(a) A STUDY OF THE DECOMPOSITION OF SODIUM CHLORITE

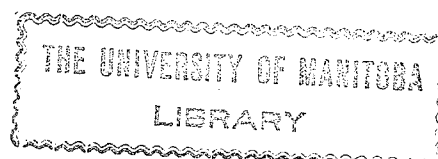UNDER CONTROLLED pH CONDITIONS

(b) THE EFFECT OF SODIUM CHLORITE ON CELLULOSE

UNDER CONTROLLED pH CONDITIONS

By

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Being a Thesis

submitted to the Committee on

Post-Graduate Studies of the

University of Manitoba in par-

tial fulfilment of the require-

ments for the Degree of

Master of Science.

April, 1941.

TO DR. H. H. SAUNDERSON

under whose very able direction

this first venture into the field

of research has been undertaken.

To him the writer offers his

most grateful thanks.

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GENERAL INTRODUCTION

The research field concerned with the improvement and development of bleaching processes has been one of great activity, and at present is still the object of a large amount of research.

The art of bleaching textiles is an ancient one, and we have advanced a long way since the elements of sun, rain, and wind were used as bleaching agents. The modern chemical methods as employed to-day, are developments brought out within the last one hundred and fifty years. Chlorine was the first chemical bleach used, but its poisonous and objectionable odour limited its use. The discovery of calcium hypochlorite or bleaching powder was the first great stride forward towards the efficient and speedy methods used to-day. Attempts have been made to use other oxidizing agents such as hydrogen peroxide, and sulphur dioxide, as a substitute for hypochlorites, but their use was limited as the demand for better grade pulps was made.

Although hypochlorite bleaching is the most commonly used method to-day, it has its limitations in the production of high grade pulp and textile products. Hypochlorites due to their strong oxidizing power will give a high brightness, but, in doing so they will weaken the fibre strength of the cellulose itself. This im-

pairs the quality of high grade pulps now in demand in the pulp and paper industry, particularly those used in the manufacture of rayons and other artificial cellulose products, which require the pulp to have high brightness along with its maximum strength. This would suggest the use of a milder bleaching agent. A possible substitute is sodium chlorite.

Sodium chlorite solutions have an oxidizing power somewhat below that of hypochlorite, the actual difference depending to a certain extent on the hydrogen ion concentration of the respective solutions. Research conducted so far indicates, that the oxidizing action of sodium chlorite is high enough to remove natural coloring material and other non cellulosic materials present in the pulp, but at the same time low enough to have little tendency to degrade the cellulose itself.

The work outlined in this thesis is an investigation of the stability of sodium chlorite solutions, and of their effect on wood pulp cellulose under different pH conditions.

THEORETICAL INTRODUCTION

(a) Preparation and Properties of Sodium Chlorite

Chlorites have been known as chemical compounds for nearly one hundred years. They were first identified by Millon (1) in 1843 and were obtained by the alkaline absorption of the greenish yellow gas formed by the partial reduction of chlorate. Millon believed this gas contained chlorine trioxide of formula Cl_2O_3. However Millon's formulation was not generally accepted and in 1881 Garzarolli-Thurnlackh (2) showed that the gas was really a mixture of chlorine dioxide and chlorine. The chlorite resulted from the hydrolysis of chlorine dioxide and gave an equimolar mixture of chlorite and chlorate, according to the equation.

$$2ClO_2 + 2KOH = KClO_2 + KClO_3 + H_2O \quad (1)$$
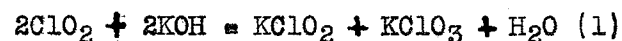
Garzarolli (2) also indicated the following method of preparing chlorine - free chlorites. A potassium hydroxide solution was treated with a stream of carbon-dioxide - containing chlorine dioxide gas protected from the light. The chlorite was separated from the chlorate by evaporation in vacuum at 45° - 50° C, and the potassium carbonate removed by treating the residue with 95% alcohol in which the chlorite was soluble.

The pure potassium chlorite was then gathered by fractional crystallization.

Rechyler (3) in 1901 investigating the preparation and analysis of chlorites reported the following reaction.

$$2ClO_2 + Na_2O_2 = 2NaClO_2 + O_2 \quad (2)$$
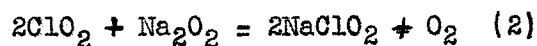
His results showed that the above reaction was instantaneous, whereas the method using potassium hydroxide instead of potassium peroxide was slow and the principal reaction was complicated by secondary transformations.

$$Cl_2 + 2KOH = KCL + KOCL + H_2O \quad (3)$$
$$2ClO_2 = Cl_2 + 2O_2 \quad (4)$$
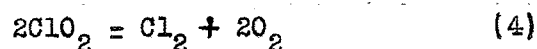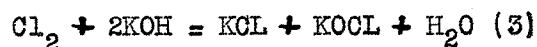
Except for the investigations mentioned above, references to chlorite are few in number prior to 1915, when Bruni and Levi (4) started an investigation which has been carried on by Levi up to the present time. This work included descriptions of various metallic chlorite salts, laboratory methods of preparation, and a few of their characteristic reactions. Little information was given of practical importance as to the commercial usefulness of chlorites.

Bruni and Levi (4, 5, 6) prepared pure barium chlorite by using the reaction as indicated by Rechyler (3) using hydrated barium peroxide instead of sodium peroxide. This reaction is important due to the relative ease with which one can prepare the chlorite in the pure state. The method they used was as follows.

A Current of chlorine dioxide containing carbon dioxide (to remove the chlorine) (7) was passed into a suspension of hydrated barium peroxide. To this solution was added three volumes of alcohol and an excess of freshly distilled ether. This separated the barium chlorite which was filtered rapidly by suction and purified in a vacuum desiccator. Using the pure barium chlorite other chlorites could be prepared by double decomposition with sulphates of various metals (8).

Sodium chlorite may exist in two solid forms, the anhydrous ($NaClO_2$), and the trihydrate ($NaClO_2 \cdot 3H_2O$). Both these forms were prepared by Levi (6). The trihydrate is the stable phase in aqueous systems at room temperature. The anhydrous form is not hygroscopic and does not cake in storage.

According to Levi, sodium chlorite is stable. He found no change in 10 hours on a water bath. At room temperature it kept the year round, and a .2N and .02N sodium chlorite solution was stable in the dark for one week. The dry salt decomposed at temperatures (9) from $180^0 - 200^0$ C. according to the

equation.

$$3NaClO_2 = 2NaClO_3 + NaCl \qquad (5)$$
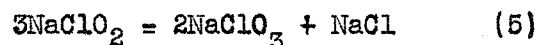
Of the characteristic reactions investigated by Bray (10) and Levi (9), the following were the most important as they were directly concerned with the methods of analysis used in determining chlorites in the presence of hypochlorites and chlorates.

Sodium chlorite reacted with arsenious acid (H_3AsO_3) in a saturated bicarbonate solution according to the equation.

$$ClO_2' + 2H_3AsO_3 = 2H_3AsO_4 + Cl' \qquad (6)$$
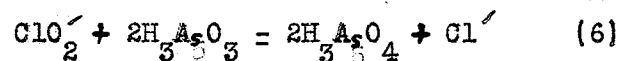
In this reaction part of the chlorite was also oxidized to chlorate.

Iodine reacted with sodium chlorite in acid solutions according to the equation.

$$5HClO_2 + 4I' + 2H_2O = 4HIO_3 + 5HCl \qquad (7)$$
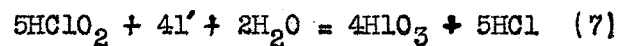
Sodium thiosulphate reacted with a neutral chlorite solution principally according to the reaction.

$$Na_2S_2O_3 + 2NaClO_2 + H_2O = 2NaCl + 2NaHSO_4 \qquad (8)$$
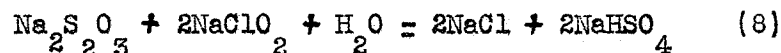
In 1927 the research and development department of the
Mathieson Alkali Works New York started the study of sodium
chlorite (11), with the aim in mind of investigating the
possible application of chlorites in industry (12), and
methods of large scale production. Their results were
highly successful and although sodium chlorite as yet is
not obtainable in large quantities their patented process
makes the production of sodium chlorite relatively simple.
From the standpoint of commercial applications, especially
in the bleaching of wood pulps and textiles, their research
has been successful and it is possible that within the next
few months sodium chlorite will be avilable in large enough
quantities to make possible its use in conjunction with hypo-
chlorites in the bleaching industry.

The investigations as to the stability of sodium chlorite
conducted by the Mathieson Alkali Works indicated that the
storage stability of dry sodium chlorite is excellent. Samples
of both the commercial and analytical quality sodium chlorite
were stored in both glass and drum containers over a period of
many months. The analysis of technical $NaClO_2$ stored in a metal
drum over a period of one year showed no decomposition whatso-
ever, while there was only a very slight decomposition when
stored in glass containers (11). Their analyses were as follows,

giving the amount of sodium chlorite in percent by weight.

Technical NaClO$_2$	Start	After one year
In drum	82.40%	82.40%
In glass	81.78%	81.02%

Analysis of analytical sodium chlorite stored in ordinary glass containers over a period of 18 months showed a decrease of about 1½% in the amount of the sodium chlorite.

