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Possible Use of Chlorine Dioxide for Bleaching Deinked Paper Stock

Donald E. Thorton

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POSSIBLE USE OF CHLORINE DIOXIDE
FOR BLEACHING DEINKED PAPER STOCK

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Submitted To

WESTERN MICHIGAN COLLEGE

JUNE 1, 1954

by

Donald E. Thornton

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ABSTRACT

The literature survey shows that chlorine dioxide can be used to bleach virgin pulp to a high brightness. The purpose of chlorine dioxide is to preserve the strength of the pulp.

The purpose of this thesis was to find out if chlorine dioxide could be used to preserve the strength of deinked paper stock.

Paper stock was found to lose strength when bleached with calcium hypochlorite and when mixed with virgin pulp the loss of strength carried over in the mixture.

When the paper stock was bleached with chlorine dioxide, there was no loss of strength in the paper stock.

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CHAPTER I

INTRODUCTION

Purpose. The purpose of this thesis is to determine whether or not chlorine dioxide can be used to an advantage for bleaching deinked paper stock, in a single stage bleaching process, to a high brightness.

To justify the use of chlorine dioxide in place of chlorine it will have to be shown that the quality of the paper stock can be improved greatly in strength, cleanliness and uniformity as compared to that obtained from hypochlorite bleaching.

By the improvement of uniformity the paper stock can be relied on to be, approximately the same from day to day.

Higher strength yield would possibly allow the management of the paper mills to use more paper stock and less virgin pulp, in at least some furnishes.

CHAPTER II

LITERATURE SURVEY

Much work has been done with chlorine dioxide in general, and in the field of bleaching cellulose with chlorine dioxide.

The cellulose bleaching with chlorine dioxide, up to date, has been limited to virgin pulps. There has been very little, if any, work done on bleaching deinked paper stock with chlorine dioxide. At the present time deinked paper stock is bleached with hypochlorite.

This literature survey will, therefore, deal with the properties of chlorine dioxide, the advantages and disadvantages in the virgin pulp industry.

It is hoped that chlorine dioxide will be as good for the deinking mills as it has been and will continue to be for the virgin pulp industry.

A brief history of chlorine dioxide. About 100 years ago Mellon obtained a gas by the partial reduction of sodium chlorate. Mellon identified this gas as chlorine trioxide (Cl_2O_3). However, in 1881 Garzarolli-Thurnalackh showed the gas to be a mixture of chlorine dioxide and chlorine.¹

This gas has, for many years now, been known to have the property of being capable of bleaching pulp to a high brightness without attacking the cellulose to any great extent. The reason it has been kept out of the pulp and paper

industry is because of the explosive properties and high cost of manufacture.

New methods of manufacture are changing this picture, until now, there are processes that bring chlorine dioxide close to a competitive range with chlorine.

More will be said about these processes later.

Properties of chlorine dioxide. Pure chlorine dioxide is very dangerous when in the pure state, either as a gas or a liquid. The gas, when dissolved in water at a concentration of twenty seven grams per liter, will crystallize out as chlorine dioxide octahydrate at a temperature below -0.79°C . If the concentration of chlorine dioxide is 108 grams per liter, the solid octahydrate will separate out at about 18.2°C . When the concentration of chlorine dioxide is between twenty seven grams per liter and 108 grams per liter, the temperature should be kept above 19°C (66°F) so that chlorine dioxide octahydrate will not crystallize out. If, however, the concentration is below twenty seven grams per liter, the temperature can go to 0°C before there is any danger of the octahydrate crystallizing out.

The danger involved, when the octahydrate comes out of solution, is that there is the possibility of liquid chlorine dioxide being formed, which is very explosive and may be set off by sun light, friction, organic matter or almost any other disturbance.²

Because of this explosive nature of chlorine dioxide, the gas cannot be cooled or compressed into either concentrated gases or liquids.

