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## Some Effects in Chlorine Dioxide Purification of Kraft Softwood Cellulose

Maynard C. Nieboer  
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SOME EFFECTS IN CHLORINE  
DIOXIDE PURIFICATION OF  
KRAFT SOFTWOOD CELLULOSE.

SUBMITTED TO THE DEPARTMENT OF PAPER TECHNOLOGY,  
WESTERN MICHIGAN UNIVERSITY IN PARTIAL FULFILMENT  
OF THE BACHELOR OF SCIENCE DEGREE.

Maynard C. Nieboer  
June, 1957 ))

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## I N T R O D U C T I O N

Up until the middle thirties, chlorine dioxide had been considered an expensive bleaching agent and also had been too explosive to ship as a gas, so it had remained a laboratory curiosity since its discovery in the 19th century. In the middle thirties, Mathieson Chemical Corporation found that solid sodium chlorite was a cheap and effective carrier of chlorine dioxide. This discovery opened the door for extensive use of chlorine dioxide and since then it has come into its own as a bleaching agent. This investigation is concerned with the three methods of generation of chlorine dioxide from sodium chlorite and their effects upon softwood cellulose.

## H I S T O R I C A L   B A C K G R O U N D

### I. BRIEF HISTORY AND BACKGROUND OF CHLORINE DIOXIDE

The history of chlorine dioxide dates back to 1815 when it was discovered by Davy.(6) He produced chlorine dioxide in one of the basic reactions which is still used today, namely by pouring strong hydrochloric acid on a chlorate and liberating the gas. While largely a laboratory curiosity, it was still the subject of considerable research effort prior to the first work done on it in the United States. (4)

Between 1815 and 1921 much of this research work was done in improving the production of chlorine dioxide and determining its potential uses. Included in these experiments are recorded instances of attempts to bleach both fibrous and non-fibrous organic materials. The bleaching action of this compound was also demonstrated on vegetable coloring matters and other dyestuffs. Chlorine dioxide was also used to bleach indigo, litmus and other organic coloring agents. (4)

In 1921, Eric Schmidt, a German chemist, found that he could dissolve the lignin from the fibers

of wood without appreciably attacking the cellulose and hemicelluloses present.(6)

Schmidt realized that he had hit upon an effective method of bleaching pulp without causing severe degradation of the cellulose fibers. But chlorine dioxide was still not regarded as practical at this time for the following reasons: (1) it was very expensive and (2) it was and still is a somewhat dangerous chemical both in the gaseous and liquid states.

Due to the unstable nature of chlorine dioxide, it was felt that if a suitable form of the solid could be developed, there would be a rapid growth in the use of it as a bleaching agent for cellulose. (6)

In 1936, the Mathieson Chemical Corporation developed a process for manufacturing sodium chlorite as a solid carrier of the chlorine dioxide. In this process, pure chlorine dioxide gas is evolved from calcium chlorate and calcium chloride by hydrochloric acid. The chlorine dioxide is then reduced in an alkaline medium and sodium chlorite is the product. However this method proved very costly and several modifications and changes have been made to

make the process more economically feasible. The final system decided upon was a sodium chlorate and sulfuric acid generation of chlorine dioxide and the subsequent reduction to sodium chlorite. (6)

Along with this process, Mathieson has further shown that the use of chlorine dioxide liberated from sodium chlorite produces very similar bleaching effects to the effects produced by direct application of the gas.

The methods of producing chlorine dioxide from chlorites have significance because they have represented the most practical and convenient way of making chlorine dioxide available to the consumer. The large-scale use of chlorine dioxide in industry has lagged far behind the discovery of useful applications principally because of the high costs and practical difficulties involved in its preparation directly from chlorate. However, the previously mentioned Mathieson process has provided industry with a source of chlorine dioxide in a convenient form, and yet, in spite of much work and experiment, high cost is the biggest drawback to the use of chlorine dioxide.

## II. THE PROPERTIES OF CHLORINE DIOXIDE (1)

Chlorine dioxide is a gas of yellowish or orange color and very closely resembles chlorine in many respects. It has the same density as chlorine and has a very similar odor differing only in the fact that it is more pungent.

The effect of chlorine dioxide and chlorine are very similar on the human breathing mechanism. However, chlorine dioxide has the extra effect of causing violent headaches and general fatigue which last for several days. Therefore the toxic qualities of the gas have to be carefully considered when industrial use is being contemplated.

Chlorine dioxide is very soluble in water and aqueous solution of various salts. In this respect, it surpasses chlorine and at equal temperatures water may contain five times as much dioxide as chlorine. This solubility differential, thus provides a convenient method of separating these similar compounds.

