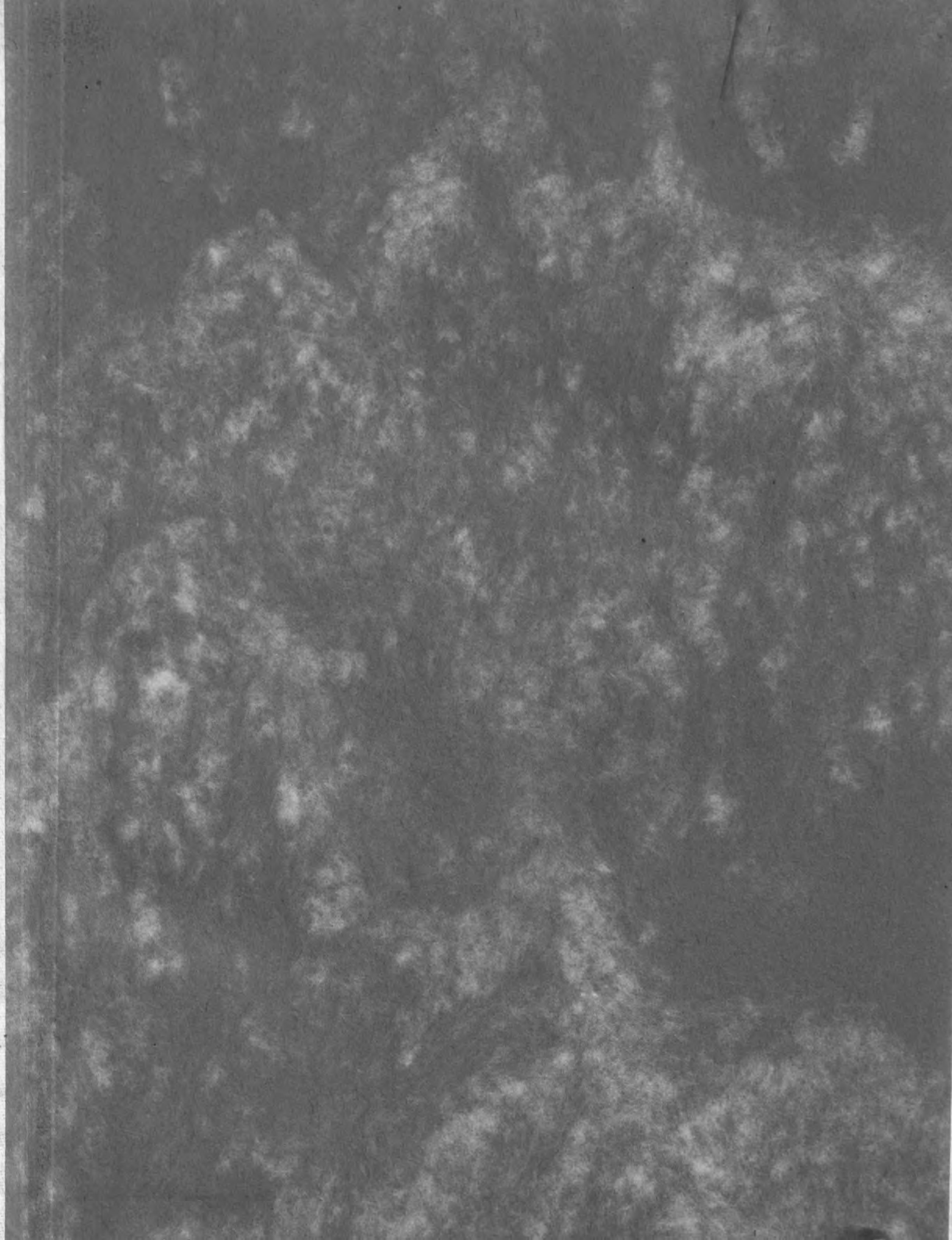
A STUDY OF THE PROGRESSIVE OXIDATION OF CELLULOSE

Thesis for the Degree of M. S.

MICHIGAN STATE COLLEGE

John D. Bartleson

1939



A STUDY OF THE PROGRESSIVE OXIDATION OF CELLULOSE

A Dissertation

Submitted to the Faculty

of

Michigan State College

of Agriculture and Applied Science

In partial fulfillment of the Requirements

for the degree of Master of Science

by

John David Bartleson

1939

ACKNOWLEDGMENT

To Prof. B. E. Hartsuch, the writer wishes to acknowledge his appreciation for the guidance and helpful suggestions which have made possible completion of this work.

Contents

Introduction

A. Purpose of the Work

In spite of the enormous amount of research which has been devoted to cellulose, many of its chemical reactions are not understood. very little is known of its degradation, either hydrolytic or oxidative. much of the study of cellulose has been carried out in the field of textiles. the greater part of this work has been done in a qualitative manner and its object has been to find simple tests which could be used to differentiate among the various modifications of cellulose. various tests have been developed which show the difference between normal cellulose and oxidized cellulose. Since these tests have been intended solely for application to commercial materials a great part of the research work has been done from the industrial rather than from the scientific viewpoint.

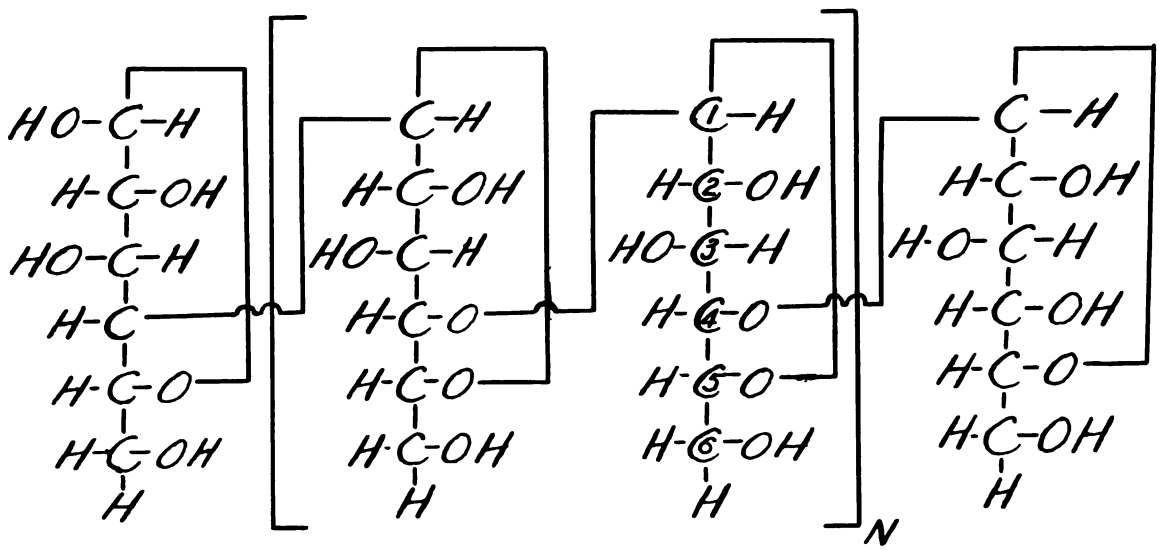
In the last few years some of these qualitative tests have been refined and developed into quantitative measurements and there have been several investigations in which these quantitative measurements have been used to follow the chemical degradation of cellulose. Their object has been the attainment of a better understanding of the chemical nature of cellulose. Unfortunately a large amount of this study has been poorly organized and has not been carried out along scientific lines. In many instances the workers have failed to state the conditions under which their research has been done and their procedures often lack many details which are necessary for a thorough understanding of their work. In these cases the results are meaningless.

The study of the oxidation of cellulose has had a gradual evolution beginning with the preparation of oxycelluloses. These oxycellulose preparations were thought to be chemical compounds by the pioneers of cellulose chemistry, each worker having his own oxycellulose and each oxycellulose having its own molecular formula. With a better understanding of the nature of oxycellulose came the realization that the oxidation of cellulose is a gradual process and that no single, isolatable oxycellulose is formed during this process. In recent years several studies have been made on the progressive oxidation of cellulose. These studies have differed in the care with which the conditions have been controlled and in the variables which have been used during the oxidations. Some of the possible variables are the nature of the oxidant employed, the strength of the oxidizing solution, the pH of this solution and the temperature at which the oxidations are carried out. The present work differs from previous work in the variable which was chosen; in the present work time is the variable.

The purpose of the present work is to make a study of the progressive oxidation of purified cotton cellulose under carefully controlled conditions and to analyze the oxidized cotton residues.

B. Nature of the Work

The structure of cellulose has been the subject of much controversy since Tollens postulated the first hypothetical formula in 1895. In the last fifty years many formulas for cellulose have been proposed, accepted and later discarded. At the present time cellulose is regarded as a chain in which a large number of cellobiose units are linked together through the one and four positions by glucosidal linkages. It is assumed that the chain is open, which means that there is no linking between the two terminal units, the first unit having a free hydroxyl in the four-position and the end unit a free hydroxyl in the one-position. The accepted formula is:



The molecular weight of cellulose is not definitely settled. Several molecular weights have been suggested depending upon the method used and the past history of the cellulose preparation used. Haworth and Machemer (1), using chemical methods, have calculated it to consist of not fewer than 100 and not more than 200 glucose units, and they regard this size to be the average lower limit of the cellulose molecule; the corresponding molecular weight of the cellulose would be between 20,000 and 40,000. The osmotic pressure method, a physicochemical method, indicates molecular

weights which range between 25,000 and 100,000 (between 155 and 600 glucose units), depending upon the degree of depolymerization through which the various preparations have passed. The most recent and most accepted method is the Svedberg ultra centrifugal method which has proved so valuable in protein chemistry. It is based upon photographic observations and records of equilibrium or velocity of sedimentation in a strong centrifugal field. The values found are much higher than those obtained with the other methods. The following figures are given: 570,000 for native cellulose (corresponding to 3,600 glucose units); 150,000 to 500,000 for purified cellulose and 50,000 to 120,000 for regenerated cellulose.

X-ray analysis has furnished definite proof of the crystalline nature of cellulose. The lattice on which the cellulose crystal is built is of the monoclinic system and there is one cellobiose unit (corresponding to two glucose units) in the unit cell. The constituent units are arranged in continuous chains which run parallel to the fiber axis through the unit cell. The glucose to glucose horizontal linkages are held together by primary valence forces while the position of the chains with respect to each other is stabilized by secondary valence forces. The cellulose crystallite or micelle, the smallest visible microscopic unit, is made up of a few chains gathered into a long, thin bundle. A micelle contains approximately 2,000 glucose units and assuming the chain to contain 200 glucose units, one micelle would comprise ten chains. The micelles are oriented parallel to the fiber axis, and in cotton are turned spirally around the axis. This orientation is directly related to the strength of the fibers. These micelles are held together by tertiary, micellar or "supermolecular" forces.

This structure explains a number of the physical phenomena exhibited by cellulose. It accounts, for instance, for the swelling in water or in other liquids not attacking the cellulose chemically. This swelling is small in the longitudinal direction.of the chains since there is apparently no opportunity for the molecules of these liquids to penetrate between the single units of the chain. In the lateral direction, however, molecules of the liquid find sufficient space to enter and in so doing widen the space still further. This theory is in agreement with the X-ray pattern of swollen (mercerized) cellulose. (The author is indebted to "Organic Chemistry" by Gilman, Volume II (1534-1595) for parts of this section; a much more thorough discussion, together with complete references, may be found there.)

These structural principles are important in the present work, in which all of the oxidation reactions were carried out in a two-phase system (liquid, solid); i.e., oxidizing solution and solid cellulose. The oxidizing solution could penetrate between the chains but not between the single units of the chains. Another method of attack for this problem would have been to dissolve the cellulose in some medium such as cupric ammonium hydroxide solution, and thus the cellulose would have been attacked in a homogeneous one-phase system; however, in this system the micellar orientation is lost and true cellulose is no longer present. Proof of this loss in micellar orientation is found in the regeneration of cellulose from the cupric ammonium hydroxide solution. The regenerated product is similar to cellulose in many respects, but has a decreased tensile strength and a lower average molecular weight.

Cellulose undergoes two types of chemical degradation; namely, hydrolytic and oxidative. Hydrolytic degradation is brought about by

the action of acids while oxidizing agents are responsible for the oxidative type. The products formed by hydrolytic degradation are usually referred to as "hydrocellulose", and the products of oxidation are termed "oxycellulose"; these are general names and their meaning is not well defined.

The first stages in any degradation of cellulose or its derivatives consists in the weakening of the supermolecular forces which hold the micelles together and in the further breakdown of the secondary valence bonds converting the micelles to their constituent chains of cellobiose molecules. It can be seen from the foregoing why in the initial stages of the formation of oxy- and hydrocelluloses, the products obtained are similar in properties; at the same time it must be realized that such a procedure must of necessity give rise to a mixture of degradation products. Thomas (2) believes that it is the end groups of these chains which are of primary importance in determining the properties of the degradation products, and he states that it is there that the difference between oxy- and hydrocellulose is to be found.