This makes it uneconomical to ship chlorine dioxide from manufacturer to consumer. If chlorine dioxide was to be shipped it would have to be shipped in a water solution or a 4% chlorine dioxide gas mixture.

Chlorine dioxide gas has an intense yellow color at ordinary temperatures with a density of approximately 2.4. It has a disagreeable odor³ and can be detected at a concentration of 14 - 17 p.p.m. At 45 p.p.m. it is irritating. "Forty-five minutes exposure in an atmosphere of 150 p.p.m. chlorine dioxide was fatal to guinea pigs, whereas, 40 minutes in 45 p.p.m. and 6 hours in 14 - 17 p.p.m. was not."⁴ Gas masks may be used for protection when chlorine dioxide is in the atmosphere.

Advantages of chlorine dioxide. When the dangers of chlorine dioxide are recognized and respected it can be a safe and valuable chemical.

The oxidation equivalent of chlorine dioxide is two and one half times that of chlorine. Taking into account the molecular weights of chlorine and chlorine dioxide, one part by weight of chlorine dioxide is equivalent to 2.63 parts by weight of chlorine.

The oxidation potential of chlorine dioxide is high

enough to attack the lignin and coloring matter of pulp, yet not high enough to attack cellulose. Chlorine not only attacks lignin and coloring matter of pulp, but also attacks the cellulose. Therefore, pulp bleached with chlorine dioxide shows less degradation and, consequently, gives more strength and higher yields.

Samuelson, Olof, Hartler and Niles showed that hypochlorite bleaching increases the carboxyl groups of the pulp in alkaline and acid bleaches. Chlorite bleaching affects the carboxyl groups the same way below a pH 4, while chlorine dioxide has no change in carboxyl groups, unless pre-bleaching with hypochlorite or chlorite has been carried too far.⁵

Chlorine dioxide bleaching usually improves opacity, alpha cellulose content, reactivity of the fiber, bleaching control,⁶ dirt count, brightness and strength.⁷

"Flash bleaching" can be obtained with chlorine dioxide. That is, most of the brightness increase is obtained in the first ten to fifteen minutes of bleaching. For example, Table I of "Bleaching Pulp With Mixtures of Chlorine Dioxide and Chlorine" by G. P. Vincent shows, in one case, an increase in brightness from 70.0 to 82.4 the first ten minutes, while at the end of two hours the brightness was only up to 84.3. This was accomplished with northern kraft at 5% consistency, 1.0% available chlorine applied, pH 9.0 and 100° F. The available chlorine was obtained from a

mixture of 2.5 parts chlorine dioxide and 1 part chlorine.

It was found by G. P. Vincent that mixtures of chlorine dioxide and chlorine gave finished pulps qualities equivalent to those of pulps bleached with chlorine dioxide alone.⁸

The brightnesses obtained from bleaching with chlorine dioxide, chlorite or mixtures of chlorine dioxide and chlorine are more permanent than those obtained from hypochlorite bleaching.⁹ Although freshly bleached hypochlorite pulps may be very high in brightness, after aging, this brightness drops appreciably. This drop in brightness is not so pronounced with chlorine dioxide or chlorite bleached pulps.

Where chlorine dioxide or chlorite is used. Chlorine dioxide is used to some extent in Sweden, Finland and Germany as a final stage for bleaching dissolving, viscose, and high alpha pulps.⁶ It is also used in the United States at Riegel Carolina Corp, Acme, N. C.¹⁰; the Brown Co., of Berlin, N. H.¹¹; the Nekoosa Edwards Paper Co. of Port Edwards and Nekoosa, Wisconsin.¹²

The use of this special bleaching agent has been used as a final stage in a multi-stage bleaching operation. If, however, a less vigorous pre-treatment of hypochlorite and two stages of chlorine dioxide are used, a higher brightness pulp can be obtained without any degradation.¹³

For the most part, chlorine dioxide has been used for bleaching kraft pulp. However, "chlorine dioxide has enabled

some sulphite manufacturers to answer the challenge of high brightness kraft pulp and retain markets which would otherwise have been lost."¹⁴

How chlorine dioxide is used. Chlorine dioxide can be generated, by the reduction of sodium chlorate, and dissolved in water and stored as bleach liquor in storage tanks until needed at the bleachery. Over a long period of time this is probably the most economical method.