Another important characteristic of chlorine dioxide is that it does not react chemically with



water even though it is so soluble. It is possible to expel the dioxide from an aqueous solution just by blowing air through it. As the gas escapes, the original yellow of the solution fades and it finally becomes colorless. If this colorless residue of water is analyzed, it is found that the solution is very weakly acid, indicating that only negligible amounts of chloric acid have been formed. From these facts we can conclude that chlorine dioxide is dissolved in water as such, without chemically reacting with it.

In spite of the easy removal of chlorine dioxide by air under pressure, an aqueous solution can be stored in the dark for weeks and months without losing strength.

The most obvious as well as dangerous characteristic of chlorine dioxide is its explosiveness. Many people, through bitter experience have found that it explodes when its temperature is being raised, or when it comes into contact with organic substances or upon exposure to light.

This inclination to blow up at the slightest provocation is still greater in the liquid state. Cases have been cited where the mere transfer from one container to another causes an explosion. The violence of these blow-ups is very similar to the power expended in the explosion of oxygen-hydrogen mixtures and the effect of liquid chlorine dioxide explosions is comparable to that of our strongest chlorate explosives.

It is known that the explosiveness of the gas is greatly diminished when it is mixed with inert gases. If, for instance, air, nitrogen, or carbon dioxide is added as a diluting agent to the extent of 90 per cent of the mixture, the  $\text{ClO}_2$  is no longer dangerous and does not react to limited temperature increases. If the chlorine dioxide percentage is still further reduced, explosions no longer happen and only gradual decomposition into chlorine and oxygen takes place in an exothermic reaction. At lower partial pressures, even this decomposition is limited.

The chemical reactivity of chlorine dioxide is very great with all known compounds and particularly with reducing agents. Therefore, it is easy to reduce it with carbon, sulfur, sulfur dioxide, hydrogen peroxide and such metals which are able to form different levels of oxides, such as nickel, chromium, manganese, lead and iron. They all reduce chlorine dioxide either to the level of chlorite or chloride, depending on the reaction conditions.

Chlorine dioxide, as a gas and in water solution is strongly oxidizing and therefore extremely corrosive.

Carbohydrates such as wood, cellulose, and pulp are also reducing agents, but of rather low reactivity, and for this reason chlorine dioxide may be used in pulp bleaching.

The most important property of chlorine dioxide as far as bleaching of cellulose is concerned is its high state of oxidation, but relatively low oxidation potential. This characteristic enables chlorine dioxide to effectively remove lignin and bleach coloring matter and yet not appreciably harm the cellulose fibers.

Thinking in terms of available chlorine as the hypochlorous acid produced in an aqueous solution and the hypochlorous acid as containing one available oxygen, we can see that  $\text{Cl}_2$  is equivalent to one oxygen ( $\text{Cl}_2 \nearrow \text{H}_2\text{O} \text{ -- } \text{HOCl} \nearrow \text{HCl}$ ). Using this as a base of comparison, we can show that chlorine dioxide has the highest theoretical state of oxidation of the following compounds in water solution:

- |  |                                      |
|--|--------------------------------------|
| (1) $\text{Cl}_2 \nearrow \text{H}_2\text{O} \text{ -- } \text{HOCl} \nearrow \text{HCl}$        | $\text{Cl}_2 \equiv \text{O}_1$      |
| (2) $\text{NaOCl} \nearrow \text{H}_2\text{O} \text{ -- } \text{NaCl} \nearrow \text{O}_1$       | $\text{NaOCl} \equiv \text{O}_1$     |
| (3) $\text{Ca(OCl)}_2 \nearrow \text{H}_2\text{O} \text{ -- } \text{CaCl}_2 \nearrow \text{O}_2$ | $\text{Ca(OCl)}_2 \equiv \text{O}_2$ |
| (4) $\text{NaClO}_2 \nearrow \text{H}_2\text{O} \text{ -- } \text{NaCl} \nearrow \text{O}_2$     | $\text{NaClO}_2 \equiv \text{O}_2$   |
| (5) $\text{ClO}_2 \nearrow \text{H}_2\text{O} \text{ -- } \text{Cl}^- \nearrow \text{O}_2$       | $\text{ClO}_2 \equiv \text{O}_{5/2}$ |

## Safety Precautions and Corrosion Resistant Containers (6)

Taking advantage of chlorine dioxide's low explosion potential in very dilute form, it is always manufactured in dilute form and shipped entirely as solid sodium chlorite.

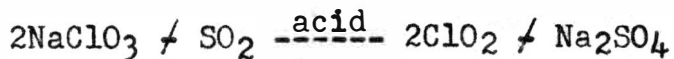
For industrial purposes the gas is applied in harmless aqueous solutions, and in manufacture, exposure to light and elevated temperatures must be excluded.

It must never be allowed to come into contact with oil, fat, coal, sulfur, rubber or any similar material.