In order to study the effect of elevated temperatures on the stability of solid sodium chlorite, portions of a product containing 68% sodium chlorite were heated in an iron crucible placed in an oil bath previously brought to the desire temperature. Thirty minutes at temperatures up to 150° C. caused no decomposition while at 200° C. less than half the chlorite was decomposed over a period of 30 minutes. A sample containing 79% sodium chlorite by weight was rapidly heated in a porcelain crucible. A thermocouple placed in the chlorite showed that decomposition started at 175° C. Within a few seconds its temperature rose to 340° C., and then the temperature commenced to fall. Analysis showed that the decomposition had taken place mainly according to the equation.

$$3NaClO_2 = 2NaClO_3 + NaCl \qquad (9)$$
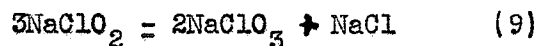
Less than 5% of the NaClO$_2$ decomposing evolved O$_2$ in accordance with the equation

$$NaClO_2 = NaCl + O_2 \qquad (10)$$
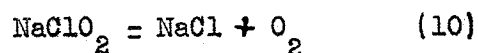
Levi (13) and Jackson and Parsons (14) showed that dilute solutions of sodium chlorite containing .5% sodium hydroxide were stable for several days if protected from the light of the laboratory. Longer tests carried out by the Mathieson Alkali Works showed that no decomposition occurred in 23 months when sodium chlorite was stored in amber bottles. The chlorite concentration ranged from .1 to 4N and the sodium hydroxide from .1 to 4M at the different chlorite concentrations used. These same solutions when stored in clear bottles showed a slight decomposition over a period of 23 months (11). Assuming that sodium chlorite could be formed only by the reaction of equation (9) complete analysis of these solutions showed that oxygen probably was evolved in accord with equation (10). It was noticed that increase in alkalinity rendered the solutions in clear glass bottles more stable.

Many of the applications of chlorite envolve its use in acid solutions, and experiments were undertaken to determine in what way sodium chlorite reacted with acid (11).

The procedure first used was to add a chlorite solution

slowly to the acid while passing nitrogen gas through the solution. The volatile products formed were thus removed and were absorbed in sodium hydroxide. The residue left in the reaction flask and the absorbing solutions were analyzed.

The various gases which might be formed would react with caustic as follows.

$$Cl_2 + 2NaOH = NaCl + NaClO + H_2O \qquad (11).$$

$$Cl_2O + 2NaOH = 2NaClO + H_2O \qquad (12).$$

$$2ClO_2 + 2NaOH = NaClO_2 + NaClO_3 + H_2O \qquad (13).$$
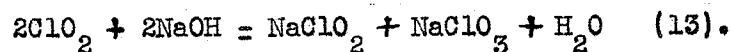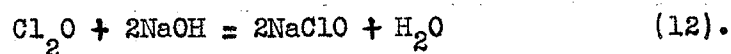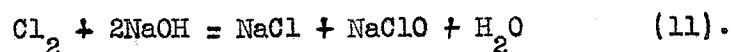
From this it was apparent that determination of Cl', OCl', ClO_2' and ClO_3' in the absorbers would disclose the composition of the gas, provided there was no secondary reaction in the absorbers, -- for instance, hypochlorite oxidation of chlorite to chlorate. A representative experiment consisted of adding a 1.3M chlorite solution slowly to a 10% acetic acid solution. Analysis of the generator residue showed that .02240 mol. of chlorite had been decomposed. The gas analysis showed that the main products were chlorite and chlorate in equimolar amounts. From this it is evident that the gas produced was almost entirely chlorine dioxide.

Although the above experiment identified the gaseous products as almost entirely chlorine dioxide, all the gaseous products released account for less than half the chlorite decomposed. The Mathieson Alkali research staff then planned further experiments in an effort to determine the nature of, and amount of non-volatile products. The absorption method used was similar to their previous experiment except that in addition to using a sodium hydroxide absorber, they followed it with an absorber containing a calcium peroxide suspension. This assured the complete absorption of ClO_2 by converting it to chlorite without formation of chlorate (11), but, as in the previous example, analysis showed that the volatile products formed were not equal to the chlorite disappearing during the course of the reaction. Perchlorate formation was first suspected, but qualitative tests did not show its presence. As yet the numerical difference between the final products and the chlorite decomposed has not been explained. It is possible that a considerable portion of the discrepancy can be attributed to the methods of and difficulties of analysis and the problem of distinguishing between the four oxidation levels of chlorine.

Chlorite undergoes two important reactions (11), namely those with hypochlorite and chlorine, both of which have become

of commercial importance. In solutions whose pH is from 11 to 12, sodium chlorite reacts with hypochlorite as follows:

$$NaClO_2 + NaClO = NaClO_3 + NaCl \qquad (14).$$
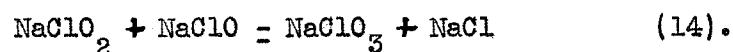
If the alkalinity is reduced below pH 11 the odour of chlorine dioxide gradually becomes perceptible. As the pH is raised above pH 12 the speed of the reaction is decreased (11).

Cunningham and Losch (15), by a method now patented discovered that when chlorine was passed into strong sodium chlorite solutions, chlorine dioxide was formed according to the equation:

$$2NaClO_2 + Cl_2 = 2NaCl + 2ClO_2 \qquad (15).$$
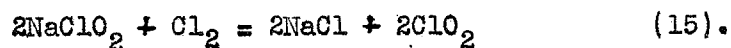
Previous to the issue of the patent mentioned above, Levi and Tabet (16) independently arrived at the same result. If, as the reaction proceeded the chlorine dioxide was removed, the efficiency of its production was high, and the reaction rate was controlled by the rate at which chlorine was introduced into the chlorite solution. If, on the other hand the chlorine dioxide was not removed as formed it dissolved in the generating solution. Under these conditions sodium chlorate was formed equivalent to 30% of the decomposed chlorite.

It appears from the reaction of sodium chlorite with hypo-
chlorite or chlorine, that acid conditions favor the formation
of chlorine dioxide, while alkaline conditions favor the produc-
tion of chlorates. These results were confirmed by Taylor,
White, Vincent, and Cunningham (11) who found that at pH4 the
formation of chlorine dioxide predominated, while at pH_s' from
8 to 10 chlorates were the main product. The equation expressing
the reaction between chlorine and chlorite under alkaline condi-
tions is represented as:

$$NaClO_2 + Cl_2 + H_2O = NaClO_3 + HCl \qquad (16)$$
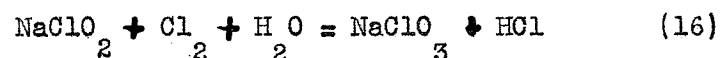
The property of sodium chlorite which forms the basis of
the more important uses so far developed, is its oxidizing
power. In cold alkaline solutions it has only mild oxidizing
action, on heating or acidification or both, sodium chlorite
solutions develop a stronger oxidizing condition.

Some preliminary determinations of oxidation potential
have been made. The values obtained for 1/142 M sodium chlo-
rite solution (1 gram of available chlorine per litre of solu-
tion) as determined by Taylor, White, Vincent, and Cunningham
(11) were found to be .79 volt at pH4 and .66 volt at pH9. The
oxidation potential of sodium hypochlorite at the same concen-
trations of "available chlorine" was found by Hisey and Koon

(17) to vary from 1.2 volts at pH7 to .95 volt at pH10 which covers its normal bleaching range. The above figures show that sodium hypochlorite is a stronger oxidizing agent under alkaline conditions than sodium chlorite is at pH4.

(b) The use of hypochlorites and chlorites in bleaching

The use of hypochlorites for bleaching wood pulp and textiles has not been entirely satisfactory. They are strong oxidizing agents which can attack the cellulose itself. This undesired reaction becomes more difficult to control as the wood pulp is more completely bleached, due to the removal of other easily oxidized products present.

Clibbens and Ridge (18), in 1927 undertook the investigation of the action of hypochlorites on cotton, and the study of the rate of oxycellulose formation. Their work was carried out using buffered hypochlorite solutions. They carried out their investigations within the pH range of 5 to 10, characteristic of technical bleach liquors in the cotton industry. Their results showed that the maximum rate of oxycellulose formation or degradation of the cellulose occurred at the neutral point, also the qualitative effects did not seem to be due to the effect of the buffer salts present

in their investigation.

Recently, Romanovsky (19) working along lines similar to those of Clibbens and Ridge, found that the maximum degradation on sulphite wood pulp occurred at the neutral point. Instead of using buffered solutions, he used a glass electrode and the required hydrogen ion concentration was maintained by adding acid or base as required.

From the work reviewed it is evident that a fairly high alkalinity must be maintained, if the resulting product is to satisfy the high quality pulps demanded.

Recently sodium chlorite has been proposed as a new bleaching agent for textiles and wood pulp (12), as it offers the possibility of securing high brightness in fully bleached pulps, with less damage to the cellulose than is found with hypochlorites.

Taylor, White, and Vincent of the Mathieson Alkali Works, undertook an extensive research of the possible use of sodium chlorite as a bleaching agent. The results of this research have been published within the last year (12, 20,) and are of such a successful nature, that it is likely that their suggested method of using sodium chlorite as a bleaching agent will be accepted by the bleaching industry.

When suggesting a new bleaching agent, comparisons with

methods now in practise are necessary. The literature regard-
ing hypochlorite bleaching shows only partial agreement, as the
optimum conditions for the bleaching stage depends upon the
species of wood, the cooking process, and all the preceding
stages of bleach.