Sodium chlorite can be purchased, however, mixed with the pulp suspension and then activated with acid, chlorine or hypochlorite. This method gives results comparable to those obtained by using bleach liquor made from chlorine dioxide gas. Chlorine dioxide can also be generated from a sodium chlorite solution by adding hypochlorite.

Chlorine dioxide or chlorite bleaching can either be carried out in an acid, neutral or alkaline medium. Results are nearly the same in all three mediums.¹²

Mixtures of chlorine dioxide and chlorine or chlorine dioxide and hypochlorite can be used with as good results as with chlorine dioxide alone.¹⁵ Chlorine dioxide-chlorine bleaching is an acid bleach. Chlorine dioxide-hypochlorite bleaching is an alkaline bleach.

If chlorine dioxide is to be used alone in an alkaline medium, caustic soda can be added to raise the pH as chlorine

dioxide solutions are acid.

Methods of manufacturing chlorine dioxide. There are six methods of preparing chlorine dioxide:¹⁶

1. Laboratory method
2. Holst process
3. Persson process
4. G. Farben process
5. Kesting or Brown process
6. Solvay process

The Holst process is the reduction of sodium chlorate with sulphur dioxide in an acid medium according to the following equation: $2\text{NaClO}_3 + \text{SO}_2 \xrightarrow{\text{H}_2\text{SO}_4} \text{Na}_2\text{SO}_4 + 2\text{ClO}_2$. Chlorine is also given off so there is a mixture of chlorine dioxide and chlorine. The gas is dissolved in water for the bleach solution. If chlorine dioxide free of chlorine is preferred, steps must be taken to remove the chlorine. Part of this may be done in the absorption tower as chlorine is not as soluble in water as chlorine dioxide.

The Persson process is practically the same as the Holst process except that chromium sulphate is used to reduce the chlorate and sulphur dioxide is used to recover the chromium sulphate.

The I. G. Farben process is the same as the Holst process to generate chlorine dioxide. The chlorine dioxide is then reacted with zinc dust to form zinc chlorite.

The Kesting or Brown process is probably the most economical of all if there is a cheap source of power. It is different from the other processes in that in this process

hydrochloric acid is oxidized to chlorine dioxide by sodium chlorate. The sodium chlorate is obtained by the electrolytic oxidation of sodium chloride. Sodium chloride is a product of the reaction of sodium chlorate and hydrochloric acid in an equivalent amount to the amount of sodium chlorate used. Theoretically, the only chemical needed is hydrochloric acid in the make up chemicals.¹⁷

The Solvay process depends on the reduction of sodium chlorate with methanol in an acid medium. Air is passed through heated methanol; and the air with the methanol vapors is passed into the acid chlorate solution. This generates chlorine dioxide and carbon dioxide: $6\text{HClO}_3 + \text{CH}_3\text{OH} = 6\text{ClO}_2 + \text{CO}_2 + 5\text{H}_2\text{O}$. The big advantage of this process is that there is very little chlorine contamination.¹¹

The laboratory method of producing pure chlorine dioxide consists of reducing sodium chlorate with oxalic acid in a sulphuric acid solution. This method gives chlorine dioxide, free from chlorine, diluted with carbon dioxide. The gas is dissolved in water.¹⁸ This method is limited to the laboratory because of the expense of chemicals.

By the use of sodium chlorite, chlorine dioxide bleaching can be accomplished (Mathieson Process); as sodium chlorite, when activated, yields chlorine dioxide. The advantage of this method in carrying out chlorine dioxide bleaching

is that no elaborate equipment is necessary to produce the bleach liquor. However, there is some indications that chlorite in the acid medium (below pH 4) is not the same as chlorine dioxide.