The choice of materials which may be used in contact with chlorine dioxide is further limited by its extreme corrosiveness in aqueous solution. In fact, so far only ceramic products like glass, porcelain, or stoneware have proven entirely resistant. Good experience has been obtained with polyvinyl chloride, but only in its pure form, which means that no fillers or plasticizers should be present. Rubber in any form is impossible. Practically all metals are attacked and only platinum and tantalum are sufficiently resistant. In addition iron silica alloys with high silica content have proven useful.

### III. METHODS FOR PREPARATION OF CHLORINE DIOXIDE

#### A. The Holst Process (9)

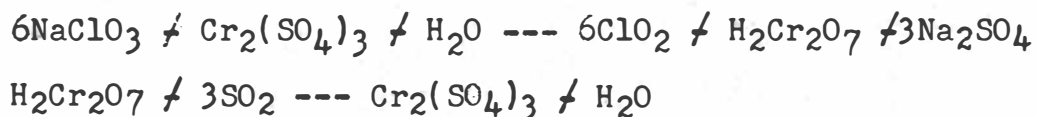


This method was invented by Gustov Holst, and has been in commercial use at Husum, Sweden for the bleaching of kraft pulp since 1946.

Production is normally on a batch basis, although continuous gas flow can be effected by use of a spare reactor. The acid sludge may be used for tall oil recovery in such mills that carry out this operation, otherwise it is normally wasted, and sulphuric acid is in either case one of the raw materials.

Sulfur dioxide gas from a burner is mixed with air in such proportions that the  $\text{ClO}_2$  - air mixture leaving the reactor is, within range, considered safe. The chlorine dioxide is then removed from the mixture by absorption in water. Less than one percent chlorine dioxide loss from the absorption tower is claimed when the  $\text{ClO}_2$  solution contains 16 - 17 grams/liter available chlorine. The yield is about 80 - 85 per cent  $\text{ClO}_2$  based on the chlorate.

B. The S. H. Persson Process (9)

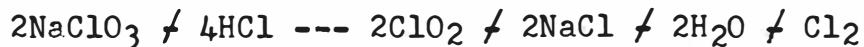


This process is in commercial use at the Stora mill in Sweden. The chief difference from the Holst process is the use of a reduction moderator, the chromium salt which is claimed to give a better  $\text{ClO}_2$  yield than when  $\text{SO}_2$  is used as a direct reducer for the chlorate.  $\text{SO}_2$  is then used to reduce the chromium.

The system may be operated batch or as a continuous process. No acid make-up is needed, and control of conditions can keep chromium sale losses low.

Glauber's salt is recovered as a by-product and is used in the mill recovery system.  $\text{ClO}_2$  gas is absorbed in water to a concentration of about 14 grams/liter available chlorine. Chlorine dioxide yields on chlorate are 90 - 95 per cent. Both the Holst and Persson process are relatively free of chlorine.

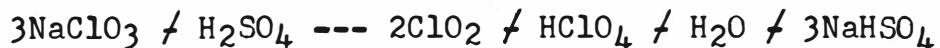
C. Hydrochloric acid reduction of chlorate (9)



Many variations of hydrochloric acid reduction have been reported, but the reaction above is economically attractive by carrying the reaction only part way to completion. It is particularly attractive to mills operating their own chlorine plant. Chlorine and hydrogen are burned and the resultant gaseous HCl mixed with air is reacted with sodium chlorate. Chlorine dioxide and chlorine gas are evolved. The two gases are separated by utilizing chlorine dioxide's greater water solubility. The amount of the chlorine in the water is used right along with the chlorine dioxide.

The yield on chlorate basis is maintained below 50 per cent. Raw material costs are low due to the recirculation of the chlorate and the claim is that savings up to 40 per cent are made over the Holst process.

D. Reduction by concentrated sulfuric acid. (3)



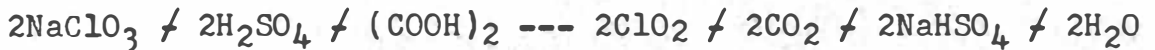
This reaction generates heat and there is considerable danger of explosion. The reaction is



carried out with greater safety if sodium bisulfate is substituted for the sulfuric acid and a means for disposing of the ClO<sub>2</sub> as it is evolved.

Even if the danger of explosion can be avoided, the process would not normally be commercially possible because of the high chlorate requirement per unit of chlorine dioxide consumed (for every one chlorate used only 2/3 of a ClO<sub>2</sub> is formed).

E. Reduction by oxalic acid (3)



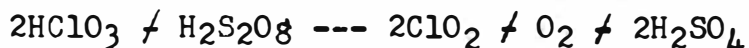
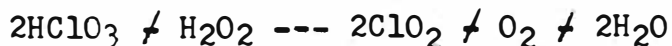
This is the common laboratory method for preparation of chlorine dioxide and it consists of gently heating a mixture of powdered chlorate and oxalic acid.

The carbon dioxide generated along with the chlorine dioxide greatly minimized the chance of explosion. By acidifying with sulfuric acid the consumption of oxalic acid is reduced.