The next stage in the formation of oxycelluloses and hydrocelluloses will therefore be an attack on the end glucose units of the chain. Thomas considers that it is possible that in the formation of hydrocelluloses the six membered rings of the end glucose units are opened to give the active reducing aldehyde form, while in the formation of oxycelluloses some or all of the exposed aldehyde groups are oxidized to carboxyl groups. It is also probable that the CH_2OH group at position number six in the glucose molecule is oxidized to an aldehyde or carboxyl group. Since there are many of these CH_2OH groups in the molecular chain, there is considerable opportunity for the formation of these groups. During

degradation further "cracking" may also occur, thus yielding shorter chains and exposing more terminal glucose units with their oxidizable aldehyde groups.

Therefore it is considered that material produced by treatment of cellulose with acid contains free aldehyde groups in its structure and corresponds to the so-called hydrocellulose, while that prepared by a mild oxidation using either an acid or alkaline oxidizing agent contains both carboxyland aldehyde groups, the carboxyl groups most probably being at the terminal position in the chain of glucose units, and corresponds to the so-called "oxycellulose." A chemical investigation of these materials is dependent upon the presence and relative amounts of these aldehyde and carboxyl groups in the molecules of the degraded cellulose. However carefully the conditions are controlled during the preparation of these materials, it cannot be conceived that the macromolecules will break down into molecular chains which are exactly equal in length.

The properties of oxy- and hydrocellulose, which are very similar, are in agreement with the structural facts which have just been discussed. As a result of the micellar breakdown the degraded cellulose has a lower tensile strength than the unmodified material. It also has a decreased viscosity in cuprammonium solution, this being ascribed to its lower average molecular weight. Many workers in this field believe the viscosity of a cellulosic product in cuprammonium solution to be proportional to its molecular weight. Two other properties which differentiate both types of degraded cellulose from the unmodified material are a marked solubility in dilute alkali and a strong reducing power, the latter property being attributed to the action of aldehyde groups. The

one property which distinguishes oxidized cellulose from acid degraded cellulose is the greater affinity of the former for basic dyestuffs.

Because of the similarity in properties of oxy- and hydrocellulose the literature is often confusing in its references to them. Thomas (2) realized the need for a better definition of the properties of these products and for a more appropriate nomenclature. Since both oxycellulose and hydrocellulose are degradation products of cellulose, in other words cellodextrin derivatives, Thomas classified them under the general name of "cotton dextrin products." As a result of his study, which showed clearly that hydrocellulose is a cellodextrin product containing free aldehyde groups and that oxycellulose is a cellodextrin product containing both free aldehyde and carboxyl groups, he proposed the new terminology "aldehydic cotton dextrin" to be applied to hydrocellulose and "carboxylic cotton dextrin" for oxycellulose.

To get a clear picture of what happens when cotton cloth is subjected to the action of various chemical agents it must be remembered that the agents attack the fiber (the basic unit of the fabric) in a two-phase system and that the reactions take place only at the surface of the fiber. There are an infinite number of stages in this process, as the point of chemical attack works its way inward from the surface of the fiber. There are several visible signs of this gradual attack. In the initial stages of degradation the modification may be detected only by certain qualitative laboratory tests. As the surface becomes more degraded the dyeing properties of the fabric are changed and it becomes partially soluble in water and alkali. When a fabric has reached an intermediate stage of degradation its strength is appreci-

ably decreased and it is no longer of any value for textile purposes. Upon washing such a fabric there is a noticeable loss in weight, and when this same material is boiled in alkali there is an even greater loss in weight and a yellow-colored solution, similar to that produced by boiling alkaline solutions of sugars, results. The modified cellulose produced in the final stages of the degradation of cotton fabric crumbles at the slightest touch, changing to a powdery, homogeneous mass which in no way resembles the original material.

Historical

The study of the progressive oxidation of cellulose has not had the logical step-by-step development that is characteristic of scientific research. The workers have not made good use of the literature,and as a result some of the more recent study has been a repetition of previous research. The lack of a single outstanding contributor or group of contributors is probably responsible for the existing state of confusion. As a result of this lack of leadership the conditions and methods of the previous studies of cellulosic oxidation have not been standardized, thus making comparative interpretations of results very hazardous.

Because of the poor continuity in the previous study of the progressive oxidation of cellulose the historical references will be listed chronologically and discussed individually.

1. In 1893 Cross, Bwan and Beadle (3) oxidized cellulose at room temperature using chromic acid as the oxidant. They found that the modified cellulose lost weight as the extent of oxidation was increased.

2. In 1922 Knecht and Thompson (4) oxidized cellulose progressively using an acid solution of potassium permanganate. Using methods which are applied to cellulosic materials they analyzed the oxidized residues for aldehydic and acidic properties and submitted the residues to various chemical reactions. They found that the increase in the reducing power of the oxidized cellulose was proportional to the amount of oxidant used up until a half atomic portion of oxygen per $C_6H_{10}O_5$ unit had been supplied, and that further oxidation caused no increase in reducing power. From this study they concluded that in the initial stages of oxidation the action is mainly to produce or liberate aldehyde or ketone groups and that the later stages involve more complicated chemical processes. From results obtained from acylating degraded cellulose they concluded that the oxidation process results in a suppression of the hydroxyl activity of these degradation products.

3. In 1923 Knecht and Egan (5) oxidized cellulose using solutions of sodium hypochlorite and hypochlorous acid of varying oxidizing strength. Measurements of the reducing power and tensile strength were made on the cotton residues. No conclusions were drawn.

4. In 1924 S. J. Lewis (6) made a study of the fluorescent properties of cellulosic products. His experimental work showed that the fluorescence of a degraded cellulose increases with a corresponding increase in alkali solubility (indicative of acid properties), but no indication of a connection between reducing properties and fluores-

cent power was found. He concluded that the form and dimensions of the fluorescent curve are an expression of the chemical constitution of the substance.

5. In 1925 Hibbert and Parsons (7) carried out a comprehensive and well-organized study of the oxidation of cellulose. They oxidized cotton cellulose progressively at room temperature (22°- 26°) over the oxidizing range 0.01 - 2.00 atomic portions of oxygen per $C_6H_{10}O_5$ unit. Potassium, magnesium and barium permanganate in neutral and slightly alkaline solutions, and chromic acid in 90% acetic acid were the oxidizing solutions. Their work included a complete analysis of the oxidized residues and a microscopic study of the fibrous structure of the residues. Some of the conclusions drawn from this important contribution were:

1. The oxidation reaction is typical of a heterogeneous system in which there is a progressive degradation of the fibres.

2. The degree of disintegration of the fibres is more pronounced in neutral, or slightly alkaline, solutions, a fine powder being obtained when the maximum amount (2.00 atomic portions of oxygen) of oxidant is employed. A marked disintegration does not appear until over 0.10 atomic portion of oxygen is consumed, although a deterioration in strength is noticeable.

3. The fibre losses are greater in neutral and slightly alkaline media, and the reaction is more rapid, than in acid solution. The losses always increase with increasing amount of oxidant used. With the permanganates, the

losses are practically independent of the nature of the metallic radical (K, Mg or Ba), and do not vary materially when the concentration of the solution is changed within a small range.

4. Carbon dioxide is one of the chief products of the oxidation.

5. Cotton cellulose when oxidized in acid solutions contains a larger amount of oxidized material than when oxidized in either neutral or alkaline solution. The ash, copper number (a measure of the reducing power), alkali-solubility, pentosan and glycurone constituents have higher values in the case of cellulose oxidized in acid solution, and the percentage yields are greater.

6. Acetylation tests indicate that for the oxidizing range studied, the number of alcoholic groups in oxidized cellulose decreases from three to nearly two for $C_6H_{10}O_5$ unit.

7. The solubility of oxidized cellulose in alkali is regarded as due not only to salt formation and to reactions involving the aldehyde group, but also to a peptisation of a portion of the unattacked cellulose.

8. The viscosities of the cuprammonium hydroxide solutions of the various oxidized celluloses are much lower than those of the original cotton. The consumption of an amount of oxidant represented by only 0.01 atomic portion of oxygen per $C_6H_{10}O_5$ unit pro-

duces a very marked decrease in viscosity. This fact, together with the alkali-solubility determinations, suggests that a portion of the unattacked cellulose - probably the layer adjacent to the oxidized portion of the fiber - is changed in some profound manner, probably the result of a depolymerization process.

9. The oxidation is accelerated by alkalis, and retarded by dilute acids, because the former act on the initially oxidized cellulose so as to give a much larger concentration of the oxidizable components. These latter are more readily oxidized, under the conditions, than cellulose itself.

10. Oxidized cellulose, as prepared in this investigation, is regarded as a mixture of a large amount of unattacked cellulose (which may exist in different degrees of polymerization or association) with relatively small quantities of degraded cellulose in the form of complex oxidation products, aldehydic and acidic in nature. The amounts of these substances formed depend on the conditions of the oxidation.

6. In 1927 Ludwig Kalb and Friedrich V. Falkenhausen (8) carried out a one-phase progressive oxidation of cellulose. They dissolved cotton cellulose in cupric oxide - ammonium hydroxide solution and oxidized it with increasing amounts of potassium permanganate. The oxidized residues were obtained by acidifying the cuprammonium solutions and were compared with the precipitates resulting from

acidification of similar non-oxidized cuprammonium solutions. From an analysis of the oxidized residues they found that their reducing power increased regularly with the degree of oxidation, but their acidity increased only in the later stages of oxidation. From these results they concluded that the first step in the oxidation is a conversion of primary alcohol groups to aldehyde groups and the second step is a conversion of the aldehyde groups to carboxyl groups.

Some of the water soluble, oxidized residue obtained by supplying 2 atomic portions of oxygen per $C_6H_{10}O_5$ unit was dialyzed until free of sulphate, cupric and manganous ions. The contents of the dialyzing thimble were found to be largely glucuronic acid and it was actually isolated in the form of its cinchonine salt. They suggested that the fact that the glucoronic acid did not dialyze away indicated that it was originally present in some chemical or adsorptive combination and was liberated only in the manipulations involved in preparing the salt.

7. In 1927 Hibbert and Hassan (9) made a study of the oxidation and hydrolysis of cotton cellulose. In one series of experiments they treated cellulose samples with constant amounts of chromic oxide dissolved in solutions of varying acid concentration, and in a second series they used varying amounts of chromic oxide dissolved in solutions of constant acid concentration. On the resultant residues they determined the reducing power, percent carbon dioxide and percent furfuraldehyde. Glucose, methyl glucoside and lactose were treated in a similar manner. No conclusions applicable to the present work were drawn.

8. In the same year Miss Elaine Alvord (10), working in this

laboratory, began the study of the progressive oxidation of cellulose using time as the variable. Calcium hypochlorite (bleach liquor) was the oxidant used. Two years later Miss Louise Drake (11), also in this laboratory, made a similar study except that she used buffered solutions of potassium permanganate. Miss Drake found that the rate of oxidation increased as the hydrogen ion concentration of the potassium permanganate solution increased, and that oxidation continued until all of the manganese had reached the bivalent form.

9. In 1930 Murray, Staud and Gray (12) made a study of the oxidation and hydrolysis of cellulose. In their oxidation experiments they used potassium permanganate and potassium dichromate and in their hydrolysis experiments they used hydrochloric, sulphuric and phosphoric acid. The work was done primarily to determine the alkali solubility and optical properties of the modified cellulosic residues.

10. In 1931 Sommer and Markert (13) searched for a test that would distinguish between the two degradation products of cellulose and show the extent of degradation. Upon examining their materials under the mercury vapor lamp they found that normally bleached cotton showed a feeble white fluorescence with a violet tinge. The fluorescence was slightly duller and had a deeper violet color when the cellulose had undergone oxidative degradation, while acid degraded cellulose showed a brilliant white fluorescence. They also found that methylene blue is an excellent indicator for showing degree of alteration, but does not differentiate clearly among hydrocellulose, oxycellulose and pectic products.

11. In 1933 Doree and Healey (14) made one of the more

important studies of the progressive oxidation of cellulose. Their investigation consisted of a series of experiments in which measurements were made of (a) the time necessary to decompose a fixed amount of potassium permanganate, in solutions of graded pH values, by a fixed weight of cellulose, (b) the modifications produced in the properties of cellulose by treatment with potassium permanganate solutions of graded pH value in definite times, (c) the properties of oxycelluloses prepared in solutions of extreme acidity and alkalinity. Some of their more important findings were:

1. The reaction of potassium permanganate with cellulose is at a minimum at a pH of 9. The measurable qualities produced have here the lowest values and they increase at the slowest rate with progressive treatment. The activity of potassium permanganate in strongly acid and alkaline solutions is high. The extreme activity in sodium carbonate solution (pH 11.2) is noteworthy.