If chlorite is mixed with the pulp and activated with hypochlorite, a careful control of pH is necessary for good results. But, if the chlorite is mixed with hypochlorite and then added to the stock, pH is not as critical.¹²

Equipment used to handle chlorine dioxide. Chlorine dioxide gas, in aqueous solutions, is extremely corrosive. Choice of materials that can be used for storage, piping and bleaching with chlorine dioxide is very limited. Some of the materials which may be used are: glass, porcelain, stoneware¹⁷ and reinforced concrete lined with acid proof bricks. Lead and stainless steel may be used¹⁹. Rubber in any form is unsatisfactory and polyvinyl chloride can only be used if it contains no fillers or plasticizers.

On page 127 of "The Bleaching of Pulp - TAPPI Monograph no. 10" 1st ed., 1953, is a list of materials resistant to chlorine dioxide.

For alkaline bleach liquors of chlorine dioxide, equipment used for hypochlorite bleaching is suitable.¹²

Costs of chlorine dioxide. Chlorine dioxide is a little more expensive than hypochlorite, but the savings in quality and yield may by far offset this added expense. One paper

mill believes that with a chlorine dioxide bleaching plant, they can reduce their pulp inventory to a few standard grades.

Their bleached kraft pulp requirement for processing will be a standard pulp of about 75 brightness. Pulps of such relatively low brightness, follow stable price trends and can be purchased at a lower cost than high brightness pulps.²⁰ The cost differential between bleaching low brightness pulps to a high brightness is usually lower than the high brightness pulps.

The initial cost of installations for the Holst, Persson and Solvay processes is from \$100,000 to \$150,000. Kesting process costs about \$500,000.²¹

Cost per pound of chlorine dioxide, for chemicals, is about 18 cents, by the Solvay process. The Holst process will probably cost a few cents a pound more, due to the low equivalent weight of methanol as compared to sulphur dioxide; as the price per pound is nearly the same for methanol as it is for sulphur dioxide. Theoretically from the equations:
 $6\text{HClO}_3 + \text{CH}_3\text{OH} = \text{CO}_2 + 6\text{ClO}_2 + 5\text{H}_2\text{O}$ and $2\text{HClO}_3 + \text{SO}_2 = 2\text{ClO}_2 + \text{H}_2\text{SO}_4$; one pound of methanol will produce $12\frac{1}{2}$ pounds of chlorine dioxide, while one pound of sulphur dioxide will produce only 2 pounds of chlorine dioxide.

The Kesting process claims 40% savings over the Holst process.¹⁹ In Germany, where power costs are high, one pound of chlorine dioxide costs about 16 cents by the Kesting

process. Where power costs are lower, as in the United States, the costs of chlorine dioxide would be lower.¹⁷ One pound of chlorine dioxide is equivalent to 2.63 pounds of chlorine.

In Germany, bleaching with chlorine dioxide, from the Kesting process, costs only about 70 cents per ton more than when chlorine is used.¹⁷ This is very cheap when compared with the advantages of high brightness without loss of strength and high yields.

The mathieson process, using sodium chlorite, costs about \$1.70 per pound of chlorine dioxide for chemicals.

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TENTATIVE OUTLINE FOR EXPERIMENTAL WORK

The purpose of this experimental work is to determine whether or not a stronger sheet of paper, made of virgin stock and deinked stock in about equal proportions, can be made from deinked stock bleached with chlorine dioxide rather than with hypochlorite in a single stage bleaching process.

The paper stock will be bleached to a photovolt brightness of 76 to 80%. This brightness will allow the paper stock to be used in some high quality papers in larger proportions.