Formic acid, calcium formate or formaldehyde may be used in place of oxalic acid. But from a commercial standpoint, these methods all have the disadvantage of requiring the use of a relatively expensive reducing agent.

F. Reduction by per-compounds (3)

The production of chlorine dioxide by the action of peracids, persalts or peroxides was first disclosed in 1942 by a German firm. In 1943, patents on basically the same process were issued in the United States covering, in one case the use of hydrogen peroxide and in the other persulfates.



Chlorine dioxide produced by this type of reaction is said to be free from chlorine. From the practical standpoint, processes of this kind would not seem feasible because of the high cost of per-compounds.

#### IV. Advantages of Chlorine Dioxide

The oxidation potential of chlorine dioxide is such that the non-cellulose materials are attacked while the cellulose remains unchanged over wide ranges of bleaching conditions.(9) The main advantage of using chlorine dioxide as a bleaching agent for pulp is derived from this selective action of the compound.

On the other hand, the hypochlorite ion is not selective in its attack on the pulp fibers. And as the non-cellulosic content of the pulp diminishes, it becomes impossible to remove all of it without breaking the cellulose chains and losing a sizable amount of the pulp. (9)

Many other benefits are derived from bleaching with chlorine dioxide. A higher brightness can be obtained without the accompanying loss of strength found in hypochlorite bleaching. The alpha cellulose content is raised due to the removal of impurities without attack on the cellulose. Strength development

is attained with a shorter beating time and in some cases there is better brightness stability and an increased yield.

In combination with other stages, proper placement of chlorine dioxide treatments will result in a whiter pulp than can be made by any other commercial bleaching agent. And with chlorine dioxide, certain levels of brightness can be reached with fewer stages of bleaching than with hypochlorite.(5)

Chlorine dioxide can be used in a very wide range of conditions, low temperature, relatively high temperatures and in acid, neutral and basic solutions. However there is a maximum and minimum p H range which must be used to maintain the selective action of chlorine dioxide. Below p H of nine and above p H of two there is little damage to the cellulose. As the p H rises above nine or falls below two, the rate of reaction is very fast and the damage to the cellulose becomes serious.(5) However, this p H range is wide enough not to cause trouble in controlling the conditions during a bleaching operation.

## V. Application of Chlorine Dioxide to Pulp

The application of chlorine dioxide to kraft and sulfite pulps has been largely confined to the final stage of a multistage bleach system. So far, the most widely accepted practice has been the application in a final acid bleaching stage.(6) However, in the use of chlorine dioxide for sulfate bleaching, several factors must be considered. If only light pre-treatment has been given to the pulp, it is sometimes found necessary to apply chlorine dioxide in two stages, separated by a caustic extraction;(9) because it has been shown any distribution of chlorine dioxide between two stages is superior to the application of all the chlorine dioxide in one stage.(7) But on the other hand, it may be possible to use extensive hypochlorite bleaching and then give a final chlorine dioxide treatment to the desired brightness without substantial cellulose degradation. In any manner, the pulp characteristics, quality demands and economics of the various methods will determine the sequence of operations.(9) In any

order that it is used, chlorine dioxide bleaching permits the use of less hypochlorite in preceding or succeeding stages, thus preserving a greater proportion of the unbleached strength. (7)

Bleaching with mixed gases, that is chlorine dioxide and chlorine, has proven at least as effective as the application of chlorine dioxide alone in giving high brightness levels with substantially no strength loss. Preliminary laboratory work also indicates that in addition to its use as a final stage treatment, mixed gas bleaching may be applied following a conventional chlorination and caustic extraction stage. This would obviously reduce the number of operations required, thus simplifying bleaching procedures and effecting operating economies.(8)

Mathieson Chemical Company has shown that activation of sodium chlorite by various means produces chlorine dioxide which bleaches to results very comparable to the results obtained in direct application of the gas.(2) There are three important methods for evolving chlorine dioxide from chlorite.

When it is activated by the action of chlorine on chlorite, it is customary to add excess chlorine.(9) And the results are similar to bleaching with mixed chlorine and chlorine dioxide. When hypochlorite is used for activation of chlorine dioxide, the chlorite solution is usually mixed with stock before the hypochlorite is added. Pulps bleached in this way have characteristics of chlorine dioxide pulps rather than hypochlorite pulps.(9) Bleaching with acid activation of chlorite is carried out much the same as when chlorine dioxide solution is used in acid medium, presenting the same corrosion problems (9) and producing very similar bleaching results.