2. The value of pH 9 differentiates the products formed. On the acid side, oxycelluloses of the reducing type are produced; on the alkaline side they are of the high methyline blue absorption type, resembling those produced with alkaline hypobromite solution.

12. In 1937 T. Brissaud (15) made the most recent study of the progressive oxidation of cellulose that is recorded in the literature. He oxidized cellulose in the dark with a neutral solution of sodium

hypochlorite, and obtained five samples which were oxidized progressively. Analysis of these samples showed that their reducing power and methylene blue absorption increased with the extent of oxidation. An X-ray examination of the dyed oxycellulose showed that the diagram was a superposition of the methylene blue on the diagram of the original cellulose, indicating that it was an absorption phenomenon.

Present Work

A. Study of the Progressive Oxidation of Cellulose

The present work is an application of quantitative methods to a study of the progressive oxidation of cellulose. Weighed amounts of pure cotton cellulose were oxidized for definite periods of time by standard permanganate solutions of different pH, one being neutral, one acid and one alkaline. Certain measurements were made as the oxidations were carried out. The amount of oxygen used and the change in hydrogen ion concentration during each oxidation were accurately measured. The loss in weight of the cellulose during oxidation was also determined.

The reduction of potassium permanganate involves more than one chemical reaction. In acid solution the oxidation of cotton by permanganate is the result of at least two reactions according to Birtwell, Clibbens and Ridge (16). The two reactions are:

1. The reduction of permanganate to manganous sulphate (sulphuric acid solutions of permanganate were used in the present work).

$$2KMnO_4 + 3H_2SO_4 + \text{Cellulose} \longrightarrow MnSO_4 + \text{Oxidation Products of Cellulose} + K_2SO_4$$

2. Its reduction to hydrated manganese dioxide by the manganous sulphate formed in the first reaction.

$$2KMnO_4 + 2H_2O + 3MnSO_4 \longrightarrow K_2SO_4 + 2H_2SO_4 + 5MnO_2 \text{ aq.-}$$

In general these two reactions proceed simultaneously and result in the formation of an oxycellulose on which hydrated manganese dioxide has been precipitated. In the presence of only small amounts of permanganate the rate of the first reaction is determined chiefly by the rate of oxidation of non-cellulose impurities in the cotton (true

bleaching effect) which is rapid compared with the oxidation of cellulose or with the reduction of permanganate by manganous salts and no precipitation of MnO_2 then occurs.

The second reaction formulated above may be retarded by increasing the concentration of acid in the solution, but it is only in the presence of acid concentrations dangerous from the point of view of cellulose hydrolysis that the precipitation of MnO_2 is entirely prevented. A further factor of some importance in this work is that hydrated MnO_2 itself oxidizes cotton cellulose, slowly compared with permanganate, but at a rate which increases rapidly with the acidity of the solution.

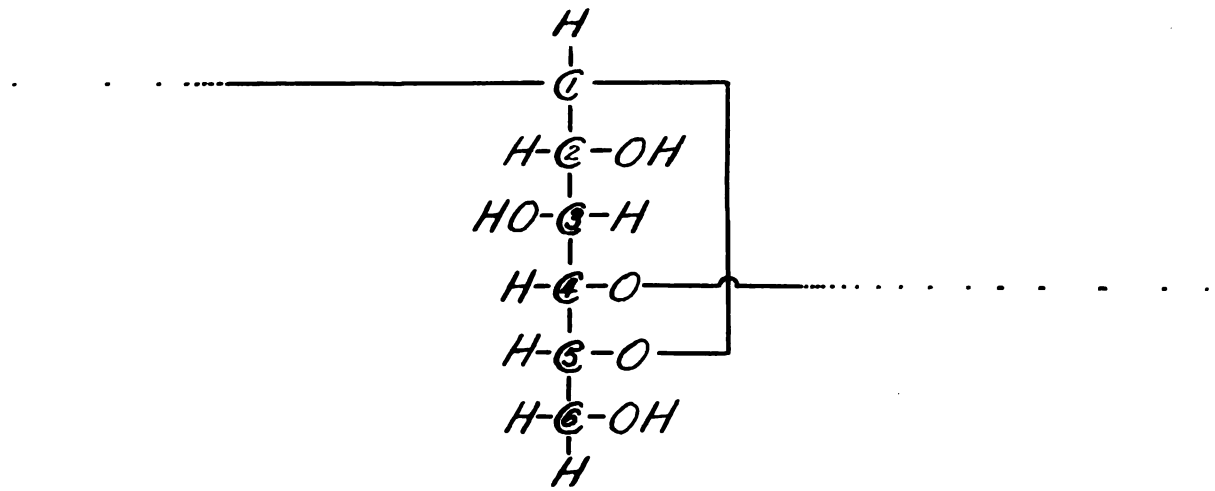
The reaction of the permanganate is more simple in neutral and alkaline media. In these solutions the reduction of the permanganate stops at the manganese dioxide stage and large amounts of the hydrated manganese dioxide are precipitated on the surface of the fabric or in the solution.

$$2KMnO_4 + H_2O + \text{Cellulose} \longrightarrow 2MnO_2 + 2KOH + \text{Oxidation Products of Cellulose}$$

Since the hydrated manganese dioxide as well as the permanganate has an oxidizing effect on the cellulose, a separate study was made of the progressive oxidation in order to determine the relative effects of the two oxidizing agents. In this study weighed samples of pure cellulose were oxidized for definite periods of time and a quantitative measurement was made of the amounts of permanganate and manganese dioxide present in the oxidizing bath at the completion of each oxidation.

B. The Nature of the Oxidized Cellulose

The structure of the anhydroglucose molecule (basic chemical grouping in the cellulose molecule) readily shows the points of oxidative attack. Besides weakening supermolecular forces and breaking down the micellar structure the oxidizing agent is believed to attack certain chemical groups within the anhydroglucose molecule.



As has already been stated, the terminal units of the long chain contain certain exposed groups that are not found in the other units of the chain. These are, namely, an exposed aldehyde group in the number one position of the anhydro glucose unit and, at the opposite end of the chain, a secondary alcohol group in the number four position. Upon breakdown of the long chain into shorter chains, more and more terminal units are exposed. In addition to these terminal units and their vulnerable groups, each anhydroglucose unit on the interior of the chain has certain chemical groups which are susceptible to an oxidizing attack. The most accessible of these is the primary alcohol group in the number six position. In a two-phase oxidizing system this primary alcohol group is more exposed to the chemical agents than the other two points of attack, the secondary alcohol groups in

positions two and three. The primary alcohol group is oxidized to an aldehyde group and then to the carboxyl group. The secondary alcohol groups are oxidized to ketones with further degradation resulting in fission.

An analysis of oxidized cellulose is based on the relative amounts of these characteristic groupings which are present in a given sample. In the present work three of the most common analytical determinations which are applied to cellulosic products were carried out on the oxidized residues. They are:

1. Copper number
2. Methylene blue number
3. Alkali solubility

The copper number determination is a measure of reducing power and is very similar to the common Munson and Walker sugar determination. It is defined as the number of grams of copper reduced from the cupric to the cuprous state under standardized conditions by one hundred grams of the sample. The reduction of cupric copper to cuprous oxide is a recognized test for the presence of "modified cellulose" in cellulosic products because both hydrolysis and oxidation of cellulose produce the aldehyde groups which are responsible for this reduction. Under the conditions of the determination, pure or unmodified cellulose has little or no reducing action.

The estimation of copper number (17) is purely empirical, and the value obtained is seriously affected by slight variations in the experimental method used. As several methods are in use the results obtained by different workers are confusing because they are not often comparable,

and the value of the test is greatly diminished by this circumstance. Due to the small amount of sample which was available, the micro-method of Heyes (18) was used in the present work.

The copper number is a valuable laboratory test for the presence of oxycellulose. It is capable of detecting the very slight changes that occur during the initial oxidation process even before the actual structural disintegration has begun. However Birtwell, Clibbens and Ridge (16) point out certain facts that should be considered when interpreting data obtained from copper number determinations. They found that when an oxycellulose is boiled with dilute alkali its copper number is reduced and may reach as low a value as that of normal unmodified cellulose; when, therefore, cotton is boiled with alkali subsequent to the injurious oxidizing treatment, measurement of copper number may not be capable of revealing the presence or extent of the oxidizing attack. Even in cases where the possibility of an alkali boil subsequent to oxidation had been excluded, they found that the determination of copper number alone could not be a quantitative basis for the measurement of the extent of oxidizing attack. This last conclusion was based on data which showed that different oxidizing agents or the same oxidizing agent used in solutions of different hydrogen ion concentration produce oxycelluloses whose copper numbers vary over a considerable range even though the extent of oxidation as measured by the consumption of available oxygen was the same.

The determination of the amount of methylene blue which a cellulosic material will absorb from a solution of the dye has long been used in the laboratory control of bleaching processes. Unbleached cotton absorbs much greater quantities of methylene-blue than bleached cotton,

a property which is due chiefly to non-cellulosic organic constituents of the raw material such as protein and pectic matter. The progressive elimination of these impurities in the bleaching process is accompanied by a gradual decrease in the absorption of methylene blue by the cotton and it is supposed that an ideal "pure cotton" from which all such impurities have been removed would show a minimum absorption characteristic of cotton cellulose itself. If the pure cotton cellulose is subjected to continued bleaching (oxidation), the absorption of methylene blue is again apparent and is believed to increase with the extent of oxidation.

In 1923 Birtwell, Clibbens and Ridge (19) made a study, the purpose of which was to determine the quantitative relationship between the extent of oxidation of cotton cellulose and its absorption of methylene blue. They did not find the cause of the methylene blue absorption in oxycellulose, but they did discover several important facts. Their experimental data showed conclusively that an increase in the ash content, or more strictly, the ash alkalinity of bleached cotton, results in an increased methylene blue absorption when all other factors are the same. Since the ash alkalinity is chiefly controlled by the nature and efficiency of washing processes, they stated that the methylene blue absorption of a material had no quantitative meaning until the disturbing effect of variations in ash alkalinity was eliminated by the careful washing of all samples with acid before examination. They also found that calendaring and mercerising, which alter the surface properties or degree of dispersion of cotton cellulose, have no effect upon the absorption. This indicates that the absorption

of methylene blue is not a surface phenomenon, but is the result of some chemical combination.

The methylene blue absorption is usually expressed as the number of millimoles of methylene blue which are absorbed by one hundred grams of dry cellulosic material. There are two methods, the colorimetric and the titrimetric, which may be used in the methylene blue determination. In the present work the titrimetric method of Pelet-Jolivet (20) was used. In both methods a weighed amount of cellulosic material is allowed to stand in a definite volume of methylene blue solution of known concentration for a standard period of time. When this time has elapsed the supernatent solution is filtered off and the excess methylene blue is determined. The titrimetric method is based upon the simple stoichiometric ratio existing between methylene blue hydrochloride, a basic dye, and naphthol yellow-S, an acid dye, one mole of the latter being equivalent to two moles of the former.

The exact cause of methylene blue absorption of an oxidized cellulose is not known, but it is the accepted belief that carboxyl groups are responsible for it to a great extent. Recently Neale and Stringfellow (21) developed a method for actually titrating the carboxyl groups present in oxycelluloses. Their method is a great improvement over the methylene blue absorption and should become the accepted method for the determination of acidic groups in oxidized cellulose.

The determination of alkali solubility is one of the standard methods of analysis which are applied to degraded cellulose. It is a gravimetric determination of the percent solubility of a cellulosic

material in an alkaline solution when treated under a carefully controlled set of standard conditions.

This determination may be used as a substitute for the measurement of copper number because the value of the result is affected by exactly the same considerations which affect the value of the results obtained by the latter determination. However, it is not nearly as accurate as the copper number, especially when the extent of the oxidizing attack is slight. Naturally, no indication of oxidizing attack can be obtained by this method from material which has already been subjected to strong alkaline treatment, and even when this has not occurred, serious damage may escape detection if sole reliance is placed on this test.

Laboratory Procedures and Calculations

The material used in the present work was 100 Berkeley cambric. Before being used it was boiled several times in distilled water and rinsed thoroughly in order to remove the sizing. It was then cut into one-quarter inch squares and allowed to come to moisture equilibrium by standing in a desiccator over calcium chloride for at least 24 hours.

A. Oxidation - Part I

In part I of the present work samples of this purified cellulose were oxidized by an acid, an alkaline and a neutral solution of 0.3N$KMnO_4$ and the resulting oxycellulose residues were analyzed. The alkaline permanganate solution was one tenth normal with respect to $NaHCO_3$ and the acid solution was one tenth normal with respect to H_2SO_4, while the neutral solution was not buffered. The same procedure was used for each oxidant.