The experimental work is outlined as follows:

- I. Make sheets of virgin pulp and deinked stock bleached with calcium hypochlorite.
 - A. Bleach deinked stock with 5 and 10% Cl_2 as calcium hypochlorite for 3 hours at room temperature; wash and check brightness.
 - B. Beat mixtures of sulphite and kraft pulp to a freeness of 500 and 300.
 - C. Make sheets of 50% deinked stock and 50% virgin pulp as prepared in A and B, also use deinked brown stock.
 - D. Test sheets for mullen, tear and fold.
 - E. Run viscosity tests on deinked stock, bleached and unbleached.
- II. Bleach deinked stock with chlorine dioxide on the acid side and on the alkaline side to determine if there is any advantage in bleaching in an acid medium with ClO_2 .
- III. Repeat I using chlorine dioxide as the bleaching agent. Bleach on the alkaline side unless II indicates otherwise.

CHAPTER III

EXPERIMENTAL WORK

Pure chlorine dioxide was prepared, upon the recommendation of the Solvay Process Division of Allied Chemical and Dye Corporation, using sulphuric acid, oxalic acid and sodium chlorate. The chlorine dioxide gas was passed through a wash bottle to take out any hydrogen chloride and then dissolved in cold water.

Calcium hypochlorite was made by passing chlorine gas in a slurry of 50 grams of lime per liter of water.

The paper stock used in the experiments was of an ordinary commercial quality deinked with caustic soda in a hydropulper. Groundwood content of the deinked stock was below 15%.

First Experiment. Paper stock was bleached with various amounts of available chlorine as calcium hypochlorite and as chlorine dioxide. The pulp was bleached for four hours at 110°F and 140°F for the hypochlorite and chlorine dioxide respectively. Hand sheets were made from the pulp and tested for mullen, tear, and fold. Table I shows a comparison of strength of pulp bleached with calcium hypochlorite, chlorine dioxide and unbleached pulp.

All strength sheets were made according to TAPPI method T 205 M-50 throughout this work.

Strength sheets were made from commercially deinked and bleached paper stock; this too shows a loss of strength.

Tests results are tabulated in Table II.

Table I
Chlorine Dioxide vs Calcium Hypochlorite

%Cl ₂	Basis Weight 25 x 38-500		Photovolt Brightness		M.I.T. Fold		Mullen ClO ⁻ ClO ₂		Elmendoré Tear	
	ClO ⁻	ClO ₂	ClO ⁻	ClO ₂	ClO ⁻	ClO ₂			ClO ⁻	ClO ₂
0%	45.4		55.6		20		19.5		57.5	
5%	43.9	44.5	69.0	67.0	12	16	17.0	21.0	43.0	56.0
8%	44.5	45.4	69.5	69.0	8	18	16.4	20.6	35.0	57.5
11%	45.2	49.2	71.0	72.5	5	20	14.7	21.9	29.5	59.0
14%	45.8	44.2	73.5	73.0	3	25	12.4	20.5	26.5	53.0

Table II
Bleached vs Unbleached

	Basis Weight 25 x 38-500	Photovolt Brightness	Mullen	M.I.T. Fold
Un Bl.	42.0	59.5	21.1	29.0
Bl.	41.4	69.5	19.9	22.0

This decrease in strength shows up throughout this work and it is therefore quite evident that hypochlorite bleaches can lower the strength of paper stock to a great extent.

Second Experiment. To confirm the first experiment, more paper stock was bleached with 5 & 10% available chlorine as chlorine dioxide and as hypochlorite. Brightness sheets were made and viscosities were run by the falling ball method

T230sm-50. Curves were drawn, fig. I, to represent the viscosity of the pulp as the time of bleaching is increased. The slight increase in viscosity when ClO_2 was the bleaching agent is probably due to the purification of the pulp by ClO_2 . The pulp shows a definite degradation when bleached with hypochlorite.

Third Experiment. Because paper stock is hardly ever used 100% in paper, it was necessary to find out how much strength paper stock contributes to a finished sheet.

This was done by making sheets with mixtures of virgin pulp, bleached and unbleached paper stock.