The following standard conditions for hypochlorite bleach-
ing as given below, are the results of an exhaustive study of
the process as conducted by the Mathieson Alkali Works' research
staff. Although their work was confined mainly to the action of
hypochlorites on kraft or sulphate pulp, which shows less degra-
dation of fibre in general than other types of pulp, the condi-
tions as set forth are comparable with results obtained on other
types of pulp, and with the investigations of various other ex-
perimentors.

The lower limit recommended for hypochlorite bleaching is
usually pH8 (21, 22). Investigations conducted indicated the
optimum pH range between pH8 and 9. Variations in temperature
showed little difference in the effect on cellulose, but the
recommended maximum temperature was 40° C. These two values
indicated above, were selected for use when studying the other
variable conditions such as consistency, time of bleaching, and
amount of avilable chlorine. Exhaustive study of the bleached
products basing the comparison of results on the physical
properties of brightness, retention of brightness, bursting

strength and tearing resistance indicated that the optimum

conditions for use of hypochlorites are (12):

pH value 8 to 9	Time 2 hours
Consistency 5%	Available
Temperature 40° C.	Chlorine - .5% - 1%

The more or less set rules which have become associated

with bleaching, because of the almost exclusive use of hypo-

chlorites, were found no longer applicable when sodium chlo-

rite was substituted for hypochlorites (20). Investigations

proved that the best results were obtained when sodium chlo-

rite was used in an acid medium. It has been frequently

stated that acid conditions damage pulp. These workers found

that as far as hypochlorites are concerned the damage done to

the pulp was due, not to the acid itself, but to the hypochlo-

rite decomposing in the presence of acids.

The ability to use chlorites in acid media permits oxida-

tion through a wide range of pH values. Such a range of selec-

tion offers the possibility of rigid control of oxidizing action,

which is not possible in the case of hypochlorites. Experiments

conducted indicated the possible use of various pH's, but general

results showed that the pH range of 3.5 to 5.5 was the most use-

ful for bleaching paper pulp. Actual experimental practise

proved that time and concentrations could be increased, without

causing the effect known as overbleaching, commonly found when the hypochlorite concentration was too high or when the alkalinity had become too low.

Although the high quality pulp obtained from bleaching with sodium chlorite merits its use, it is unsuitable yet from an economic standpoint as a bleaching agent alone. Further investigations indicated that there was an alternative method, by using a mixture of hypochlorite and chlorite.

Taylor, White, and Vincent (12) found that chlorite activated by hypochlorite gave more desirable physical properties to bleached pulps than could be obtained by using hypochlorites alone. The peculiarity found with this method was that the results were characteristic of chlorite bleaching. This effect was believed due to the removal of the hypochlorites by reaction with chlorite to form chlorine dioxide. In the case of hypochlorites alone the more active chlorine and chlorine monoxide are released.

Bleaching by the hypochlorite activation of chlorite was found not to be limited to any particular pH range. In general the same conditions suitable for hypochlorite bleaching alone were applicable for this method. The best pulps were obtained within the alkaline range of pH8 to pH9.

A comparison of the experimental results of the three methods indicated, that when the same degree of high brightness was attained there was a loss in physical strength of 5% from the hypochlorite-chlorite method, and a loss of 10% or more from hypochlorite bleaching as compared to the acidified chlorite process (12, 20). Comparisons based on the physical properties of brightness, maximum bursting strength, and tearing resistance, definitely showed the superiority of the acidified chlorite method over the alkaline hypochlorite method. The properties of pulp bleached by mixed hypochlorite and chlorite are in most cases comparable with those bleached by the acid-chlorite process. Fig. (1) shows a graphical comparison between hypochlorite and chlorite bleaching, the comparison based on maximum mullen strength and brightness (23).

FIG. 1
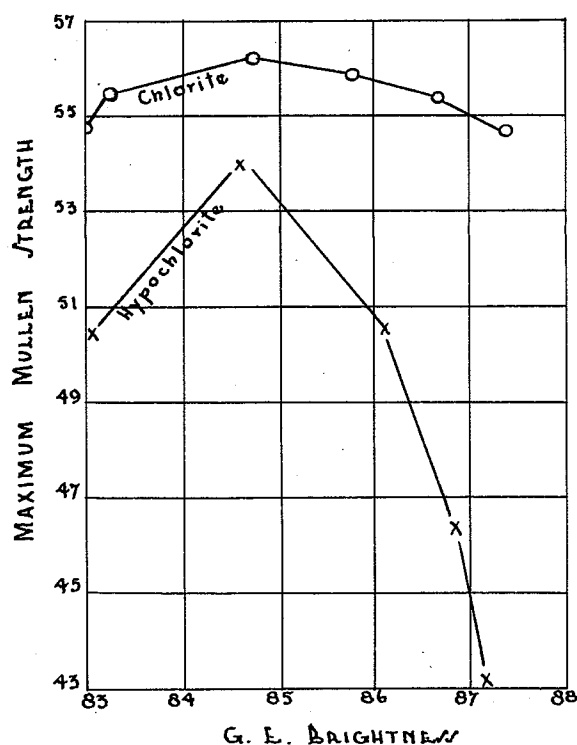
G. E. BRIGHTNESS

Table 1. Shows a comparison of physical tests on unbleached and bleached sulphite pulps. (12).

Process	Bright-ness	Bursting Strength	Folding Endurance	Tearing Strength	Viscosity
Unbleached pulp (original)	64	52	950	51	86.4
Hypochlorite (single stage)	87.5	44	600	49	17.2
Chlorine-hypo-chlorite (2 stage)	88.5	47	925	50	21.9
Chlorine-chlo-rite (2 stage)	88.6	49	1250	65	84.6

This superiority of properties was not only found in the case of various types of wood pulp, but textile chemists have found the same superiority extends to cotton and rayon. The results do not depend on the exact nature of the impurities and colored bodies present, but do depend upon the inability of chlorite to react with cellulose.

(c) Structure and degradation of Cellulose

In order to understand the physical and chemical proper-

ties of cellulose, it is necessary to consider the nature of cellulose, its structure, and the possible manner of its degradation.

Cellulose, the chief constituent of all living plants is built up of glucose anhydride units ($C_6H_{10}O_5$) and this suggests that it owes its formation in the plant to a condensation of glucose units with loss of water. These units are arranged in long chains, but the number of units in a chain is as yet unknown, and seems to vary from sample to sample. However, the number is large, endowing this substance with all the properties of a high molecular weight compound. X-ray analysis has definitely revealed the crystalline nature of cellulose. It is assumed that within the geometrical unit all the individual molecular chains are arranged parallel to each other, and that this arrangement is laterally stabilized by secondary valence forces exerted by quadrivalent oxygen atoms. These chain bundles have varying lengths, and are arranged in units called micellae. These micellae are held together by "tertiary" or micellar valencies to build up the fibrillae, the smallest constituent of the fibre which may be detected under the microscope (24).

Careful degradation of cellulose, and chemical analyses have confirmed that the high molecular weight polysaccharides are constituted on the bases of long chain mono-saccharide residues or B - glucose anhydride units, and are linked together in a mode

corresponding to that of cellobiose, namely, through the 1 and

4 carbon atoms of the glucose units by oxygen bridges to form a

primary valence chain of unstated length. Fig. 2 indicates the

cellulose molecule, and indicates the 1:5 internal glucose

linkage (amylene oxide linkage) and the 1:4 glycosidic linkage

between the glucose units.
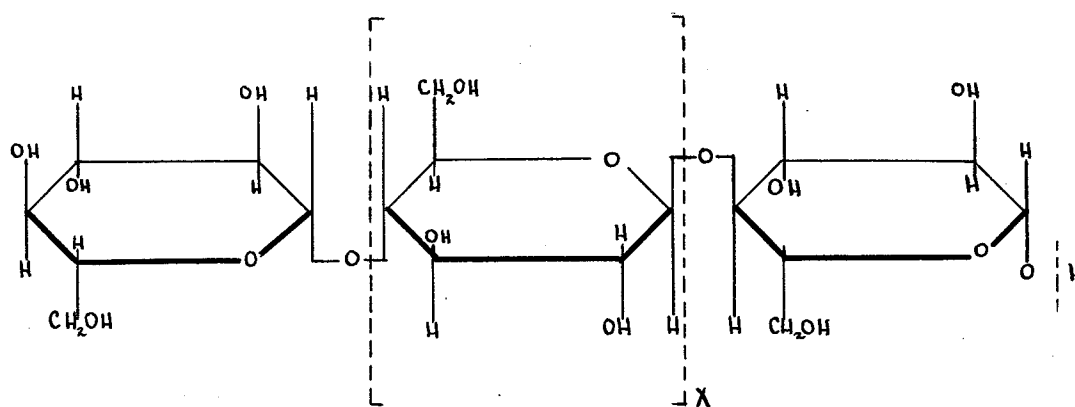
FIG. 2

Cellulose, when subjected to the action of dilute mineral acids undergoes a modification due to hydrolysis, the extent of which depends on the conditions and severity of the treatment. Hydrolysis carried out under mild conditions leads to the formation of products which have undergone various stages of degradation, from almost untouched chains down to the monomeric glucose. These heterogeneous degradation products are due to the slowness and irregularity of the hydrolytic process on cellulose, and to the fact that degradation starts on the surface of the fibre and works inwards. These complex products of varying chain length are generally grouped together under the name of "hydrocellulose." When the hydrolytic process was carried out under special conditions and reached completion, it was found that there had been a complete break-down of the primary valence chains with little or no oxidation, and the final product was glucose (24).