L I T E R A T U R E   C I T E D

- (1) Manufacture and Properties of ClO<sub>2</sub>  
Pulp and Paper Magazine of Canada  
Volume 53, No. 8, Pages 99-104
- (2) Technical Production of ClO<sub>2</sub>  
Paper Trade Journal, Volume 128  
January 6, 1949, Page 21
- (3) The Preparation of ClO<sub>2</sub>  
Paper Trade Journal, Volume 135, No. 10  
Page 22
- (4) Uses of ClO<sub>2</sub> and Chlorites in Pulp and Paper  
Ferri Cascioni, Niagra Alkali Company  
Paper Trade Journal, Volume 136, No. 10  
Pages 21-25
- (5) Ultra-High density Bleaching of Chemical Pulp  
by W. Howard Rapson  
Paper Mill News, Volume 77, No 34 Pages 15-18
- (6) ClO<sub>2</sub> for Pulp Bleaching by Vernon Woodside and  
K. S. Mac Leod  
Paper Trade Journal, Volume 137, No. 8, Pages 26-31
- (7) A comparison of Bleaching Agents for Kraft Pulp  
by R. L. Miller, R. A. Dando and R. P. Hamilton  
Tappi, November 1956, Pages 826-829
- (8) Bleaching Pulp with mixture of Chlorine Dioxide  
and Chlorine. By G. P. Vincent  
Paper Trade Journal, Volume 124, No. 26 Pages 53-55
- (9) Chlorine Dioxide Bleaching of Kraft Pulp  
By D. M. Reid  
Pulp and Paper Magazine of Canada, Volume 52  
October, Pages 112-112



## EXPERIMENTAL PROCEDURE

This experiment was conducted with unbleached, softwood kraft pulp having a permanganate number of 24.

The first step in the procedure included two direct chlorinations with a water wash between. The first chlorination was for 45 minutes at five per cent available chlorine, three per cent consistency and 20° C.

The second chlorination consisted of two per cent available chlorine for 45 minutes at 20° C.

This pulp was given a hot caustic extraction. The retention time was 90 minutes in two per cent caustic soda at 55 - 60° C. The pulp was washed in hot water, dewatered and air dried for storage purposes.

The permanganate number of this pulp was six.

The chlorinated and caustic extracted pulp was analyzed for alpha cellulose content, one per cent caustic solubility and cupraethylenediamine viscosity.

Handsheets were made from pulp refined in a Waring Blendor for four minutes. The handsheets were tested for burst and tearing resistance.

A series of four bleaches were made on separate samples of the chlorinated and caustic extracted pulp, one with calcium hypochlorite, and three with chlorine dioxide. The chlorine dioxide was generated from sodium chlorite by three methods: (1) sulfuric acid (2) chlorine gas and (3) sodium hypochlorite.

The bleaching conditions of these four treatments were held constant. The bleaches were made at five per cent consistency, five per cent available chlorine and in the temperature range of 40 -50° C. The calcium hypochlorite bleach was made at 40 -45° C. The retention time was 90 minutes in each case.

The final experimental bleach was a combination of calcium hypochlorite in a third stage and chlorine dioxide generated from sodium chlorite by sodium hypochlorite in a fourth stage.

The calcium hypochlorite stage was at two per cent available chlorine, five per cent consistency and in the temperature range 45 - 50° C. The retention time in each stage was 45 minutes.

The pulps bleached by these five different methods were analyzed and evaluated in the same manner as the chlorinated and caustic extracted pulp.

The alpha cellulose content of the pulps was determined according to TAPPI Standards T203m - 55. The one per cent caustic solubility was made according to T212m - 54. The handsheets for burst and tear tests were made in the British sheet mold after refining in the Waring Blendor.

The brightness of the handsheets was determined by the Photovolt Brightness tester.

The cupraethylenediamine viscosity was performed according to T230 SM - 46 using the viscosity pipette method. The pipettes were calibrated according to ASTM specifications. ASTM constants and calculation methods were used.

T A B L E I R E S U L T S

Treatment	Initial p H	Viscosity	% alpha Cellulose	1% Causti solubility	Brightness	tear	mullen
chlorination- caustic ext.	--	14.6 cp	89.6%	2.5%	29	173	27
Ca(OCl) <sub>2</sub>	8.5	4.1 cp	85.1%	7.8%	78	140	22
ClO <sub>2</sub> activated by H <sub>2</sub> SO <sub>4</sub>	1.9	9.6 cp	88.3%	2.6%	67	149	22
ClO <sub>2</sub> activated by NaOCl	9.4	8.6 cp	88.1%	2.6%	78	150	19
ClO <sub>2</sub> activated by chlorine	6.8	12.7 cp	89.3%	2.9%	73	157	21
hypochlorite bleach							
ClO <sub>2</sub> activated by NaOCl	8.9	7.7 cp	86.8%	4.0%	83	160	23