Eight 2.5000 gram samples of the purified cellulose were weighed out into 500 ml Erlenmeyer flasks for each series of oxidations. Two hundred milliliters of 0.3N standard $KMnO_4$ was pipetted into each flask, which was then immediately transferred to a constant temperature bath which was maintained at 50°C. The flasks were stoppered with corks wrapped in lead foil to prevent evaporation, and were shaken every 15 minutes. Their time of entry into the bath was accurately recorded and at the end of exactly one hour intervals the flasks were removed from the bath. The period of oxidation varied from one to eight hours and was measured accurately (within 15 seconds).

Upon removal of a sample from the bath approximately 30 ml. of the supernatent liquid were poured off, and to the remainder of the solution a measured volume of .7464 N oxalic acid, sufficient to reduce all manganese present to the colorless divalent form and to provide an excess, was added (pipette) immediately so that the oxidation process might be stopped at that time. Fifteen ml. of 6.0 NH_2SO_4 was added to the oxalic acid - permanganate - MnO_2 - mixture and it was heated gently in order to hasten the reaction because the MnO_2 which is precipitated on the fabric is very stubbornly held and is reduced with difficulty. The 30 ml. portion of the oxidizing solution was used for the determination of pH and was then transferred quantitatively to the oxalic acid - oxidizing solution mixture. A Beckmann pH meter was used for the pH measurements.

As soon as the oxalic acid had reduced all of the $KMnO_4$ and MnO_2, the solution was cooled to 60°C and filtered through a weighed, modified Gooch crucible. The solid cellulose residue was transferred quantitatively to the crucible and was washed thoroughly, first with dilute H_2SO_4 and then several times with distilled water. The crucible was then dried at 60°C in a vacuum oven and weighed and then redried and reweighed until a constant weight was obtained. Several weighings were required because oxidized cellulose is slightly hygroscopic. The vacuum oven was used for drying because the modified cellulose tends to char and decompose when heated in an ordinary 110°C oven. From the difference between the final weight of the oxidized residue and the original 2.5000 gms. the percent loss in weight was calculated. These dried residues were the samples which were used for the analytical determinations.

To the above filtrate was added 10 ml. of conc. H_2SO_4. It was then heated to boiling and the excess oxalic acid was backtitrated with a standard 0.3N $KMnO_4$ solution. By subtracting the number of milliequivalents of $KMnO_4$ which were used in the backtitration from the number of milliequivalents of oxalic acid which were added, the number of milliequivalents of $KMnO_4$ which were left after the oxidation of the cellulose was obtained. By subtracting this value from the number of milliequivalents of $KMnO_4$ which were present originally, the number of milliequivalents of $KMnO_4$ which disappeared during the oxidation was obtained. This figure takes into account the fact that the $KMnO_4$ may be reduced to either MnO_2 or divalent manganese and represents the amount of oxygen which disappeared during the oxidation process. In part A of this work the milliequivalents of oxygen which disappeared during the oxidation was multiplied by .008, thus converting the result to grams of oxygen used up during the preparation of each modified cellulose sample. This value was then used in calculating the number of atomic portions (16 grams is one atomic portion or gram atom) of oxygen which were furnished for every $C_6H_{10}O_5$ unit (equivalent to 162 grams of cellulose).

A. Oxidation - Part II

In part II of the present work, samples of the purified cellulose were oxidized by an acid, an alkaline and a neutral solution of 0.3N $KMnO_4$ and quantitative measurements were made of the amounts of $KMnO_4$ and MnO_2 present in the oxidizing mixture at the end of each oxidation period.

The preparation of the samples, their entry into the constant

temperature bath and time of removal from the bath were exactly the same operations that were carried out in part I of this work. It was in the treatment of the contents of the flasks after their removal from the bath that the two experiments differed.

In this experiment a sample, upon removal from the bath, was placed in ice water for exactly five minutes so that it would be cooled to room temperature. Then 25 ml. of the solution was drawn up into a pipette through a piece of glass tubing packed with glass wool. The purpose of the glass wool was to filter out all of the MnO_2 which was carried up with the solution. This 25 ml. of MnO_2-free $KMnO_4$ solution was transferred to a 200 ml. Erlenmeyer flask and 10 ml. of .7830N oxalic acid (an excess) and 20 ml. of 4.0N H_2SO_4 were added to it. The pipette and glass tube were then washed thoroughly and their washings allowed to drain into the original flask. Then 100 ml. of .7830N oxalic acid (an excess) and 25 ml. of 4.0N H_2SO_4 were added to the original flask, and it was heated gently to accelerate the reduction of the MnO_2 which was precipitated on the oxidized residues.

The contents of the 200 ml. Erlenmeyer flask were then heated to boiling and the excess oxalic acid was backtitrated by .1N $KMnO_4$.

The original flask was then cooled to room temperature and filtered through an asbestos-matted Gooch crucible. The flask and residue were washed several times with distilled water and the filtrate was then carefully transferred to a 500 ml. volumetric flask, and made up to volume.

In the oxalic acid - $KMnO_4$ titrations in part I the endpoints were evanescent due to the soluble degradation products of cellulose. In

order to avoid the troublesome endpoint in this second experiment, a combination of gravimetric and volumetric methods was used to determine the excess oxalic acid. A 25 ml. aliquot portion was removed from the volumetric flask by a pipette and transferred to a 400 ml. beaker. Then 25 ml. of distilled water was added and the solution was heated to boiling. Then 15 drops of phenol red and 25 ml. of 1.0M $CaCl_2$ were added to the hot solution and finally 0.5N NH_4OH was added slowly with constant stirring until the red color had changed to a faint purple (pH= 8). (If the pH of the solution goes above 8, the manganous ions are oxidized by the air to MnO_2 which precipitates out. The MnO_2 oxidizes some of the oxalate and makes the determination worthless.) The beaker was then set aside for at least 24 hours to allow the precipitation of calcium oxalate to be completed. After standing for this period of time the calcium oxalate was filtered off and the filtrate discarded. The beaker was rinsed with 50 ml. of 4.0N H_2SO_4 which was then poured over the precipitate and the solution collected in a 500 ml. Erlenmeyer.

The beaker and filter paper were then washed with hot 0.2N H_2SO_4 until no test for chlorides was obtained from the washings. To the filtrate which contained approximately 300 ml. was added 5 ml. of conc. H_2SO_4. It was then heated to boiling and titrated with 0.1N $KMnO_4$.

The results from the titration of the 25 ml. sample which was withdrawn from the original oxidizing solution gave a measure of the $KMnO_4$ which was present in the solution. By subtracting the number of milliequivalents of $KMnO_4$ which were used in the backtitration from the number of milliequivalents of oxalic acid which were added to the 25 ml. sample, the number of milliequivalents of $KMnO_4$ actually

present in the 25 ml. sample was obtained. When this figure was multiplied by eight the number of milliequivalents of $KMnO_4$ present in the entire 200 ml. of oxidizing solution was obtained.

The analysis of the solution in the volumetric flask gave a measure of the total oxidizing power (both $KMnO_4$ and MnO_2) which was present in the original oxidizing solution when it was removed from the water bath. By multiplying the number of milliequivalents of $KMnO_4$ which were used in the titration of the filtrate, obtained by dissolving the calcium oxalate, by twenty the number of milliequivalents of $KMnO_4$ which would have been necessary to titrate the oxalic acid present in the entire 500 milliliters was obtained. When this value was subtracted from the number of milliequivalents of oxalic acid which were added to the 175 ml. of oxidizing solution, the number of milliequivalents of active oxygen ($KMnO_4$ + MnO_2) present in the 175 ml. of solution was found. When this last value was added to the number of milliequivalents of $KMnO_4$ which were present in the 25 ml. sample that was removed at the close of oxidation, the total number of milliequivalents of active oxygen ($KMnO_4$ + MnO_2) present in the flask was obtained. This value was used in two calculations; first by subtracting it from the number of milliequivalents of $KMnO_4$ (or active oxygen) which were added to the flask originally, the loss in oxidizing power (expressed in milliequivalents of oxygen) which resulted from oxidation of the cellulose was found, and second, by subtracting the number of milliequivalents of $KMnO_4$ which were present in the entire flask at the close of oxidation from the number of milliequivalents of active oxygen ($KMnO_4$ + MnO_2) which were present in the entire flask

when oxidation was stopped, the number of milliequivalents of active oxygen which were present as MnO_2 was obtained. The number of milliequivalents of active oxygen which were present as MnO_2 had resulted from a valence change in the manganese from seven to four. The difference between this value and the total number of milliequivalents of oxygen which disappeared during the oxidation had evidently been lost in a valence change of manganese from seven to two.

B. Analysis of Residues

The methods of analysis which were used in the present work are empirical, and the relative value of the results depended on a strict adherence to the procedures which were used.

1. Alkali solubility

In the determination of alkali solubility 0.5000 gram samples of the oven-dried oxidized residues were used. The sample was placed in a 200 cc. Erlenmeyer flask which was then connected to a short reflux condenser. Fifty ml. of 3% (.75N) NaOH was pipetted into the flask and a strong Bunsen flame was immediately placed under the flask. As soon as the solution came to a boil the flame was adjusted so that it would reflux gently. The residue was subjected to this alkaline treatment for exactly one hour starting from the time that the flame was placed under the flask. At the end of the hour the hot, alkaline solution was filtered through a weighed, modified Gooch crucible. The residue was washed with water, then with dilute HCl and finally with water again. The crucible was then dried in a 105°C oven and weighed, and this was repeated until a constant weight was obtained. The final weight times

one hundred divided by the original sample weight was the alkali solubility.

2. Copper number

In the determination of copper number the micro-method of Heyes (18) was followed very closely. The samples of air-dried oxidized residue weighed 0.25 gm. and were placed in a 6" x 5/8" test tube. Into a similar tube were placed 0.5 ml. of a copper sulphate solution (100 grams $CuSO_4$ per liter) and 9.5 ml. of an alkaline solution (150 grams anhydrous Na_2CO_3 and 50 grams $NaHCO_3$ per liter). These two solutions were mixed thoroughly and were then placed in a boiling water bath. As soon as the solution reached the temperature of the bath it was removed and poured over the oxycellulose sample. The tube containing the sample was then stoppered with a loose-fitting glass stopper and placed in the boiling water bath where it was left for exactly three hours. When the three hours had elapsed the tube and its contents were cooled to room temperature and filtered through a modified Gooch crucible. Two ml. of distilled water were used to rinse out the tube and to wash the solid residue in the crucible. Then the crucible was placed in a rubber diaphragm which fitted the top of a short-stemmed 2" funnel, which in turn was connected to a 50 ml. suction flask by a rubber stopper. The original test tube was then rinsed with 3 ml. of a ferric sulphate solution (40 gm. $Fe_2(SO_4)_3$ + 100 ml. conc. H_2SO_4 per liter) and then this rinse solution was poured over the contents of the crucible. The ferric sulphate solution was allowed to react with the Cu_2O in the crucible for three minutes and was then drawn through the

crucible by applying suction. This treatment was then repeated with 2 ml. of ferric sulphate solution. During this treatment the red Cu_2O which was precipitated on the surface of the fabric during the three hour digestion period was dissolved by the ferric sulphate solution and a light green solution resulted, the copper being oxidized from the cuprous to the cupric state and an equivalent amount of iron being reduced from the ferric to the ferrous state. The test tube and crucible were then washed three times, using 2 ml. of distilled water for each wash. The filtrate in the suction flask was then titrated by a 0.0410N $KMnO_4$ solution. A microburette which was calibrated to read to .001 ml. was used for the titration. The endpoint of the titration was a change from a pale green solution to a colorless one and was easily discernible. The blank correction for the titration, as determined in the laboratory, was 0.030 ml. of the $KMnO_4$ solution.

In calculating the copper number the blank correction was subtracted from the number of milliliters of $KMnO_4$ used in the titration, and the remainder converted to its equivalent in grams of copper. Since this weight of copper was reduced by .25 grams of sample, it was multiplied by 400 so that it would represent 100 grams of sample.

3. Methylene blue number

The method of Clibbens and Geake (22) which involves the use of a buffered solution of methylene blue was used in the determination of the methylene blue number. In this method the methylene blue solution is buffered with KH_2PO_4 and NaOH. The purpose of the buffer is to stabilize the hydrogen ion concentration and neutralize the effect of traces of

acid or alkali which may be introduced with the cellulosic residue.