The degradation of cellulose by oxidation caused the cellulose to be irreversibly modified in such a way that its intrinsic strength and viscosity in cuprammonum solutions were decreased, and chemical properties appeared which were foreign to the natural material. It would seem possible from the structure, that cellulose could be oxidized without the oxygen bridges between glucose anhydride units being ruptured. Results of oxidation experiments, however, have indicated that oxidation is normally accompanied by

hydrolysis to a greater or less extent. The products formed consisted of polysaccharides of varying chain length with an increase in reducing properties. These degradation products were classed together into one group and called "oxycellulose". Severe oxidation does not result in the formation of glucose, but simpler ketonic, aldehydic, and carboxylic materials.

The extent of hydrolysis can be followed by determination of the viscosity in cuprammonium solution or the alpha cellulose content of the pulp. As the chains decrease in length, the viscosity decreases and the pulp becomes more soluble in sodium hydroxide solutions, giving a lower alpha cellulose value. The reducing power found on the breakdown of the structure due to oxidation and hydrolysis will be indicated by the determination of copper numbers, i.e. the reduction of copper from cupric to the cuprous state.

DISCUSSION OF THE PROBLEM

It is the problem of the author to examine the decomposition of sodium chlorite solutions at constant temperature, and under definite pH conditions. Throughout the course of each experiment these conditions were maintained as closely as possible. At various intervals of time, determination of strength was carried out by volumetric analysis. Once establishing the stability of sodium chlorite at various pH's, the author undertook to investigate the action of sodium chlorite on commercial sulphite wood pulp, under the same conditions of pH, and temperature used in the previous part of the work. The time of the reaction was set at six hours, and at set intervals within this time limit samples of the treated cellulose were taken from the water bath and analyzed for alpha cellulose content and copper numbers, to give a measurement of the degradation of the cellulose.

EXPERIMENTAL

(a) Apparatus

The apparatus used consisted of a Leeds and Northup Type K Potentiometer and a Leeds and Northup Galvanometer, Weston Standard Cell and two standard glass electrodes, one a calomel-KCl electrode, the other a quinhydrone electrode. Also a constant temperature water bath and the usual standardized chemical analyses equipment, burettes, beakers and flasks.

The galvanometer was used as a null point instrument and was a type sensitive to .00075 milliamperes.

The potentiometer used was a standard type K instrument sensitive to .00005 volt.

The apparatus used in the work on the degradation of cellulose included the equipment mentioned above, except that a Beckman pH meter was used instead of the Leeds and Northup potentiometer and galvanometer. The second section of the work included equipment suitable for mechanical stirring, and refluxing reactions such as one litre round bottom flasks and glass condensers.

The constant temperature water bath used was a copper tank insulated with asbestos and controlled by a mercury-ether thermo-regulator running two 500 watt carbon filament lamps as heating units. The bath was kept at a temperature of 35° C and the maximum variation was from 34.9° to 35.1° .

The glass electrodes used were Leeds and Northup standard electrodes. The quinhydrone electrode was made up of quinhydrone in the internal electrode, the outer part being filled with 1pH hydrochloric acid solution. These were renewed every three weeks. When not in use the complete cell was kept immersed in distilled water.

The calomel electrode also in two parts, the outer being the salt bridge, the inner the calomel electrode which was made by putting 1 gram mercury and 0.25 grams of mercurous chloride and moistened with saturated potassium chloride solution and thoroughly shaken till the mercury and mercurous chloride appeared to be emulsified. The salt bridge outer section was filled with saturated potassium chloride and the ground glass tip loosened until potassium chloride dripped through. The electrode was then ready for use. Before using each time bridge was flushed as described above.

(b) Standardization of Potentiometer and Glass Electrodes

As the potentiometer and glass electrodes were to be used
for measuring the pH of the solutions, the instrument was stan-
dardized against buffer solutions of known pH, prepared by the
standard methods given in Clark's "Determination of Hydrogen
Ions."

The type of buffers used and their pH's were as follows.

pH 6   - acid potassium phthalate + NaOH.

pH 7   - acid potassium phosphate + NaOH.

pH 8   - Boric Acid, KCl + NaOH.

pH 9.19   - Boric Acid + NaOH.

pH 9.87   - Boric Acid + NaOH.

pH 10.93 - Boric Acid + NaOH.

The potentiometer was connected up with the electrodes and
the buffer solution supported in the water bath. The electrodes
were immersed in the solution and the buffer solution allowed to
come to constant temperature. A series of potentiometric readings
were taken with the various buffer solutions until a series of
constant results were obtained. The buffer solutions were kept
in stock bottles fitted with ground glass stoppers. The poten-
tiometer was standardized against these buffer solutions occasion-
ally to make sure no asymmetric potential was set up in the elec-
trodes.

POTENTIOMETER READINGS

CALOMEL ELECTRODE −   CALOMEL ELECTRODE +

.10   .08   .06   .04   .02   .00   .02   .04   .06   .08   .10   .12   .14

5

6

7

8

9

10

11   PH VALUES

STANDARDIZATION GRAPH
FOR POTENTIOMETER
AND ELECTRODES

Form No. 5780E—20 Squares per Inch

Made in U.S.A.
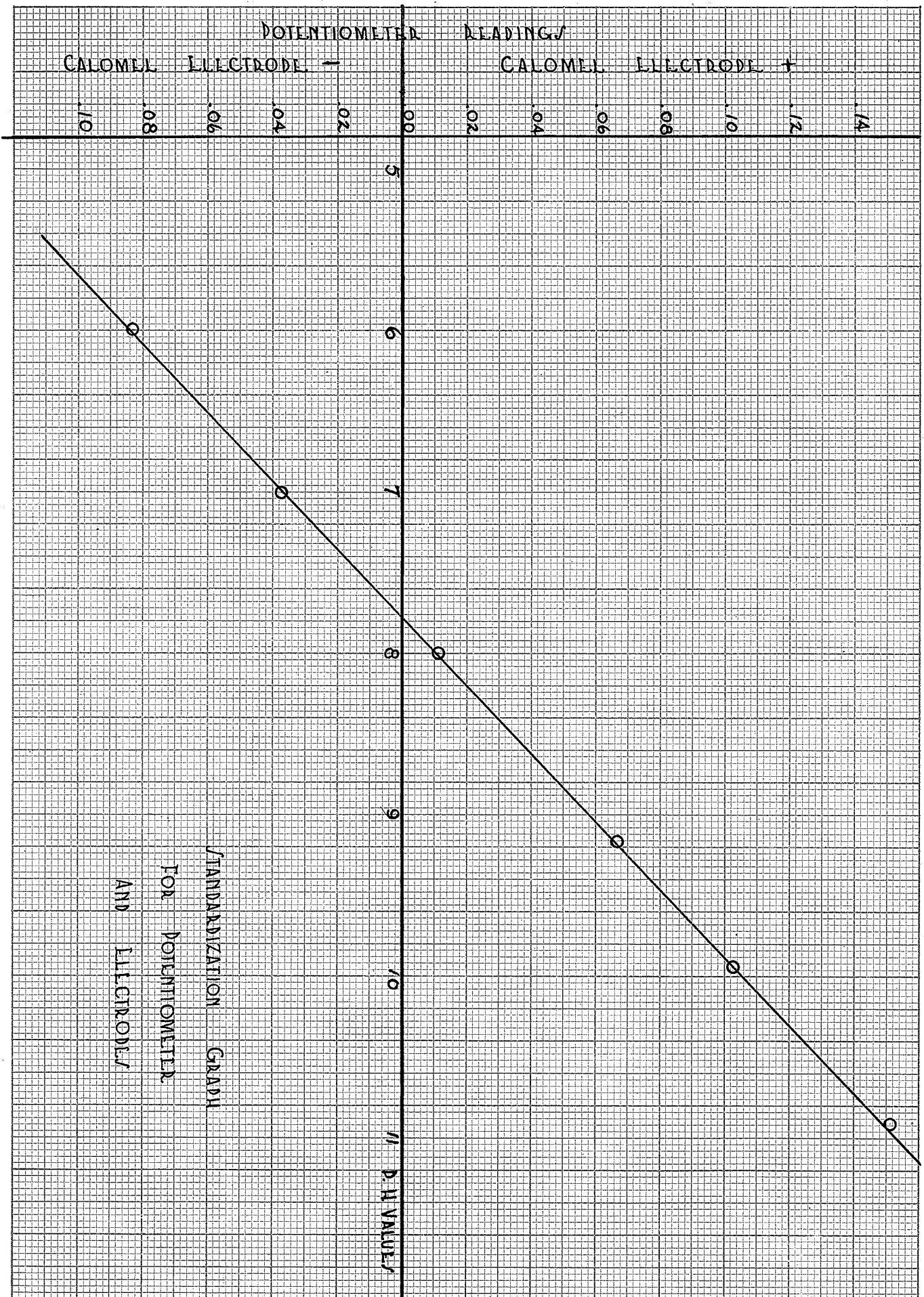
NATIONAL

The results of the standardization are shown in table (2) and graphically in Fig. 3.

Table 2.

pH Value of Buffer Solution	Potentiometer Reading	Calomel Electrode Polarity
6	.0828	—
7	.0365	—
8	.0110	+
9.19	.0672	+
9.87	.1030	+
10.93	.1508	+

The Beckman pH meter used in Section II of the experimental work instead of the Leeds and Northup Potentiometer, was standardized against a buffer supplied with the instrument.