GRAPH NO. 1

% SOLUBLE IN 17.5% CAUSTIC SODA

% ALPHA CELLULOSE

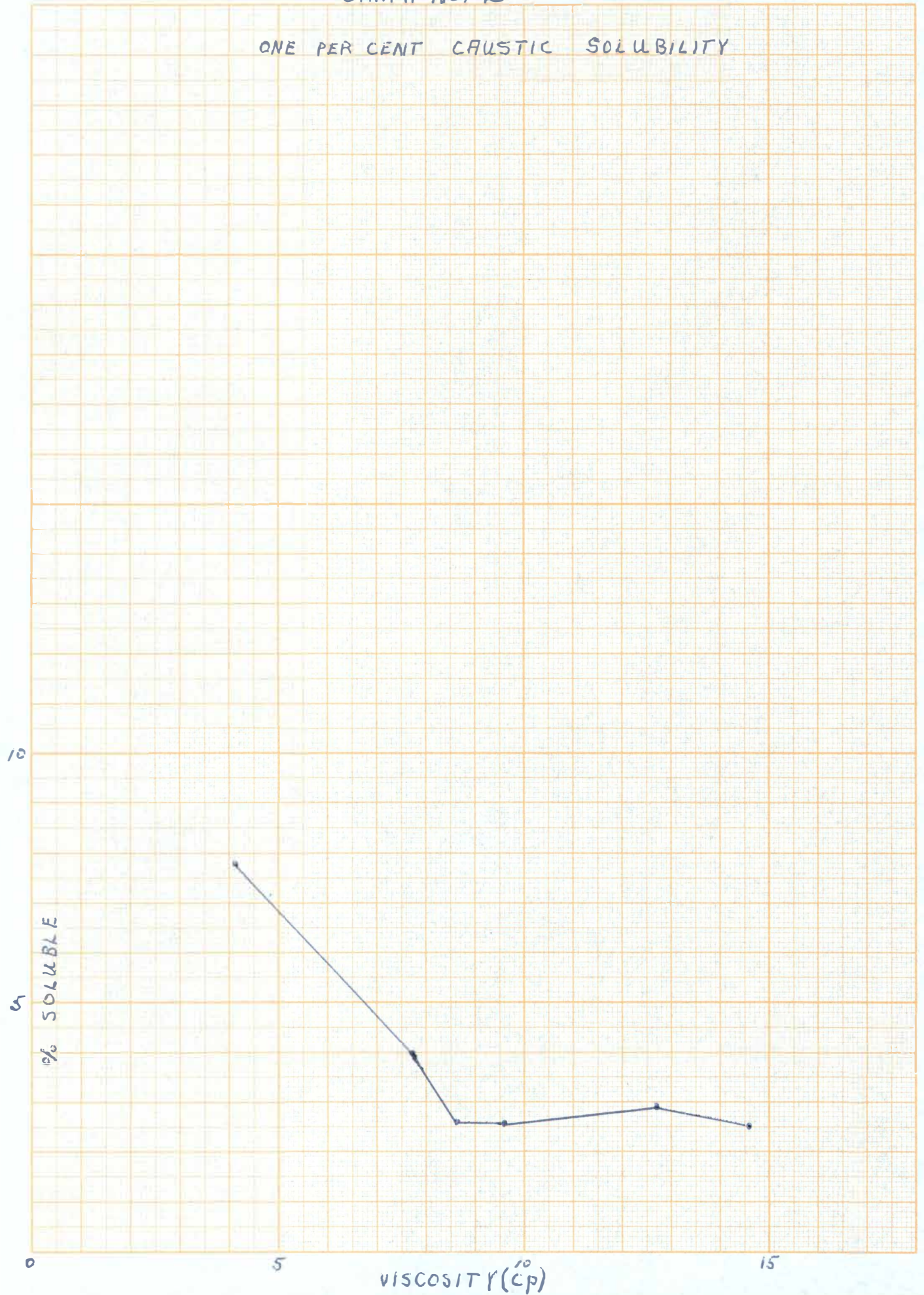
VISCOSITY (CP)