Five pulps were prepared for this work as follows:

- A- 50% Kraft and 50% sulphite beaten in a Valley Beater to a C.S. Freeness of 580.
- B- 50% Kraft and 50% sulphite beaten in a Valley Beater to a C.S. Freeness of 378.
- C- Unbleached deinked stock.
- D- "C" bleached for three hours at 80°F with 5% Cl_2 as CaOCl_2 .
- E- Same as "D" except with 10% Cl_2 .

Sheets were made with mixtures of these pulps and tested at 50% R.H. and 72°F . The results are tabulated in Table III.

Fourth Experiment. The above sheets were made with paper stock that was not degraded to much of an extent.

More pulp was then bleached with the intention to degrade it more. The same virgin pulp mixtures were used, and the same unbleached deinked stock.

Viscosity vs Time of Bleaching

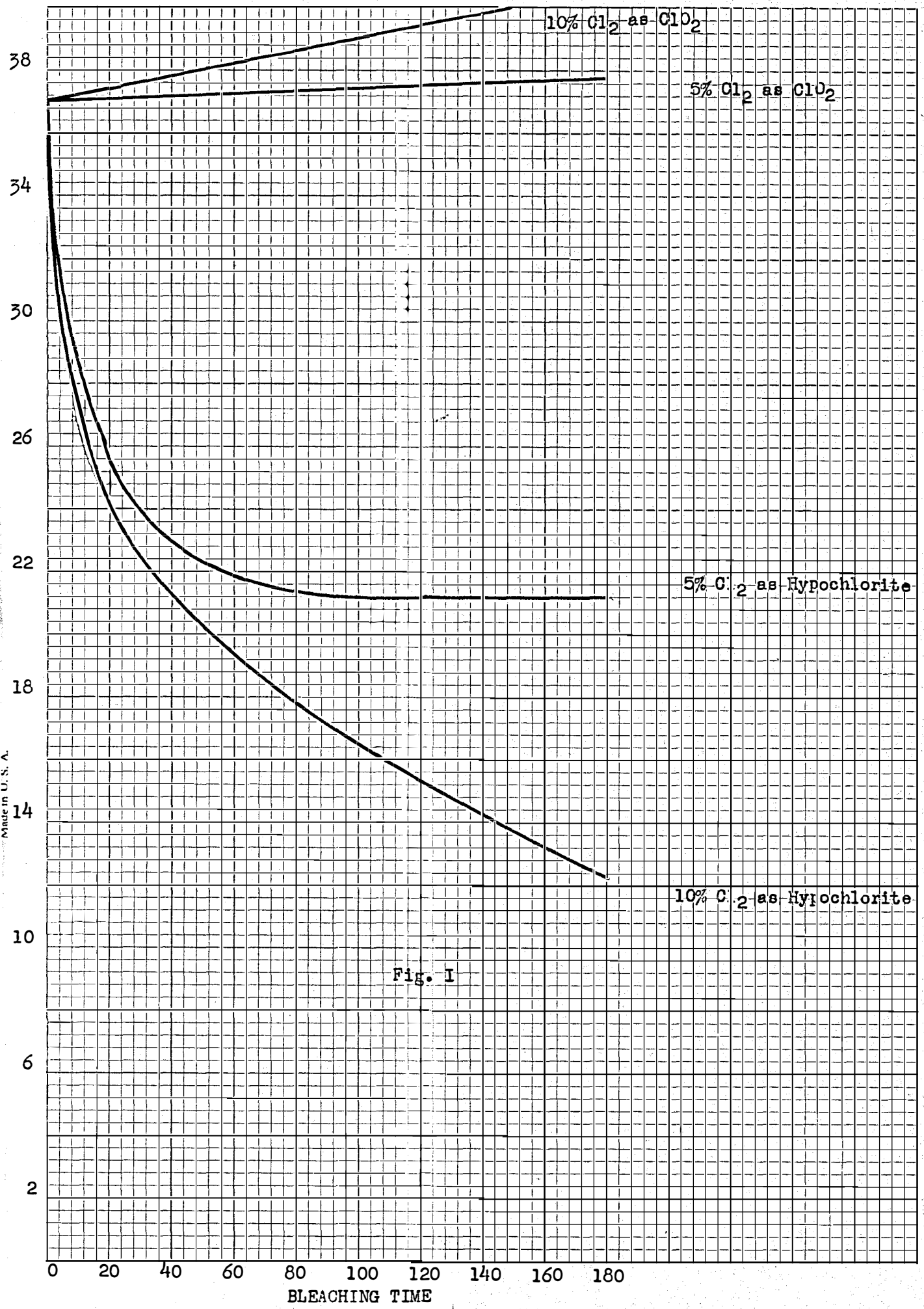


Fig. I

Made in U. S. A.

One new pulp was prepared as follows:

F- "C" bleache with 10% calcium hypochlorite at 110°F for 5 hours.

Sheets were made with "A", "B", "C", and "F" pulps and tested. Results are tabuated in Table IV.

Table III

Sheet	Pulps Used	Basis Wt.	Brightness	Mullen	Tear	Fold
1	A	39.2		27.0	57.3	95
2	B	40.7		34.2	43.2	278
3	C	44.6	53.0	19.9	51.1	20
4	D	44.6	71.0	20.2	48.0	17
5	E	44.8	74.5	20.1	41.6	15
6	50% A 50% B	38.2		30.8	48.1	146
7	40% A 60% C	46.6		26.8	62.3	66
8	40% A 60% D	46.6		27.5	60.0	55
9	40% A 60% E	45.0		26.4	51.2	57
10	40% B 60% C	46.6		28.0	54.5	67
11	40% B 60% D	46.2		28.8	52.8	75
12	40% B 60% E	46.2		28.2	48.0	95

Table IV

Sample	Pulps Used	Basis Wt. 25 x 38-500	Mullen	Tear Cor. to 45#	Fold
1	C	43.7	18.0	59.2	14
2	60% C 40% A	43.6	22.8	64.4	43
3	60% C 40% B	43.6	27.0	53.6	51
4	F	45.0	17.0	36.0	7
5	60% F 40% A	43.8	24.5	49.4	42