(c) <u>Reagents used and their standardization</u>

In all cases the reagents used were of analytical quality where possible.

1. Potassium permanganate solution exactly .1N. This solution was standardized against Mohr's salt, and was prepared from a stock solution of permanganate prepared as follows. The potassium permanganate was made up to a fairly concentrated solution, stored in brown glass Winchester bottles and allowed to stand for two weeks in order to allow any decomposition products to settle out. The top layer of the solution was siphoned off and diluted with carbon-dioxide free water to the required strength.

2. Sodium Thiosulphate solution, exactly .1 Normal. This solution was standardized against a potassium permanganate solution of known strength, prepared from the stock solution.

3. Potassium Iodide)   used together as external

   Starch Solution)   indicators

4. Ferrous ammonium sulphate.

5. Silver nitrate solution of .1 Normal strength standardized against an exactly .1 Normal potassium thiocyanate solution using ferric indicator.

6. A .1N potassium thiocyanate solution standardized against sodium chloride of analytical quality.

(d) Preliminary Investigations

A preliminary investigation was carried out by the author on

the analysis of chlorite by itself, and also in the presence of

chlorates and chlorides, in order to establish the accuracy of

the method suggested by Bray (25) and Foerster (26), and to es-

tablish an accurate analytical technique.

Foerster in his research on the transition of hypohalites

into halates, and the part played by halites in this transition

in alkaline solution, used the following method of analysis.

Analyzing for hypochlorites alone Foerster used a solution

of alkaline sodium arsenite. He found if chlorites were present

this direct method of analyzing for hypochlorites gave erroneous

results, because with the addition of less than 2cc of the bi-

carbonate - containing arsenite solution, the color and smell of

chlorine dioxide occurred. This formation of chlorine dioxide

was due to the reaction of the hypochlorous acid freed by the

bicarbonate with the chlorite. This difficulty was overcome by

running the hypochlorite-chlorite solution into an excess of the

arsenite solution and immediately back titrating with an iodine

solution. Under such conditions the hypochlorous acid was given

no time to react with the chlorite, while it was taken into union

at a much greater rate by the arsenious acid.

After the determination of the hypochlorite, the chlorites

were analyzed (25) for by taking the previously mentioned solution

and adding 50cc of .2NKl and acidifying with $2NH_2SO_4$. This solution
was allowed to stand from 3-5 minutes in order to allow the reaction
to reach completion. The liberated iodine was then titrated with
.1N sodium thiosulphate. The reaction according to Bray (25) is:

$$ClO_2' + 4I' + 4H^. = 4I + Cl' + 2H_2O \quad (17)$$
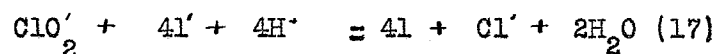
The estimation of chlorates present was carried out indirectly
by establishing the total active oxygen and subtracting that due to
chlorite and hypochlorite. In the absence of chlorite the determina-
tion of chlorate can be achieved by distillation with Hcl, but in
presence of chlorites, chlorine dioxide is formed thus rendering
the distillation method unsuitable. The method of analysis used in
this case was to allow the solution under investigation to react
with a neutral solution of ferrous sulphate then quickly acidify,
and titrate the excess ferrous sulphate with potassium permanganate.

The author, when analyzing for chlorates using the above method,
used a solution of ferrous sulphate instead of individual solid samples
for each determination. This was done for ease of manipulation
during the experiment. From time to time a potassium permanganate
titration was run on the ferrous sulphate solution in order to detect
any change of strength over a period of time. The author also found
that if chlorates were present the reaction between the ferrous
sulphate and chlorate was slow, and if the reaction was carried out

in the cold it didn't reach completion. Best results were obtained
by heating the solution to the boiling point and gradually acidify-
ing after the sodium chlorite, sodium chlorate and iron salt had
been added.

The total amount of chloride present was analyzed for by
taking the previous solution and adding an excess of .1N silver
nitrate. The precipitated silver chloride was filtered off and
the excess silver nitrate was titrated with .1N potassium thio
cyanate using ferric indicator.

In several preliminary experiments the author found that in
the samples of sodium chlorite used there was no sodium hypochlo-
rite, and consequently in the method used, analyses were made only
for chlorites chlorates and chlorides.

In order to check these methods the author carried out ana-
lysis on accurately weighed samples of (a) sodium chlorite, (b) a
mixture of sodium chlorite and potassium chlorate, (c) a mixture
of sodium chlorite, potassium chlorate, and sodium chloride.
Solutions of the single and mixed salts were prepared in the follow-
ing manner. In the case of (a) 2.5 gms. of sodium chlorite were
made up to one litre of solution, and the analysis was made on a
10cc sample of this solution. The mixture of sodium chlorite and
potassium chlorate (b) consisted of 5 grams of sodium chlorite and
5 grams of potassium chlorate made up to one litre of solution, 10cc
of this solution contained .05 grams of each constituent. In the

case of (c) 5 grams of sodium chlorite, potassium chlorate, and

sodium chloride respectively were accurately weighed out and made

up to one litre of solution, 10cc of this solution contained .05

grams of each constituent. As the sodium chlorite used was 98.5%

pure its theoretical and analytical value was less than .05 grams

per 10cc of solution.

The analyses for chlorite, chlorate, and chloride were

carried out on duplicate 10cc samples of the solutions. The chlo-

rite determination was carried out on one of the two 10cc samples

by means of the thiosulphate titration. The other 10cc was used

to determine the amount of chlorate and chloride by the methods

previously indicated.

The titration and standardization values of the solutions

used in the preliminary investigations are given in Table 3. The

amounts of chlorite, chlorate, and chloride were calculated and

are shown in Table 4, which indicates the accuracy of the analy-

tical method used.

Table 3   -   Titration Values

Ex. (a)   Sodium Chlorite (single salt)

    (1)   10cc of sodium chlorite solution $= \dfrac{.025 \times 98.5}{100}$ grams

    (theoretical) required 10.7cc of .1024N $Na_2S_2O_3$. (chlorite

    Analysis).

    (11)   .8544 grams of Fe" (solution) added to duplicate 10cc

sample, excess iron required 143.0 cc of $K.MnO_4$:

lcc $KMnO_4$ is equivalent to .005545 grams Fe" (chlorate Anal.)

(111) 50cc $AgNO_3$ added to solution (11), excess A_9NO_3 titrated with 34.9cc of KCNS.

25cc $AgNO_3$ requires 18.53 KCNS

lcc $AgNO_3$ is equivalent to .005847 grams NaCl (chloride Anal.)

Ex. (b) $NaClO_2$ + $KClO_3$

_____

(1) 10cc of solution $=$ $\frac{.05 \times 98.5}{100}$ grams $NaClO_2$ and .05 grams $KClO_3$ (theoretical) required 21.02cc of .1016N $Na_2S_2O_3$ (chlorite Anal.)

(11) .7120 grams Fe" (solution) added to duplicate 10cc sample, excess iron required 77.9cc of $KMnO_4$:

lcc $KMnO_4$ is equivalent to .005843 grams Fe" (chlorate Anal.)

(111) 25cc $AgNO_3$ added to solution (11), excess A_9NO_3 titrated with 9.8cc KCNS.

25cc $AgNO_3$ requires 16.63cc KCNS

lcc $AgNO_3$ is equivalent to .00525 grams NaCl. (chloride Anal.)

Ex. (c) $NaClO_2$ + $KClO_3$ + NaCl

_____

(1) 10cc solution $=$ $\frac{.05 \times 98.5}{100}$ grams $NaClO_2$, and .05 grams of $KClO_3$ and NaCl respectively (theoretical), required 21.45cc of .1016 N $Na_2S_2O_3$ (chlorite Anal.)

(11) 1.4220 grams Fe" (solution) added to duplicate 10cc sample, excess iron required 98.4cc $KMnO_4$

1cc $KMnO_4$ is equivalent to .01182 grams Fe" (chlorate Anal.)

(111) 50cc $AgNO_3$ added to solution (11), excess $AgNO_3$ titrated with 20.1cc KCNS.

25cc $AgNO_3$ requires 16.63cc KCNS

1cc $AgNO_3$ is equivalent to .00525 grams NaCl. (chloride Anal.)

The detailed method of calculating chlorites, chlorates, and chlorides using (a) as an example was as follows.

(1) 10cc of solution required 10.7cc of .1024 N $Na_2S_2O_3$

Amount of chlorite =

$$\frac{10.7 \times .1024 \times 22.6135}{1000} = .02476 \text{ grams } NaClO_2$$

(11) $NaClO_2 + 4FeSO_4 + 2H_2SO_4 = 2Fe_2(SO_4)_3 + NaCl + 2H_2O$
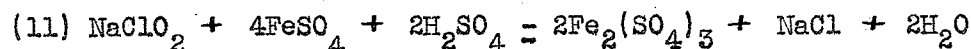
90.45 grams $NaClO_2$ requires 55.84 x 4 = 223.36 grams Fe"

1 gram $NaClO_2$ is equivalent to 2.4688 grams Fe"

Excess Fe" required 143cc $KMnO_4$ =

Excess Fe" = 143 x .005545 =   .7924 grams

Fe" reducing $NaClO_2$ = .02476 x 2.4688 =   .0611 grams

                   Total   .8535 grams

Difference =

    .8544 - .8535 =   .0009 grams Fe"

$$NaClO_3 + 6FeSO_4 + 3H_2SO_4 = 3Fe_2(SO_4)_2 + NaCl + 3H_2O$$
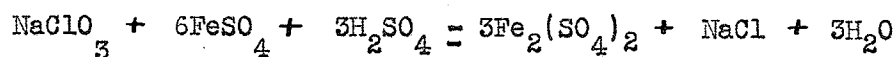
106.45 grams $NaClO_3$ requires 55.84 x 6 = 335.04 grams Fe"

1   gram $NaClO_3$ is equivalent to $\frac{55.84}{17.742}$ grams Fe"

Amount of chlorate =

$\frac{17.742}{55.84}$ x .0009 = .0003 grams $NaClO_3$

(111) 50cc $AgNO_3$ added to (11), excess $AgNO_3$ required

34.9 cc KCNS.