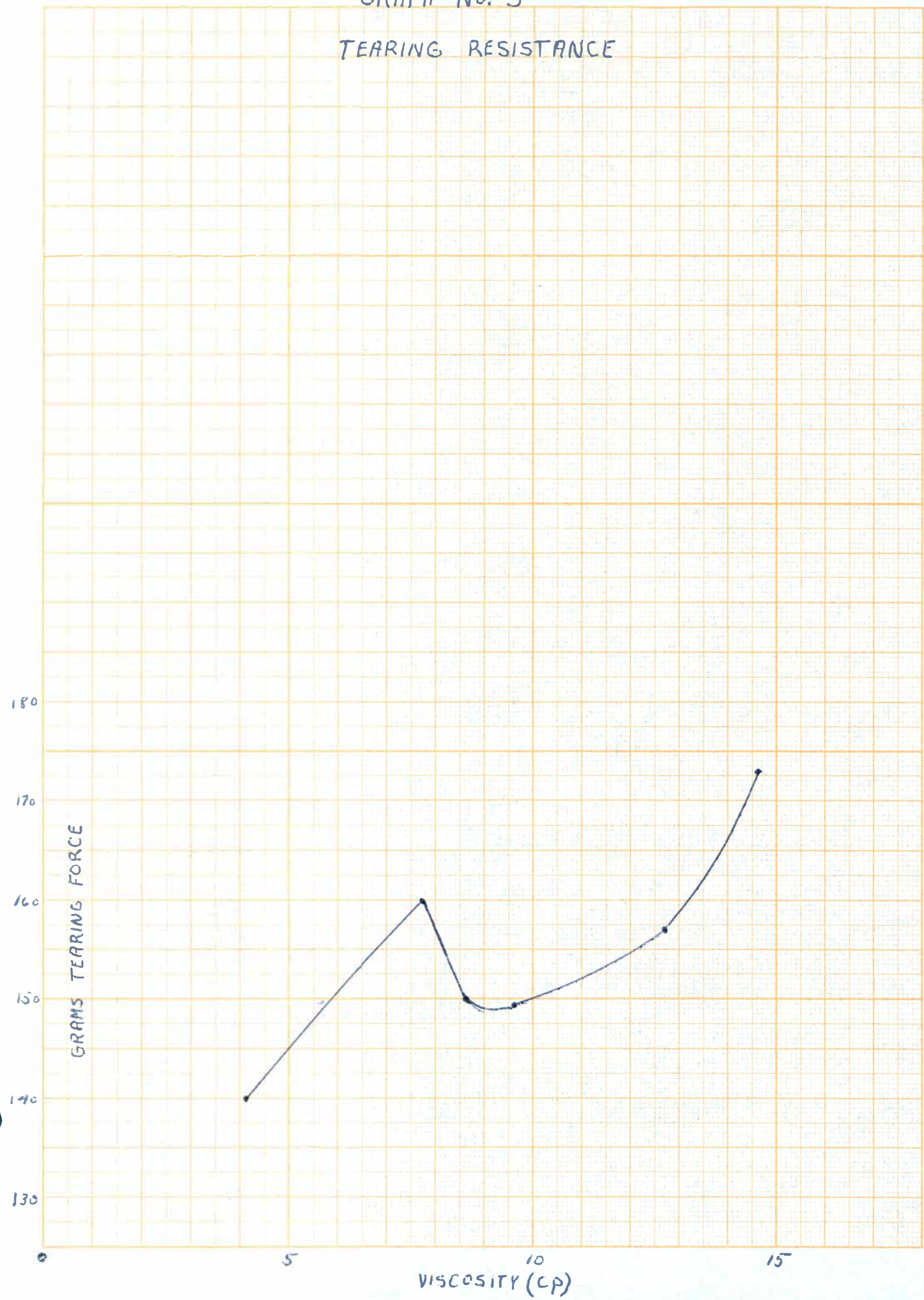
# GRAPH NO. 2

## ONE PER CENT CAUSTIC SOLUBILITY





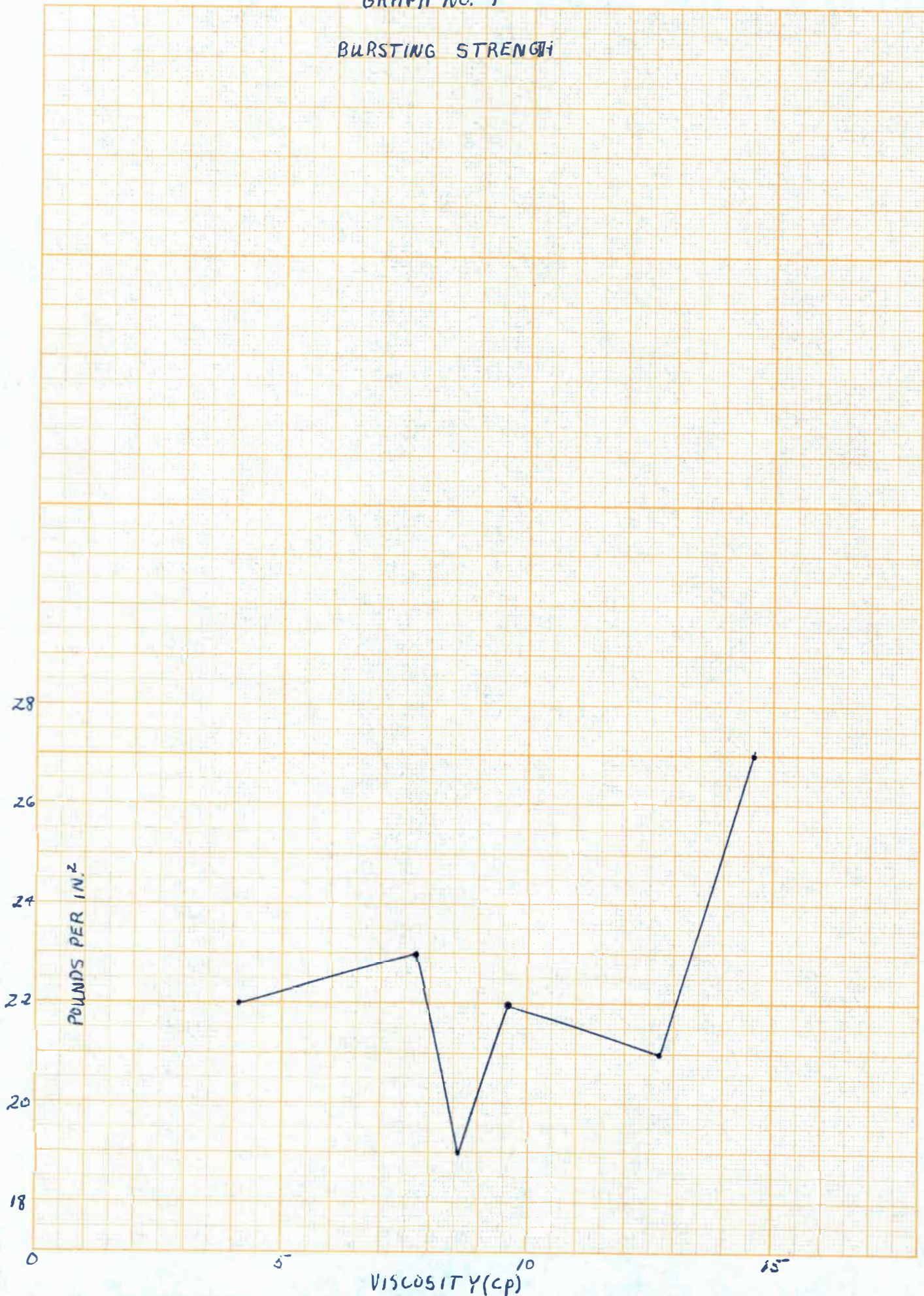
GRAPH NO. 3  
TEARING RESISTANCE





GRAPH No. 4

BURSTING STRENGTH





## E V A L U A T I O N

Results -- The results showed that the calcium hypochlorite bleached pulp, as would be expected, had a large drop in viscosity, in alpha cellulose content and a high increase in one per cent caustic solubility when compared with the chlorinated pulp.

The pulp purified with sulfuric acid activated sodium chlorite showed a viscosity drop of approximately one third the unbleached value with relatively little increase in one per cent caustic solubility and a very slight decrease in alpha cellulose content.

The pulp purified with sodium hypochlorite activated sodium chlorite showed a viscosity decrease of a little less than half the value of the unbleached with relatively little increase in caustic solubility and a small decrease in alpha cellulose content.

The multistage system, hypochlorite and sodium chlorite, showed a viscosity drop of about half the value of the unbleached with an increase in one per cent caustic solubility and a decrease in alpha cellulose content but at a brightness level of 83%.

The strength test could not be directly correlated with the chemical tests. Perhaps the variation was due to the error present in small quantity refining in a condition where the conventional beater method was replaced by a Waring Blendor.

Discussion -- The chlorine activated  $\text{ClO}_2$  bleach showed the least degradation because the pH of the solution was in an ideal position to prevent degradation. The range for no degradation with  $\text{ClO}_2$  ranges between two and nine. The acid activation bleach showed low brightness and more degradation because the pH of the solution was below the safe value.