A .5 gram sample of the oxidized cellulose was used in this determination. The sample was placed in a thick-walled pyrex test tube of 1" diameter and 50 ml. capacity. At one-third of the distance from the top of the tube there was a constriction which was designed to prevent the passage of the cellulosic residue when the tube was inverted and centrifuged. The sample was pushed down through the constriction into the lower part of the tube and 15 ml. of buffered methylene blue solution, containing 4.00 millimoles per liter, was pipetted into the tube. Another heavy-walled pyrex test tube of slightly larger diameter was then fitted over the original tube to prevent evaporation. The residue was then left in the methylene blue solution for eighteen hours. When the time had elapsed the two tubes were inverted and centrifuged, thus driving 13 or 14 ml. of the original 15 down into the outside tibe and leaving the residue in the constriction. Ten ml. were then removed from the outside tube by a pipette and placed in a similar tube. The methylene blue in this 10 ml. sample was then titrated by a solution of naphthol yellow-S containing 2.24 millimoles per liter (.9 gms. per liter). The naphthol yellow, when run into the methylene blue solution, produces at first a reddish-brown precipitate, the color of the solution becoming at the same time less and less blue until it finally changes to yellow. This gradual change is largely obscured by the precipitate, which does not settle readily. The approach of the endpoint was detected by observing a drop of the liquid suspended from a glass rod, and when the end point was nearly reached, the tube was centrifuged for thirty seconds. This separates the precipitate, and the color of the supernatent liquid is

clearly seen. The endpoint is a change from a light blue to a green, and is not difficult to see. The results were calculated by multiplying the number of ml. of naphthol yellow - S used in the titration by 1.5 and subtracting the value of this volume of naphthol yellow - S expressed in millimoles of methylene blue from the number of millimoles of methylene blue which were originally added to the sample. This value was then converted to millimoles of methylene blue absorbed by 100 gms. of sample.

DATA

I-A. Neutral Oxidation

Conditions of oxidation:

1. Weight of sample = 2.5000 gms.
2. Temperature = 50°C
3. 200 cc. of oxidizing solution (.3016N $KMnO_4$) equivalent to .4826 grams of active oxygen

	DATA OF OXIDATION PROCESS						ANALYSIS OF RESIDUES		
Sample Number	Hours in Oxidizing Bath	Final pH	% Loss in Weight During Oxidation	Grams Oxygen Used	% of Available Oxygen Used	Gm. Atoms of Oxygen used per $C_6H_{10}O_5$ Unit	Alkali Solubility	Copper Number	Methylene Blue No.
A - 0	0	6.67					3.42%	0.20	1.61
A - 1	1	7.24	6.30%	.0679	14.07%	.2750	25.30%	5.34	9.72
A - 2	2	7.34	8.98	.1222	25.37	.4949	27.22	5.63	10.52
A - 3	3	7.46	10.87	.1636	33.83	.6626	27.74	5.67	10.68
A - 4	4	7.60	13.18	.1960	40.53	.7938	29.04	5.72	10.58
A - 5	5	7.61	14.26	.2248	46.51	.9104	29.76	5.74	10.61
A - 6	6	7.74	15.15	.2417	50.07	.9789	31.26	5.75	8.66
A - 7	7	7.86	17.07	.2671	55.27	1.0817	32.50	5.76	10.71
A - 8	8	7.84	17.06	.2743	56.72	1.1109	31.52	5.77	10.04

These results are expressed graphically on Graph I-A (page 44)

DATA
I-B. Acid Oxidation

Conditions of oxidation:
1. Weight of sample = 2.5000 gms.
2. Temperature = 50°C
3. 200 cc. of acid oxidizing solution (.3009N $KMnO_4$ - 0.1N H_2SO_4) equivalent to .4806 gms. of active oxygen

	DATA OF OXIDATION PROCESS						ANALYSIS OF RESIDUE		
Sample Number	Hours in Oxidizing Bath	Final pH	% Loss in Weight During Oxidation	Grams Oxygen Used	% of Available Oxygen Used	Gm. Atoms of Oxygen used per $C_6H_{10}O_5$ Unit	Alkali Solubility	Copper Number	Methylene Blue No.
B - o	0	1.60					3.42%	0.20	1.61
B - 1	1	1.71	11.18%	.1791	37.15%	.7253	42.66	7.49	11.53
B - 2	2	1.85	14.25	.3028	62.95	1.2263	44.88	7.49	11.67
B - 3	3	1.90	15.96	.3304	68.70	1.3381	44.30	7.50	11.23
B - 4	4	1.99	16.07	.3454	71.75	1.3989	45.34	7.49	11.28
B - 5	5	2.05	15.57	.3502	72.80	1.4183	44.36	7.23	11.62
B - 6	6	2.14	15.85	.3541	73.60	1.4341	46.22	6.99	11.37
B - 7	7	2.28	15.28	.3583	74.35	1.4511	45.84	6.96	
B - 8	8	2.31	15.85	.3632	75.30	1.4710	45.36	7.36	11.66

These results are expressed graphically on Graph I-B (page 45)

DATA
I-C. Alkaline Oxidation

Conditions of oxidation:
1. Weight of sample = 2.5000 gms.
2. Temperature = 50°C
3. 200 cc. of alkaline oxidizing solution (.2979N $KMnO_4$ - 0.1N $NaHCO_3$) equivalent to .4766 gms. of active oxygen

	DATA OF OXIDATION PROCESS							ANALYSIS OF RESIDUES		
Sample Number	Hours in Oxidizing Bath	Final pH	% Loss in Weight During Oxidation	Grams Oxygen Used	% of Available Oxygen Used	Gm. Atoms of Oxygen used per $C_6H_{10}O_5$ Unit		Alkali Solubility	Copper Number	Methylene Blue No.
C - 0	0	8.18						3.42%	0.20	1.61
C - 1	1	8.22	7.63%	.0687	14.39%	.2782		27.00%	5.43	10.14
C - 2	2	8.22	12.11	.1394	29.20	.5646		30.02	5.92	9.45
C - 3	3	8.13	13.58	.1510	31.60	.6115		28.54	5.62	10.36
C - 4	4	8.11	14.88	.1794	37.55	.7266		29.86	5.81	8.42
C - 5	5	8.06	16.13	.2062	43.21	.8351		29.38	5.83	10.26
C - 6	6	8.10	17.28	.2334	48.85	.9453		28.92	5.78	10.75
C - 7	7	8.16	18.38	.2507	52.55	1.0153		31.42	5.53	9.81
C - 8	8	8.18	17.97	.2654	55.75	1.0749		31.32	5.72	10.81

These results are expressed graphically on Graph I-C (page 46)

DATA
II-D. Neutral Oxidation

Conditions of oxidation:
1. Weight of sample = 2.5000 gms.
2. Temperature = 50°C
3. 200 ml. of oxidizing solution (.2948N $KMnO_4$) equivalent to 58.96 milliequivalents of active oxygen

Sample Number	Hours in Oxidizing Bath	Initial Milliequivalents of Oxygen Present	Final Milliequivalents of Oxygen Present	Milliequivalents of Oxygen Lost	Gm. Atoms of Oxygen used per $C_6H_{10}O_5$ Unit	Final Milliequivalents of Oxygen Present as $KMnO_4$	Final Milliequivalents of Oxygen Present as MnO_2	M.Eq. of Oxygen Lost in Valence Change 7-2	M.Eq. of Oxygen Lost in Valence Change 7-4
D - 1	1	58.96	52.77	6.19	.2005	48.08	4.69	1.50	4.69
D - 2	2	58.96	46.99	11.97	.3880	39.28	7.71	4.26	7.71
D - 3	3	58.96	41.43	17.53	.5690	30.94	10.44	7.09	10.44
D - 4	4	58.96	37.42	21.54	.6980	24.45	12.97	8.57	12.97
D - 5	5	58.96							
D - 6	6	58.96	32.27	26.69	.8680	15.26	17.01	9.68	17.01
D - 7	7	58.96	29.38	29.58	.9590	11.82	17.76	11.82	17.76

In this table the $KMnO_4$ and MnO_2 are expressed in terms of their maximum available oxygen. The $KMnO_4$ representing a valence change from 7 to 2 and the MnO_2 a valence change from 4 to 2.

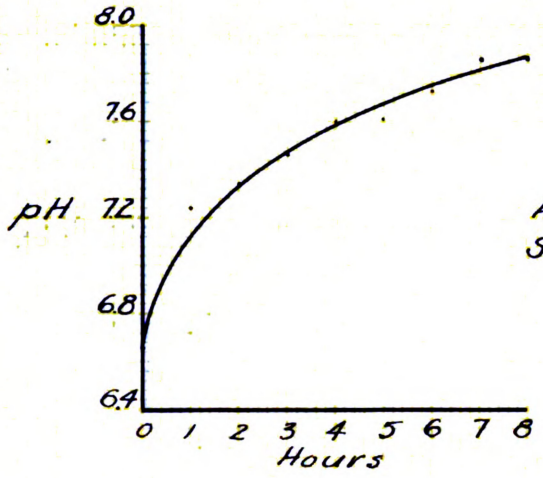
DATA
II-E. Acid Oxidation

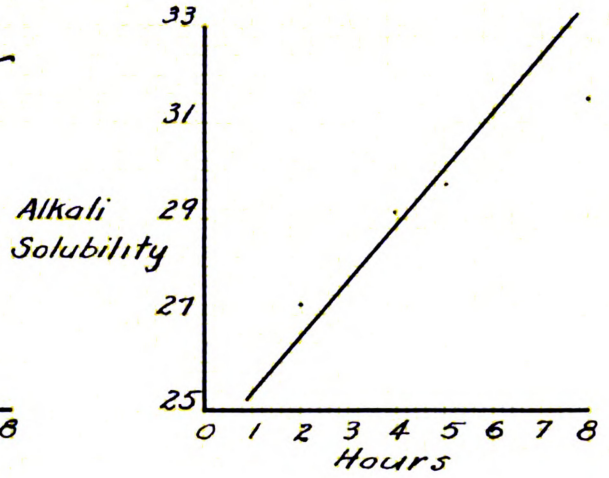
Conditions of oxidation:
1. Weight of sample = 2.5000 gms.
2. Temperature = 50°C
3. 200 ml. of acid oxidizing solution (.3069N $KMnO_4$ - 0.1N H_2SO_4) equivalent to 61.38 milliequivalents of active oxygen

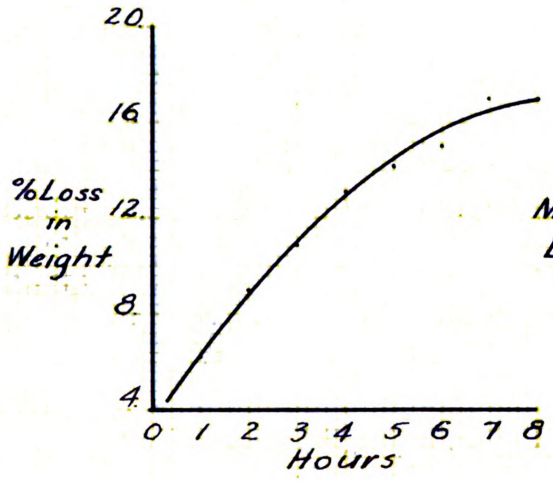
Sample Number	Hours in Oxidizing Bath	Initial Milliequivalents of Oxygen Present	Final Milliequivalents of Oxygen Present	Milliequivalents of Oxygen Lost	Gm. Atoms of Oxygen used per $C_6H_{10}O_5$ Unit	Final Milliequivalents of Oxygen Present as $KMnO_4$	Final Milliequivalents of Oxygen Present as MnO_2	M.Eq. of Oxygen Lost in Valence Change 7-2	M.Eq. of Oxygen Lost in Valence Change 7-4
E - 1	1	61.38	42.34	19.04	.6180	26.74	15.60	3.44	15.60
E - 2	2	61.38	24.77	36.61	1.185	00.24	24.53	12.08	24.53
E - 3	3	61.38	21.80	39.58	1.283		21.80	17.78	21.80
E - 4	4	61.38	20.50	40.88	1.325		20.50	20.38	20.50
E - 5	5	61.38	19.25	42.13	1.364		19.25	22.88	19.25
E - 6	6	61.38	18.42	42.96	1.395		18.42	24.54	18.42
E - 7	7	61.38	17.17	44.21	1.430		17.17	27.04	17.17
E - 8	8	61.38	16.82	44.56	1.445		16.82	27.74	16.82

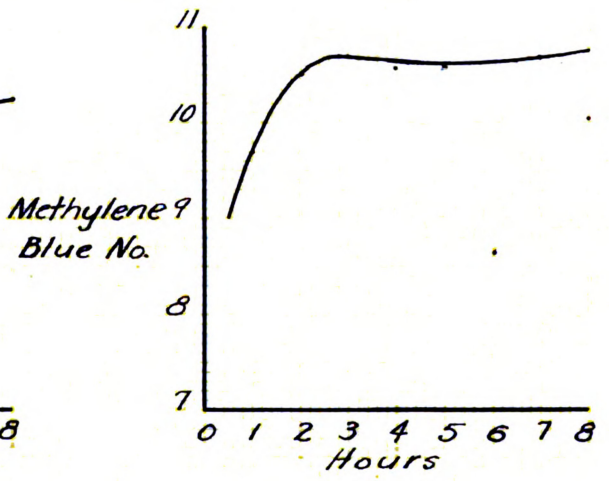
In this table the $KMnO_4$ and MnO_2 are expressed in terms of their maximum available oxygen. The $KMnO_4$ representing a valence change from 7 to 2 and the MnO_2 a valence change from 4 to 2.