Amount of $AgNO_3$ required to react with chloride reduced from

sodium chlorite and sodium chlorate,

50 - ($\frac{25}{18.53}$ x 34.9) = 2.8cc $AgNO_3$

1cc $AgNO_3$ is equivalent to .005847 grams NaCl

Amount of chloride =

2.8 x .005847 = .0164 grams NaCl.

(1v) Amount of chloride calculated from chlorite and chlorate.

From $NaClO_2$ $\frac{58.45}{90.45}$ x .02476 =   .0160   grams NaCl

From $NaClO_3$ $\frac{58.45}{106.45}$ x .0003 =   .0001   grams NaCl

Calculated Total   .0161   grams NaCl

Analysis =   .0164

Calculated =   .0161

Difference =   .0003   grams NaCl

Table 4.   Check on Analysis

Sample		NaClO$_2$ grams	KClO$_3$ grams	NaCl grams
(a) NaClO$_2$	theoretical	.0246		
	By analysis	.0247	.0003 (as NaClO$_2$)	.0003
(b) NaClO$_2$ + KClO$_3$	theoretical	.0492	.0500	
	By analysis	.0483	.0504	.0007
(c) NaClO$_2$ + KClO$_3$ + NaCl	theoretical	.0492	.0500	.0500
	By analysis	.0493	.0502	.0494

PROCEDURE

   (a) Decomposition of sodium chlorite

   A one percent solution of sodium chlorite was placed in a one
litre beaker, in the water bath, and brought to the required tem-
perature of 35° C. The electrodes were then immersed in this
solution, and the required pH adjustment was made as quickly as
possible using a .01N sodium hydroxide or .01N sulphuric acid
solution as the case may be. Timing was started immediately and
at stated intervals two - 2cc portions of the solution were re-
moved and quickly analyzed by volumetric methods. A careful watch
was made of the solution and the necessary adjustments for the pH
value in question were made as required. The solutions under in-
vestigation especially when kept over a period of days were kept
in glass stoppered bottles to prevent any evaporation.

   The analysis of each sample withdrawn was carried out using
the volumetric methods for determination of sodium chlorite, sodium
chlorate, and sodium chloride as previously indicated in the section
on preliminary investigations. One of the two - 2cc portions with-
drawn was used for the determination of sodium chlorite, the other
2cc sample for the estimation of sodium chlorate and sodium chloride.

   The author noted that the alkaline solutions on long standing
turned slightly yellow, and with the decrease in alkalinity this
coloration appeared more quickly. This coloration of the solution

indicated the possibility of decomposition, but no change could be
detected in the analysis. It was first believed that the fault was
due to the solutions being kept in sealed bottles, thus preventing
any gaseous decomposition products from escaping. Investigations
of solutions kept in open beakers, after noting that evaporation
was negligible over a short period of time, showed that no decom-
position had taken place that could be detected by titration, although
these solutions also turned yellow. There remained the possibility
that if decomposition had taken place, the products were dissolved
in the solution including the chlorine dioxide which gives the
solution its yellow color. To investigate this possibility the
author took a solution which had stood for 200 hours in a glass
stoppered bottle, the titration value of which was known accurately.
Air was bubbled through this solution until it was free of any
coloration. Analysis of this aerated solution showed a change
in the titration value of about one half of one percent.

The author concluded that the development of the yellow color
in the solution was independent of the type of vessel used, and
that the titratable concentration of the solution was not affected
by it.

This complete procedure of analysis was carried out in duplicate
for each determination of pH values of 10, 9, 8, 7, 6.5, 6, 5, and 4.

The amounts of sodium chlorite, sodium chlorate, and sodium chloride
were calculated and averaged; these amounts were used in the prepara-
tion of the following Table 5. Column 9 of Table 5 refers to the
total sodium chloride found by analysis, and includes chlorite present
in the sodium chlorite as an impurity, and the chloride resulting
from the reduction of sodium chlorite and sodium chlorate by the ferrous
salt. The amount of sodium chloride other than that from sodium chlo-
rite and sodium chlorate was normally $\pm$ .0004 grams.

Table 5 Results

Time Hours	Na$_2$S$_2$O$_3$ Soln. ccs. 1	2	Av.	NaClO$_2$ in gms	Gms. Fe" in 25 ccs of soln.	KMnO$_4$ Soln. ccs. 1	2	Av.	NaClO$_3$ in gms.	AgNO$_3$ Soln. ccs. No. of ccs.	KCNS Soln. ccs. for sample # 1	2	Av.	NaCl in gms.
P.H. Value = 10														
0	8.70	8.70	8.70	.0196	.3545	54.40	54.50	54.45	.0005	25	21.80	21.80	21.80	.0132
18	8.60	8.60	8.60	.0194	.3545	54.60	54.60	54.60	.0004	25	21.87	21.94	21.90	.0126
70	8.65	8.65	8.65	.0196	.3546	54.50	54.40	54.45	.0005	25	21.80	21.80	21.80	.0132
185	8.65	8.65	8.65	.0196	.3535	54.30	54.20	54.25	.0006	25	21.80	21.80	21.80	.0132
P.H. Value = 9														
0	8.80	8.75	8.78	.0197	.3522	54.05	53.86	53.95	.0007	25	22.00	22.13	22.07	.0118
50	8.65	8.70	8.68	.0196	.3507	53.70	53.70	53.70	.0007	25	21.87	22.00	21.94	.0126
73	8.70	8.65	8.68	.0196	.3493	53.60	53.50	53.55	.0005	25	21.87	21.94	21.90	.0126
143	8.90	8.85	8.88	.0198	.3436	52.40	52.47	52.44	.0005	25	21.87	21.87	21.87	.0128
P.H. Value = 8														
0	8.90	8.90	8.90	.0199	.3567	54.75	54.66	54.70	.0006	25	22.00	22.00	22.00	.0121
23	8.90	8.90	8.90	.0199	.3552	54.57	54.40	54.48	.0005	25	21.87	21.94	21.90	.0126
48	8.95	8.90	8.93	.0199	.3545	54.22	54.22	54.22	.0007	25	21.94	21.94	21.94	.0124
96	8.90	8.85	8.88	.0199	.3516	53.86	53.86	53.86	.0004	25	22.00	21.94	21.97	.0122

Time Hours	Na₂S₂O₃ Soln. ccs 1	2	Av.	NaClO₂ in gms.	Gms. Fe" in 25 ccs of Soln.	KMnO₄ Soln. ccs 1	2	Av.	NaClO₃ in gms.	AgNO₃ Soln. ccs No. of ccs.	KCNS Soln. ccs for sample = 2 1	2	Av. = 2	NaCl in gms.
P.H. Value = 8 (contd.)														
142	8.90	8.85	8.88	.0199	.3547	54.40	54.30	54.35	.0006	25	22.00	22.07	22.04	.01185
190	8.80	8.75	8.78	.0198	.3517	53.95	53.86	53.90	.0004	25	21.94	22.00	22.97	.0122
238	8.80	8.90	8.85	.0199	.3491	53.35	53.35	53.35	.0006	25	21.94	21.94	21.94	.0124
P.H. Value = 7														
0	8.75	8.75	8.75	.0197	.3525	53.95	53.95	53.95	.0007	25	21.94	21.94	21.94	.0124
48	8.60	8.60	8.60	.0194	.3506	53.70	53.78	53.74	.0007	25	21.87	21.94	21.90	.01243
94	8.65	8.75	8.70	.0196	.3547	54.30	54.40	54.35	.0008	25	21.80	21.87	21.84	.0128
142	8.75	8.75	8.75	.0197	.3517	53.86	53.86	53.86	.0006	25	21.87	21.94	21.90	.0126
190	8.75	8.70	8.73	.0197	.3497	53.45	53.45	53.45	.0007	25	21.80	21.87	21.84	.0126
P.H. Value = 6.5														
0	8.60	8.60	8.60	.0194	.3571	54.96	54.96	54.96	.0007	25	21.90	21.90	21.90	.0127
43	8.55	8.60	8.58	.0194	.3544	54.54	54.54	54.54	.0006	25	21.90	21.90	21.90	.0127
145	8.55	8.55	8.55	.0194	.3514	54.00	54.00	54.00	.0006	25	21.90	21.90	21.90	.0127
237	8.60	8.70	8.70	.0196	.3470	53.06	52.94	53.00	.0008	25	21.93	21.90	21.92	.0125
330	8.60	8.70	8.70	.0196	.3425	52.20	52.10	52.15	.0008	25	21.93	21.90	21.92	.0125