6	60% F 40% B	44.9	26.4	41.8	49

Fifth Experiment . So far the sheets have been made without first beating the paper stock. The following experiment was done to show the advantage of beating the paper stock before making sheets.

Four pulps were prepared as follows:

- B- 50% Kraft and 50% sulphite beaten to a C.S. freeness of 430.
- C- Unbleached paper stock.
- E- "C" bleached with 10% Cl_2 as $CaOCl_2$ at $110^{\circ}F$ for three hours.

Sheets were made using the above pulps. Also "C" and "E" were beaten in a valley beater for 15 minutes without the beater weights on, these pulps are C_1 and E_1 , and sheets made from these pulps. Tests results are tabulated in Table V.

Table V

Sample	Pulps Used	Basis Wt. 25 x 38-500	Mullen	Tear Cor. to 45#	Fold
1	C	45.6	18.2	53.8	9
2	E	44.0	17.1	37.7	3
3	C ₁	46.4	20.0	51.1	11
4	E ₁	44.6	16.0	35.5	5
5	50% B 50% C	48.0	29.0	66.0	55
6	50% B 50% E	46.5	29.0	62.0	36
7	50% B 50% C	47.0	30.0	65.0	58
8	50% B 50% E	47.0	30.0	54.2	53

Conclusion. If paper stock is bleached too hard with hypochlorite bleach, the strength of the paper stock can be considerably lowered. When the degraded paper stock is used to make paper, the finished paper will show a lower strength than if the paper stock has not been degraded.

This lowered strength of finished paper can be overcome by bleaching with chlorine dioxide. When the paper stock is bleached with chlorine dioxide, there is no decrease in the strength of the paper stock or the finished paper.

The amount of strength that can be saved with chlorine dioxide depends on the type of paper to be made and the quality of the deinked stock.

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