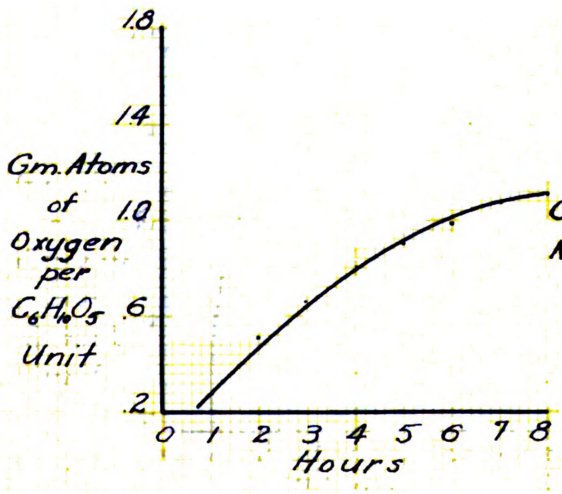
Graph I-A
Neutral Oxidation

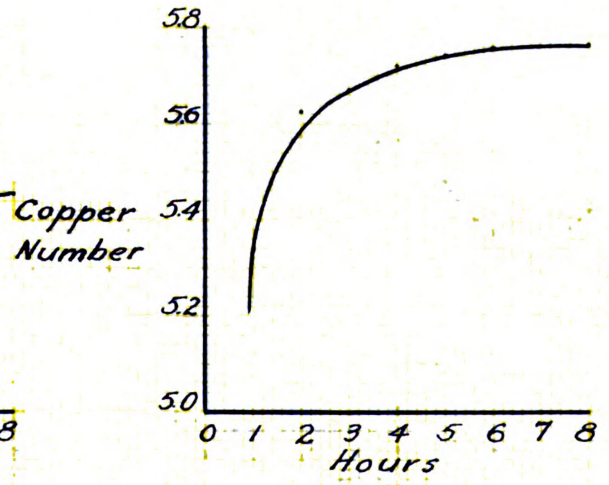


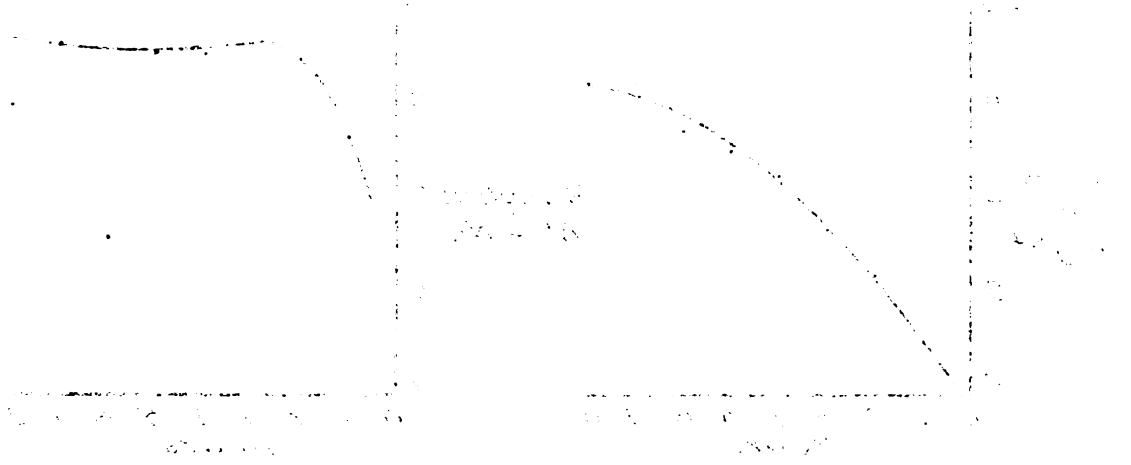


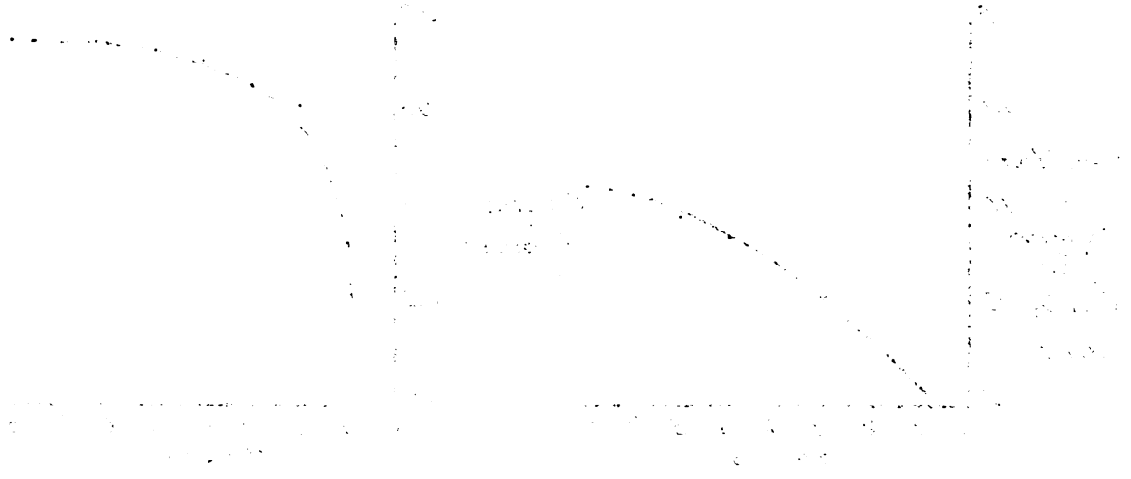




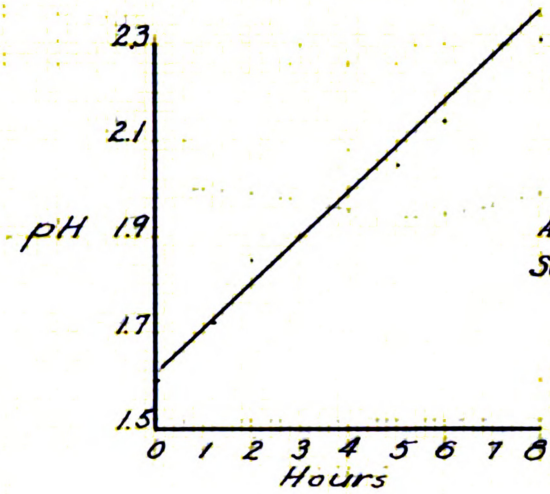


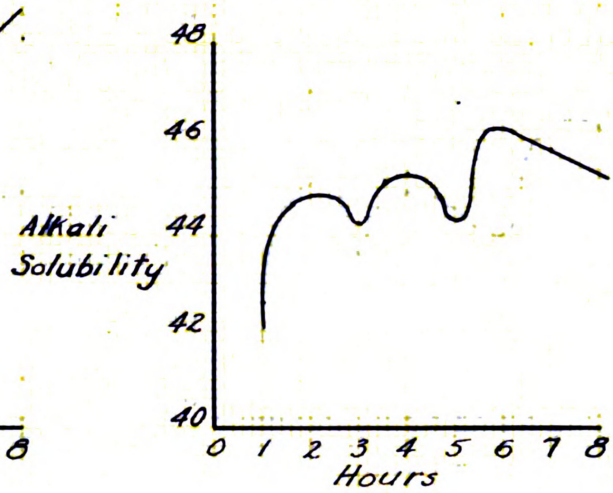


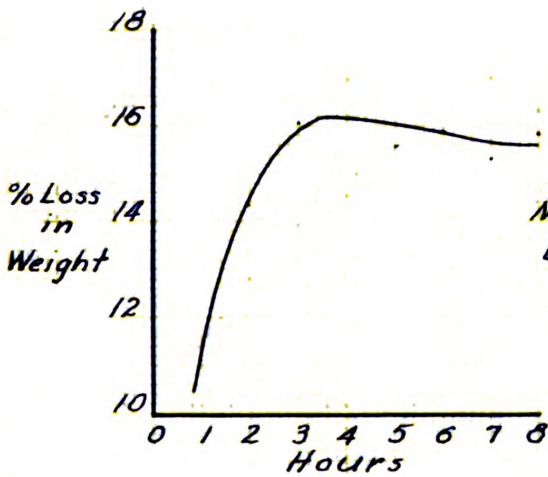


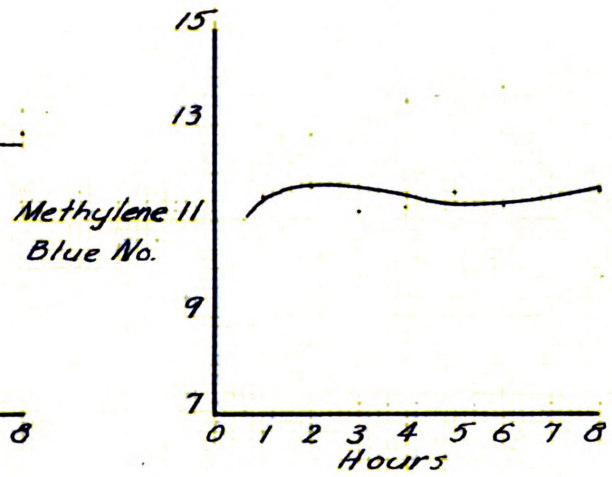


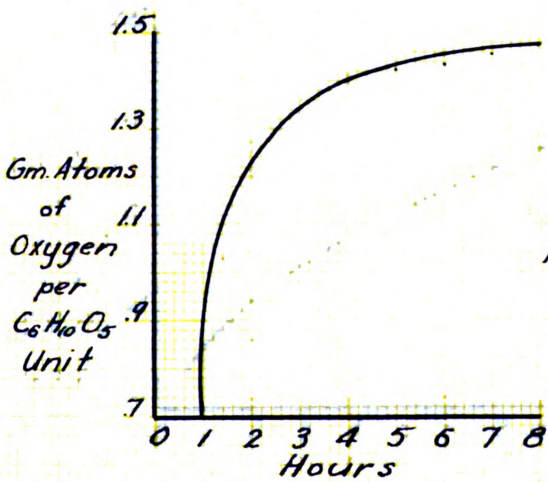
Graph I-B
Acid Oxidation

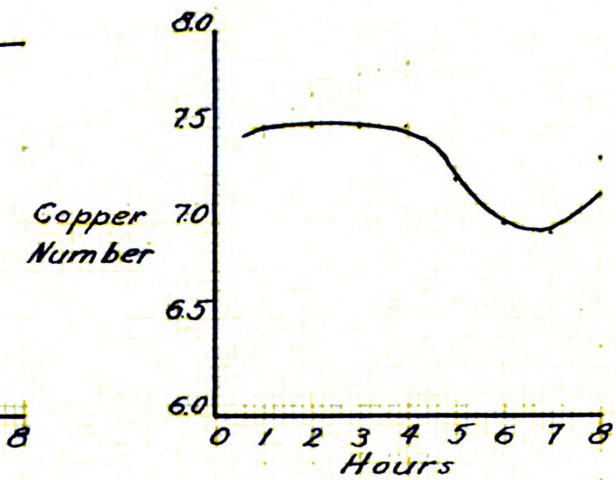


