at 20° C.

These results, therefore, indicate that the method of applying correction, as suggested by Nabar, Scholefield and Turner,<sup>1</sup> though satisfying the requirements at 20° C., is not applicable to the results at 30° C.; otherwise a complete similarity in the shape of the following curves, *viz.*, pH-corrected oxidation

potential, pH-oxygen consumption and pH-cuprammonium fluidity, both at 20° C. and 30° C., would have been obtained. It appears, therefore, that their suggestion that the 'corrected oxidation potentials' should represent the measure of the oxidising intensity does not appear to be substantiated at 30° C.

#### SUMMARY

(1) The measurement of oxidation potential of dilute solutions of sodium hypochlorite has been carried out at 30° C. by a method used successfully by various investigators.

(2) The values of the oxidation potential at 30° C. are higher than those at 20° C. The differences in the potentials become more and more marked with reduction in the pH of the hypochlorite solution.

(3) A correction of  $\text{pH} \times 0.06$  volts to the measured potentials at 30° C. does not show any maximum value over the pH region examined. A sharp change in the direction of pH-corrected oxidation potential curve, however, occurs at about the same pH at which a maximum is obtained at 20° C.

(4) There exists no similarity between the corrected oxidation potential-pH curve at 30° C. and a curve showing relation between oxygen uptake or fluidity and pH at 30° C. Nabar, Scholefield and Turner<sup>1</sup> had shown a striking resemblance between these curves at 20° C.

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