Time Hours	Na₂S₂O₃ Soln. ccs. 1	2	Av.	NaClO₂ in gms.	Gms. Fe" in 25ccs of Soln.	KMnO₄ Soln. ccs. 1	2	Av.	NaClO₃ in gms.	AgNO₃ Soln. ccs.	KCNS Soln. ccs. 1	2	Av.	NaCl in gms.
P.H. Value = 6									No. of ccs. for sample = 2					
0	8.65	8.65	8.65	.0195	.3545	54.63	54.60	54.60	.0004	25	21.93	21.93	21.93	.0123
4	8.60	8.60	8.60	.0195	.3545	54.48	54.50	54.50	.0006	25	21.93	21.93	21.93	.0123
8	8.65	8.70	8.68	.0195	.3545	54.56	54.48	54.52	.0006	25	21.93	21.93	21.93	.0123
33	8.70	8.75	8.72	.0196	.3542	54.50	54.40	54.45	.0007	25	21.93	21.93	21.93	.0123
38	8.70	8.70	8.70	.0196	.3542	54.50	54.50	54.50	.0006	25	21.93	21.90	21.92	.0123
P.H. Value = 5														
0	8.90	8.75	8.83	.0198	.3462	53.13	52.90	53.00	.0008	25	21.93	21.92	21.93	.0123
2	8.80	8.85	8.83	.0198	.3462	53.00	52.90	52.95	.0008	25	21.92	21.90	21.92	.0123
4	8.75	8.70	8.73	.0197	.3462	53.00	52.83	52.90	.0008	25	21.93	21.93	21.93	.0123
6	8.80	8.75	8.78	.0198	.3462	52.83	52.83	52.83	.0007	25	21.92	21.93	21.92	.0123
34	8.75	8.70	8.73	.0197	.3474	53.10	53.17	53.15	.0006	25	21.90	21.98	21.93	.0123
37	8.70	8.75	8.73	.0197	.3473	53.15	53.20	53.17	.0006	25	21.90	21.93	21.92	.0123

4?

Time Hours	Na₂S₂O₃ Soln. ccs. (P.H Value = 4)			NaClO₃ in gms.	Gms. Fe" in 25 ccs of Soln.	KMnO₄ Soln. ccs.			NaClO₃ in gms.	AgNO₃ Soln. ccs (No. of ccs for sample =)	KCNS Soln. ccs. (sample = 2)			NaCl in gms.
	1	2	Av.			1	2	Av.			1	2	Av.	
0	8.75	8.70	8.73	.0197	.3440	52.63	52.70	52.67	.0004	25	21.98	22.04	22.00	.0123
1	8.65	8.65	8.65	.0195	.3440	52.65	52.60	52.63	.0006	25	22.04	21.98	22.00	.0123
2	8.60	8.65	8.63	.0195	.3440	52.65	52.60	52.63	.0006	25	22.04	22.04	22.04	.0123
4	8.65	8.65	8.65	.0195	.3440	52.53	52.50	52.50	.0008	25	21.93	21.93	21.93	.0123
6	8.60	8.65	8.63	.0195	.3440	52.63	52.60	52.60	.0007	25	21.93	21.98	21.95	.0122
9	8.65	8.60	8.63	.0195	.3440	52.53	52.47	52.50	.0008	25	21.90	21.93	21.92	.0125
11	8.65	8.65	8.65	.0195	.3440	52.47	52.47	52.47	.0009	25	21.92	21.93	21.93	.0123

CONCLUSIONS

From the investigations carried out on sodium chlorite solutions the author concluded the sodium chlorite was stable under alkaline and neutral conditions. Under acid conditions the analyses of sodium chlorite solutions showed no significant change. Although the solutions gradually turned yellow, indicating the presence of dissolved chlorine dioxide. This indicates a slight decomposition into products which remain dissolved, and which have practically the same effect on the analytical reagents as sodium chlorite solutions have. If the gaseous decomposition products were removed by aeration the equilibrium of the system would be destroyed and a continual evolution of chlorine dioxide would take place with the corresponding decomposition of sodium chlorite. The author investigated this by aerating a solution at pH5 which had stood for 200 hours and then titrating the solution when it was colorless. Analysis showed a decomposition of one half of one percent. Although investigations were not carried below pH4, the rate of decomposition increased as acidity increased. This was indicated by the deepening of the color and its more rapid appearance under stronger acidity. Even at pH4 analysis showed a consistency in titration values: from this the author concluded that under the conditions at which the investigations were carried out the chlorine dioxide remained dissolved in the solution and its presence was recorded in the titration values as sodium chlorite.

(b) Effects of Sodium Chlorite on Cellulose

The cellulose used in this part of the work was bleached sulphite wood pulp. In order to make easier handling the cellulose which was in thin compressed sheets was torn into little pieces approximately one square inch in size and soaked in water. An electric eggbeater was then used to beat up the cellulose until it was completely broken up. The cellulose was filtered out on a large Buchner funnel and the loosely knit cellulose torn into fluffy particles and allowed to dry in open dishes. The dry cellulose was then stored in large metal capped sealers until required.

A 3% cellulose suspension was prepared to which was added a weight of sodium chlorite equal to 25% of the weight of cellulose used.

To 1925 grams of distilled water, was added 15 grams of sodium chlorite. This chlorite solution was placed in the water bath and brought to the required temperature of 35° C. Acid or base was then added to bring the solution to the required pH. To this solution was then added 60 grams of air dried cellulose, the moisture content of which was known. The cellulose-chlorite suspension was quickly and thoroughly mixed with the electric eggbeater and the time was recorded.

The initial chlorite solution was analyzed previous to the addition of the cellulose, in order to determine the exact strength of the chlorite content. As the reaction proceeded 2cc of the solution were

removed from time to time and analyzed.

At regular intervals a portion of the cellulose was removed. To maintain the cellulose-chlorite ratio as accurately as possible, a portion of the solution was also removed. Cellulose samples were removed at the end of fifteen minutes, one hour, three hours, and six hours.

The cellulose on removal from the solution was poured immediately into a large beaker of ice water to check the reaction. It was then filtered through a Buchner funnel, washed with a weak acidified bi-sulphite solution to remove all traces of chlorite remaining in the cellulose. The cellulose was thoroughly washed with distilled water, removed from the Buchner funnel and shredded by hand. The shredded pulp was allowed to dry in the air under ordinary conditions. The air dried cellulose was then stored in labelled moisture tight jars for 48 hours to make sure that any remaining moisture was distributed uniformly throughout the cellulose.

This complete procedure was carried out for each determination of pH values 10, 9, 8, 7, 6, 5, and 4, respectively.

Methods of Analysis

The chemical effect of chlorite on cellulose under controlled pH conditions was determined by the use of copper number determinations and alpha cellulose content. The author attempted to use silver numbers in conjunction with the Cu No. determination, but the results were not satisfactory and the method was abandoned.

The method used for the determination of alpha-cellulose content, was the method number four approved by the Division of Cellulose chemistry of The American Chemical Society (27). This method was the result of a wide spread investigation and review of all existing literature, supplemented by certain experimental work on variables, with the aim of drawing up a tentative standard method accurate enough to give results that would be comparable when carried out by analysts, who are analyzing the same materials.

An approximately 3 gram sample of the treated cellulose was weighed accurately in a weighing bottle. The sample was placed in a 250cc pyrex beaker, and 35cc of 17.5% carbonate-free sodium hydroxide was added and the solution allowed to stand for 5 minutes. With a thick glass rod, the end of which had been rounded in the flame of a bunsen burner, the pulp was macerated for 10 minutes, adding intermittently in 10cc portions a total of 40cc of the 17.5% sodium hydroxide (20° C), during this interval. The beaker was covered with a watch glass and the contents of the beaker were subjected to an additional 30 minutes

mercerizing treatment on the water bath at 20° C. (total mercerization time 45 minutes). 75cc of distilled water (20° C.) were then added, and the contents of the beaker were filtered by suction on a large Gooch crucible having a finely perforated bottom, allowing the cellulose to form its own mat. The filtrate was poured through the mat a second time and a third time if necessary, to catch any fine material.

The cellulose residue in the Gooch crucible was washed with 750cc of distilled water (20° C.) by means of suction, then the suction tube was disconnected, and 40cc's of 10% acetic acid (20° C.) were added and allowed to soak 5 minutes. Suction was again applied to remove the acid, and the filtrate was tested for acid using litmus paper. The accurately weighed Gooch containing the alpha cellulose was dried at 105° C. to a constant weight--that is, the first constant consecutive weights obtained after 1 hour heating interval following an initial drying of at least 6 hours. The Gooch crucible and contents were allowed to cool in a desiccator for 30 minutes and then weighed.

The alpha-cellulose yield was calculated on the oven dry weight of the material. (see Table 6).

Duplicate samples for moisture determinations were weighed out at the same time that the samples for the alpha-cellulose determinations were taken.

The method of preparing the 17.5% carbonate-free sodium hydroxide used in extracting the beta-cellulose and gamma-cellulose from the alpha-cellulose was as follows. Sodium hydroxide sticks were dissolved in an equal weight of water. This concentrated hydroxide solution was allowed to stand 10 days to give the sodium carbonate and other impurities present time to settle. The clear supernatant liquid was decanted and diluted with carbonate free water until its density at 15° C. was 1.197. This solution contained 17.5 ± 0.1 grams of NaOH per 100 grams of solution. To protect the solution from the air the sodium hydroxide container was fitted with a siphon delivery tube and a drying tube.

The copper number of cellulosic material is defined as the weight of copper reduced by 100 grams of the sample from the cupric to the cuprous condition.