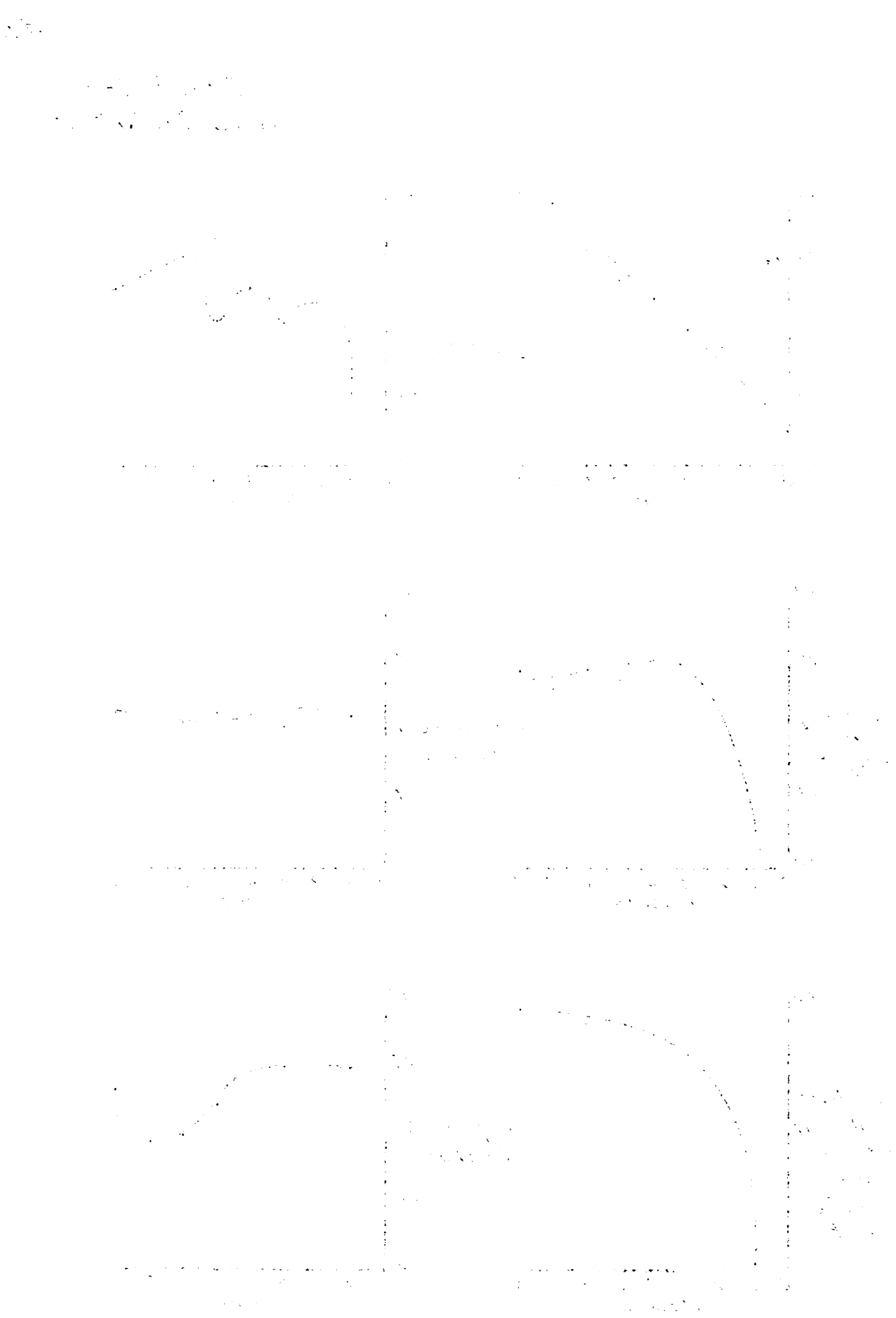




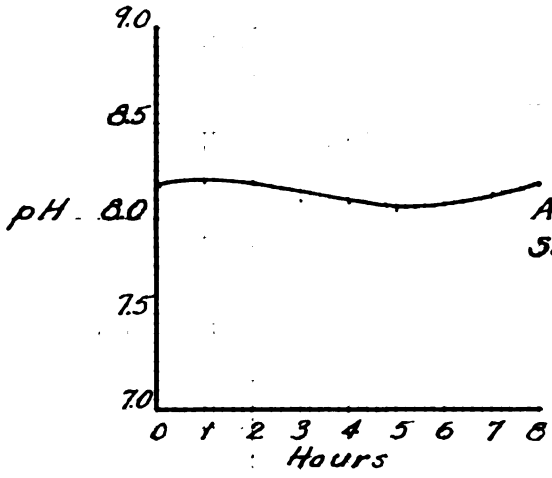


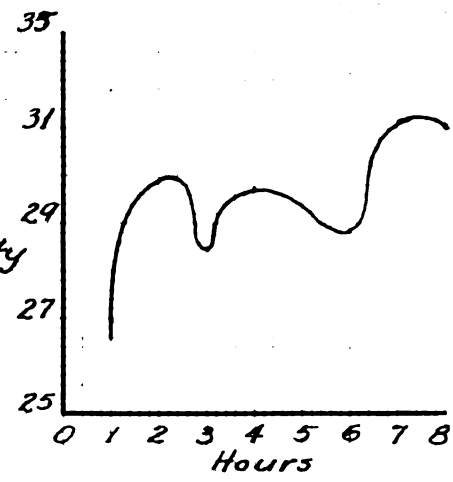


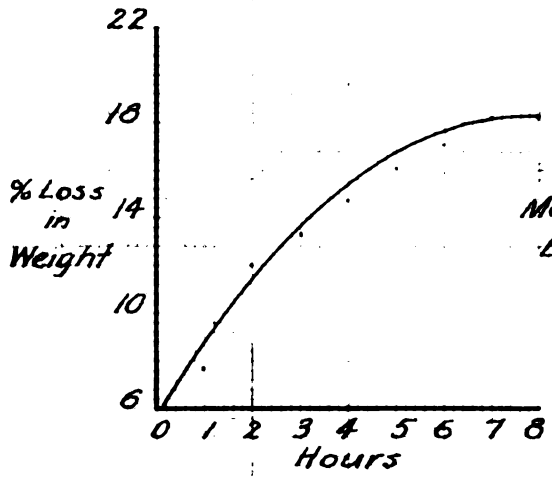


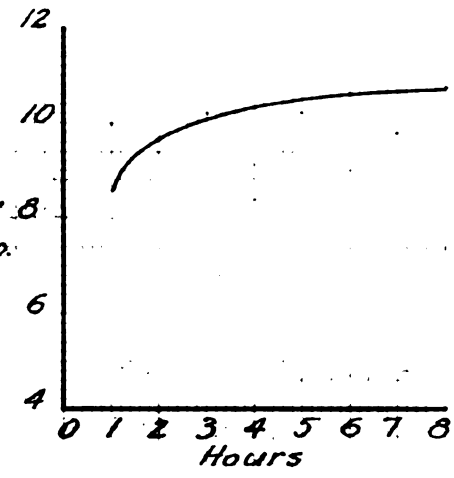


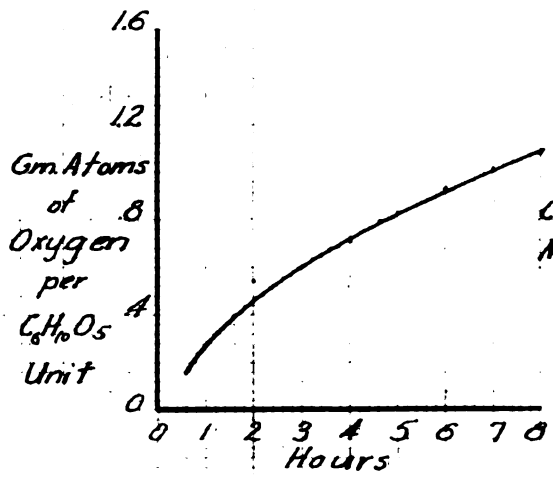
Graph I-C
Alkaline Oxidation

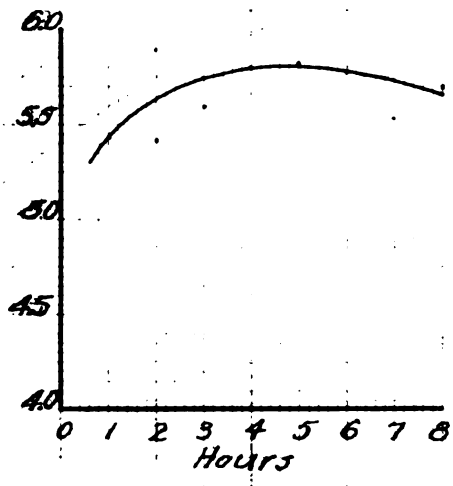


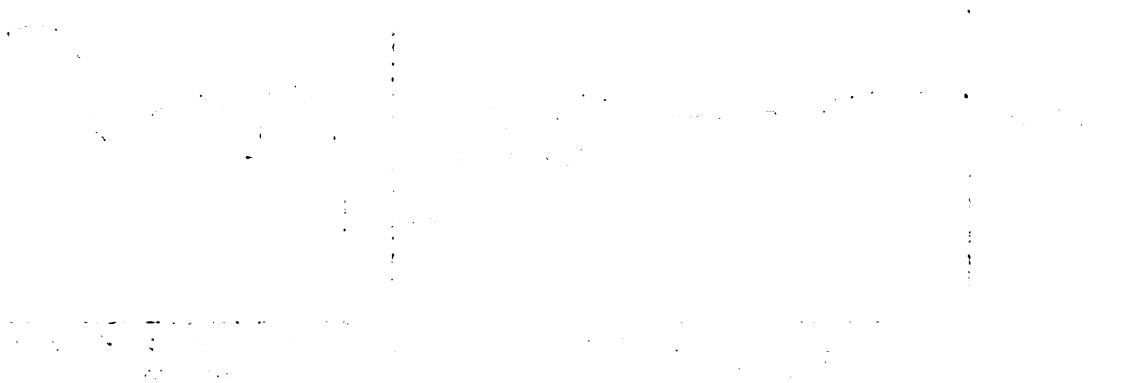


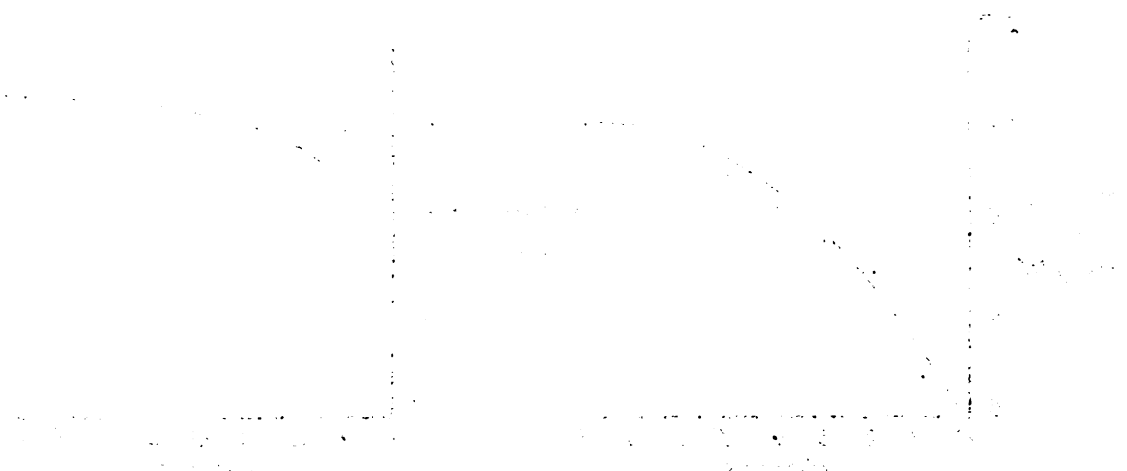


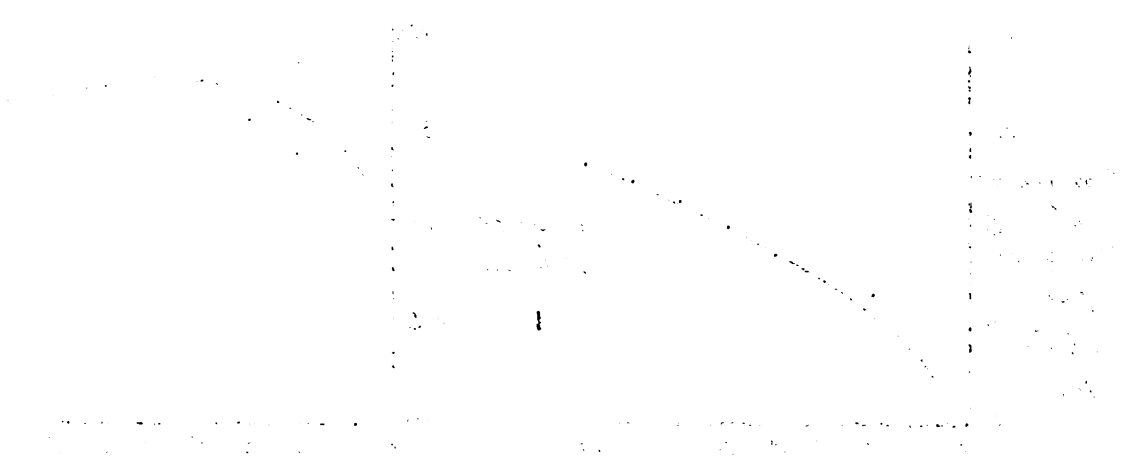


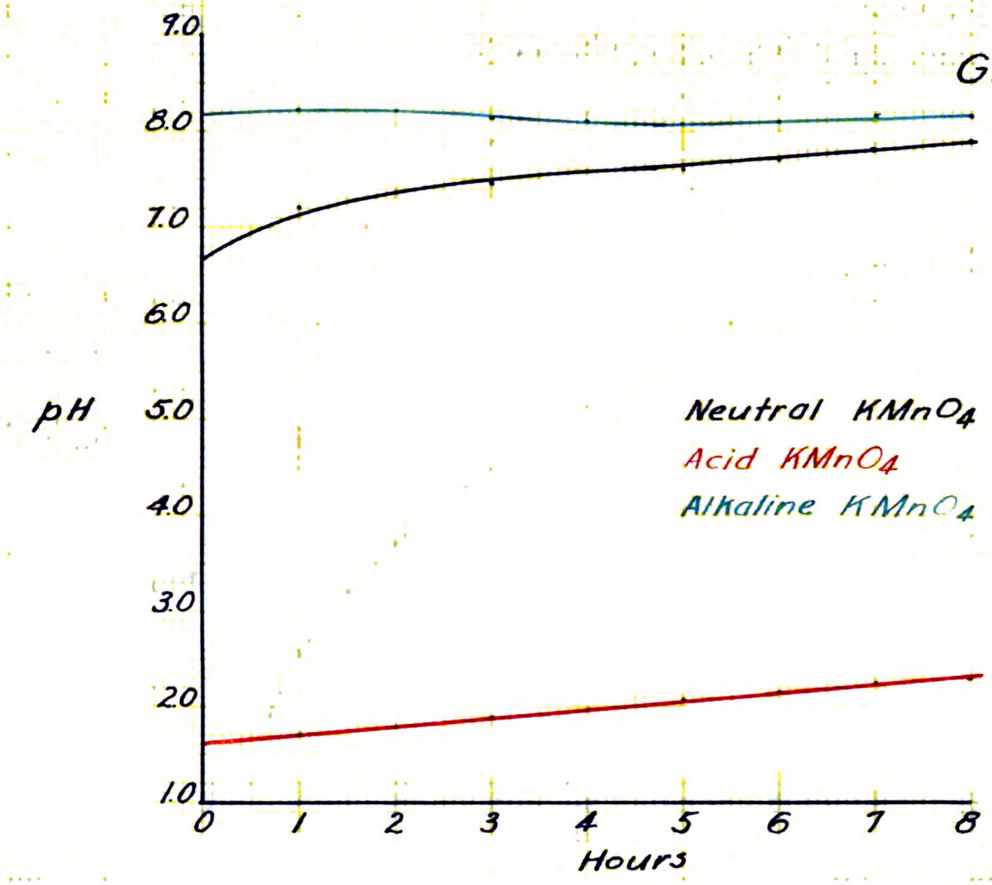