Severe degradation took place in the  $\text{Ca}(\text{OCl})_2$  bleach because the pH dropped from an initial 8.5 toward the neutral point and the danger zone for  $\text{Ca}(\text{OCl})_2$ .

The strength test did not give much of an indication of the relative strengths of the pulp or reflect the degradation. The general trend of the strength tests just indicated that the strength went down when the last bleaching stages were performed

on the chlorinated pulp and that the hypochlorite bleached pulp was the weakest.

The two stage bleaching system showed satisfactory results in both brightness and degradation effects. The viscosity was slightly less than double the viscosity of the  $\text{Ca}(\text{OCl})_2$  pulp. However the alpha cellulose content and 1% caustic solubility indicated that there was a considerable amount of oxidation and formation of carboxyl groups but not enough to shorten the chains too severely.

Conclusions -- In evaluating these results, we find that they agree with the known fact that calcium hypochlorite harms the cellulose molecule more than chlorine dioxide.

Under the given conditions, chlorine gas activated sodium chlorite does less harm to the fibers than acid or hypochlorite activated sodium chlorite.

The p H of chlorine dioxide bleach liquor is instrumental in controlling the selective action of the gas on the fibers.

And finally less degradation will occur on a high brightness level when calcium hypochlorite is used in combination with chlorine dioxide generated from sodium chlorite.