Various methods are referred to in the literature, the most notable being those outlined by Schwalbe (28), and Braidy (29) which is a modification of the Schwalbe method. The author used the Schwalbe method with some recommended modifications. Even with this method, the results of which show a fairly uniform consistency, there are many variables which can still be standardized as the empirical nature of these measurements renders it highly dependent upon the details of procedure. Results obtained by slightly differing methods are seldom comparable.

Approximately 3 grams of treated cellulose was accurately weighed out in a weighing bottle. This sample was placed in a 1 litre round bottomed flask fitted with a double holed stopper. A short reflux condenser bent at an angle of 45° was inserted through the cork, the other hole in the cork was fitted with a piece of glass tubing about 6 inches long and of a diameter just large enough to accommodate the shaft of a glass stirrer fitted to an electric motor. 250cc of boiling distilled water were run into the flask and brought to the boil, at the same time stirring was commenced just fast enough to prevent bumping. To the boiling water-cellulose suspension was added 20cc of the $CuSO_4$ solution and 30cc of the alkaline tartrate solution, which had been boiled separately and mixed just before adding to the flask. The Fehling's solution was washed from each of the beakers with 100cc of boiling water and added to the flask. The cellulose sample was heated with this solution on a sand bath for 45 minutes from the time bubbles first appeared.

The flask was then removed and 300cc of ice-cold water were added to prevent further reaction, and the solution was then immediately filtered by suction on a 17-G3 Jena glass filter.

The material on the filter was then washed with 300cc of cold distilled water, then with 750cc of boiling water, taking precautions that the pulp was not sucked to complete dryness. All filtrate and

washings were discarded.

The contents on the filter were then treated with 100cc of ferric sulphate solution, allowed to stand 5 minutes and the filter sucked dry. The pulp was washed with two-100cc portions of 2 Normal H_2SO_4 and further washed with 300cc of distilled water. The filtral and washings were titrated with .025 Normal $KMnO_4$.

The copper number determinations were carried out in duplicate, and duplicate samples for moisture determinations were weighed out at the same time as those for the actual determination. (See Table 6).

The solutions used and their preparation were as follows.

1. 692.0 grams Rochelle salt.

    200.0 grams NaOH.

    Dissolved in 2 litres of distilled water

    and filtered through glass wool.

2. 138.6 grams $CuSO_4$, dissolved in 2 litres of

    distilled water and filtered through glass

    wool.

3. Ferric Sulphate - 100 grams in 1 litre of water

    to this added 220cc of Conc. H_2SO_4. This solution

    was boiled 5 minutes and diluted to 2 litres.

    This solution should not reduce $KMnO_4$.

The number of grams of copper reduced by 100 grams of cellulose was calculated as follows.

$$\frac{\text{cc's of KMnO}_4 \times \text{Normality of KMnO}_4 \times .06357 \times 100}{\text{dry weight of cellulose}} = \text{Cu. No.}$$

Table 6.   Results

Time	Copper Numbers			Alpha Cellulose		
	1	2	Av.	1	2	Av.
			Grams			%
P.H. 10						
15 mins.	1.99	1.96	1.97	90.43	90.24	90.33
1 hour	2.00	1.99	1.99	90.53	89.83	90.18
3 hours	1.92	1.93	1.93	88.73	89.33	89.03
6 hours	1.87	2.01	1.94	89.86	90.26	90.06
P.H. 9						
15 mins.	1.94	1.83	1.88	90.76	90.62	90.69
1 hour	1.97	1.97	1.97	90.26	90.23	90.24
3 hours	1.85	1.93	1.89	89.89	89.95	89.92
6 hours	1.91	1.82	1.87	89.83	90.32	90.07
P.H. 8						
15 mins.	1.77	1.65	1.71	90.43	90.78	90.60
1 hour	1.78	1.76	1.77	90.20	90.63	90.41
3 hours	1.75	1.77	1.76	90.30	90.28	90.29
6 hours	1.67	1.70	1.69	90.24	90.05	90.14
P.H. 7						
15 mins.	1.64	1.79	1.71	89.81	89.80	89.80
1 hour	1.65	1.79	1.71	90.50	90.56	90.53
3 hours	1.69	1.77	1.73	90.94	90.76	90.85
6 hours	1.78	1.73	1.75	90.91	90.20	90.50

Time	Copper Numbers			Alpha Cellulose		
	1	2	Av. Grams	1	2	Av. %
P.H. 6						
15 mins.	1.83	1.84	1.83	91.46	91.10	91.27
1 hour	1.62	1.62	1.62	91.60	91.45	91.52
3 hours	1.85	1.76	1.80	91.54	91.45	91.50
6 hours	1.87	1.93	1.90	91.60	91.60	91.60
P.H. 5						
15 mins.	1.44	1.49	1.47	90.60	90.70	90.65
1 hour	1.60	1.44	1.52	90.50	90.60	90.55
3 hours	1.65	1.55	1.60	90.66	91.00	90.88
6 hours	1.43	1.58	1.50	90.65	90.68	90.66
P.H. 4						
15 mins.	1.30	1.31	1.30	90.60	90.35	90.47
1 hour	1.53	1.64	1.58	91.20	90.75.	90.97
3 hours	1.40	1.34	1.37	90.20	90.45	90.33
6 hours	1.55	1.55	1.55	90.45	90.56	90.50
Originals			1.70	90.24	90.39	90.30
	1.673					
	1.674					
	1.630					
	1.736					
	1.727					
	1.731					
	1.698					

CONCLUSIONS

The data presented show that throughout the pH range investigated sodium chlorite has had little damaging effect on the cellulose. This conclusion was drawn from the fact that analyses of alpha-cellulose content on the various treated samples remained practically the same as those of the original, and had even a tendency to show a slight increase.

Copper number determinations showed an increase over the original on the alkaline side. Although this rise above the original under alkaline conditions was difficult to explain, it was due possibly to alkaline hydrolysis of non-cellulosic materials present in cellulose fibres to give reducing substances. In any case it was not due to degradation of cellulose as this would be indicated by a decrease in alpha cellulose content, which has remained stable. Within the neutral zone the treated and untreated cellulose show the same approximate copper number, while under acid conditions there was a decrease especially in the pH range of 4 to 5. This decrease in copper number was more than likely due to the oxidation by sodium chlorite of this non-cellulosic reducing material, as cellulose degradation was excluded by the stability of alpha cellulose content within this pH range.

GENERAL DISCUSSION OF RESULTS

The chemical properties of treated cellulose investigated by the author have a direct bearing on the structure of cellulose, and also on the possible use of sodium chlorite in the bleaching of wood pulps and textiles.

The quality of wood pulp for many purposes depends on its alpha-cellulose content. Hence, the object in pulp manufacturing processes is to remove as completely as possible the non-cellulosic constituents of the raw stock, with minimum damage to the alpha cellulose fibres.

Hypochlorite bleaching to a greater or less extent destroys alpha-cellulose even when carried out with the utmost care. This destruction can be followed by alpha-cellulose determinations. A decrease in alpha cellulose content is directly concerned with the structure of cellulose, and means that there has been a rupture of the primary valence bonds with the corresponding shortening of the chain length. A further indication of degradation is given by determinations of copper numbers, which depend on the reducing properties of the material. Any sudden rise would indicate that reducing groups are appearing from the destruction of the 1:4 oxygen bridges and the appearance of the free aldelydic groups and the oxidation of the primary alcohol group to aldelyde. This rise of copper number is observed when hypochlorite bleaching is carried too far or if the alkalinity of the solution falls to unsuitable pH conditions.

In contrast to hypochlorites, sodium chlorite tends to decrease the copper numbers below the value determined from the original untreated pulp, and to increase the alpha cellulose content. These tendencies indicate that the structure of the cellulose is still unchanged, and that the action is only a case of removing the non-cellulosic carbohydrates remaining in the pulp after the initial bleaching.

Although no equipment was available to determine such physical properties as brightness, it was observed that the pulp treated with sodium chlorite under acid conditions had a brightness higher than the original which was a commercially bleached sulphite pulp.

These experiments lead to the conclusion that sodium chlorite is a high grade bleaching agent. In comparison to hypochlorites it is far more stable even under acid conditions, it has little or no tendency to attack cellulose, a property possibly due to its lower oxidizing power, and there is the possibility of achieving fully bleached pulps of high brightness without any apparent damaging effect on the cellulose.

SUMMARY

1. A Study of the decomposition of sodium chlorite solutions was made under controlled pH conditions.

2. The stability of sodium chlorite solutions under alkaline conditions were independent of their pH value. Under acid conditions this stability was still indicated in solutions in which the gaseous products of decomposition remained dissolved.

3. Sodium chlorite solutions under acid conditions showed a decomposition when the chlorine dioxide was removed by aeration. The rate of decomposition increased with increased acidity.

4. A study of the effects of sodium chlorite on cellulose were made under controlled pH conditions.

5. Chemical determinations on treated wood pulp indicated that under alkaline conditions the tendency was for the alpha cellulose to remain stable, and the copper numbers to increase: This, due to the alkaline hydrolysis of non-cellulosic materials present with the formation of reducing materials.

6. Under acid conditions the alpha cellulose tends to increase and the copper numbers to decrease. These properties suggest the oxidation and removal of the non-cellulosic material present in the cellulose fibres.

7. Sodium chlorite offers the possibility of securing fully bleached pulps without damage to the cellulose.

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