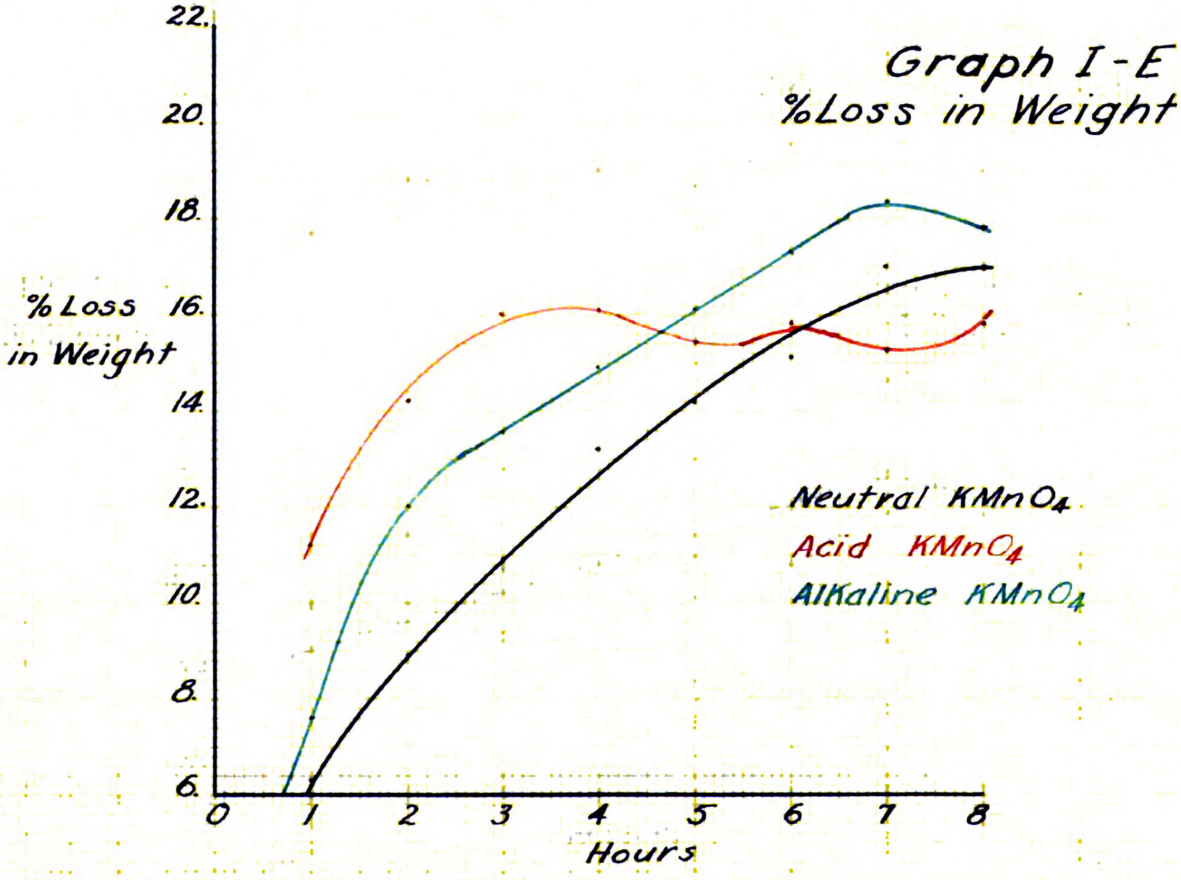






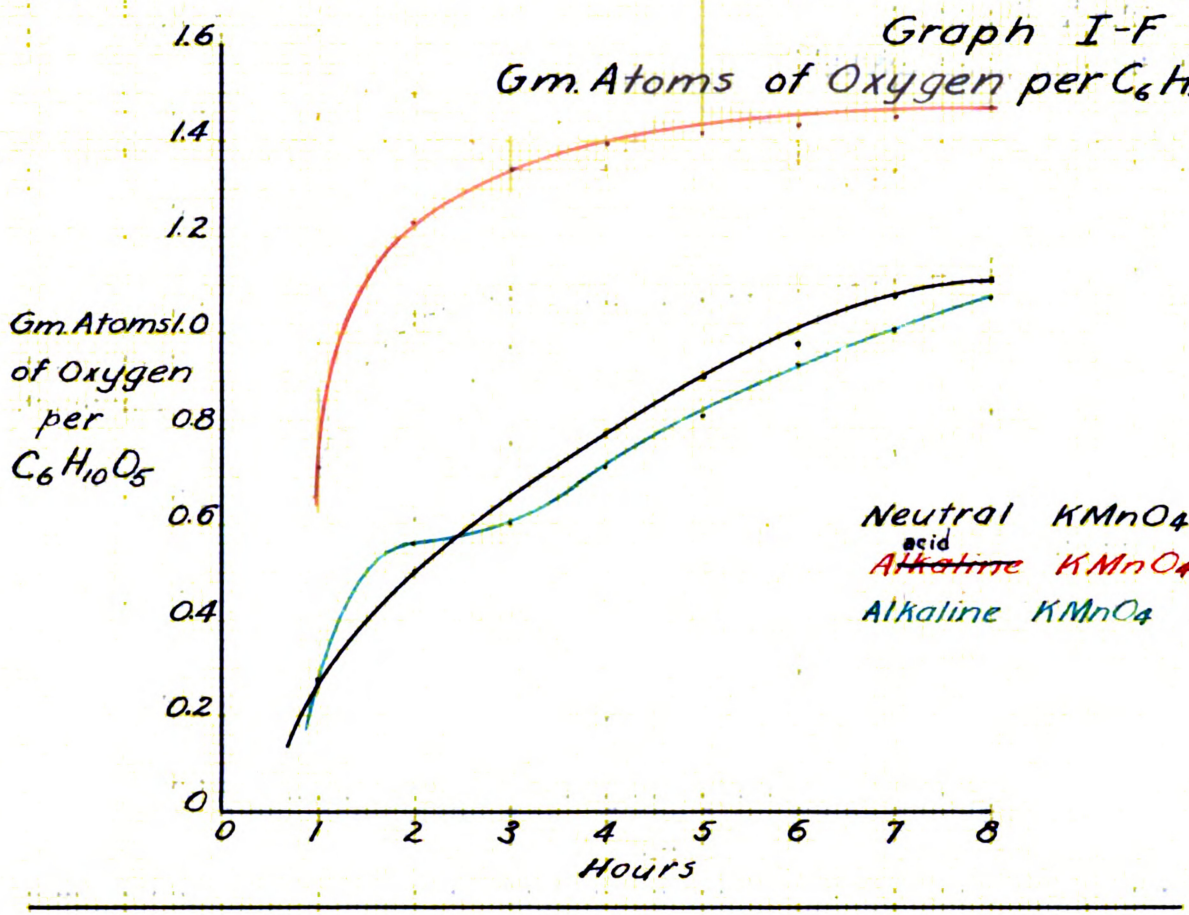



Graph I-D
pH
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
pH
Neutral KMnO4
Acid KMnO4
Alkaline KMnO4
0 1 2 3 4 5 6 7 8
Hours


Graph I-E
%Loss in Weight
22.
20.
18.
16.
14.
12.
10.
8.
6.
% Loss in Weight
Neutral KMnO4
Acid KMnO4
Alkaline KMnO4
0 1 2 3 4 5 6 7 8
Hours

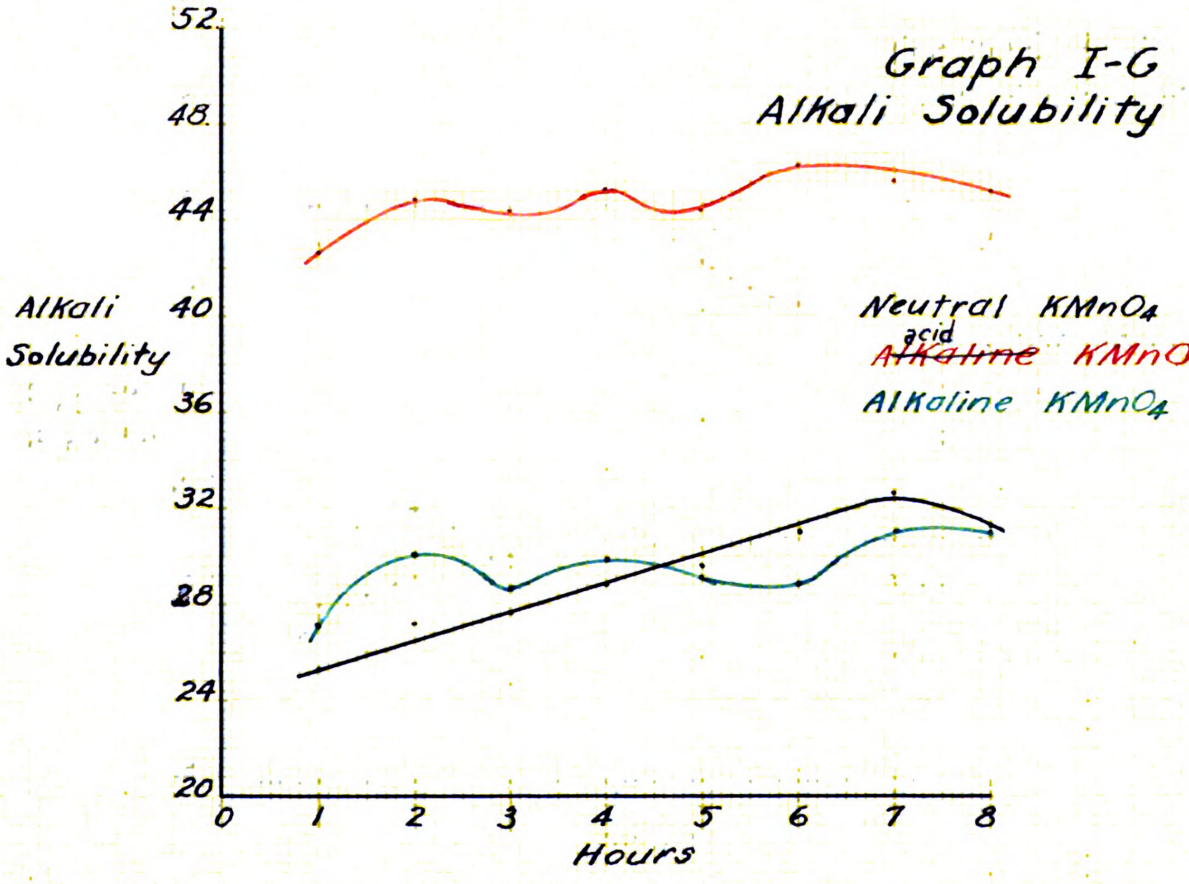
Graph I-F

Gm. Atoms of Oxygen per $C_6H_{10}O_5$ Unit

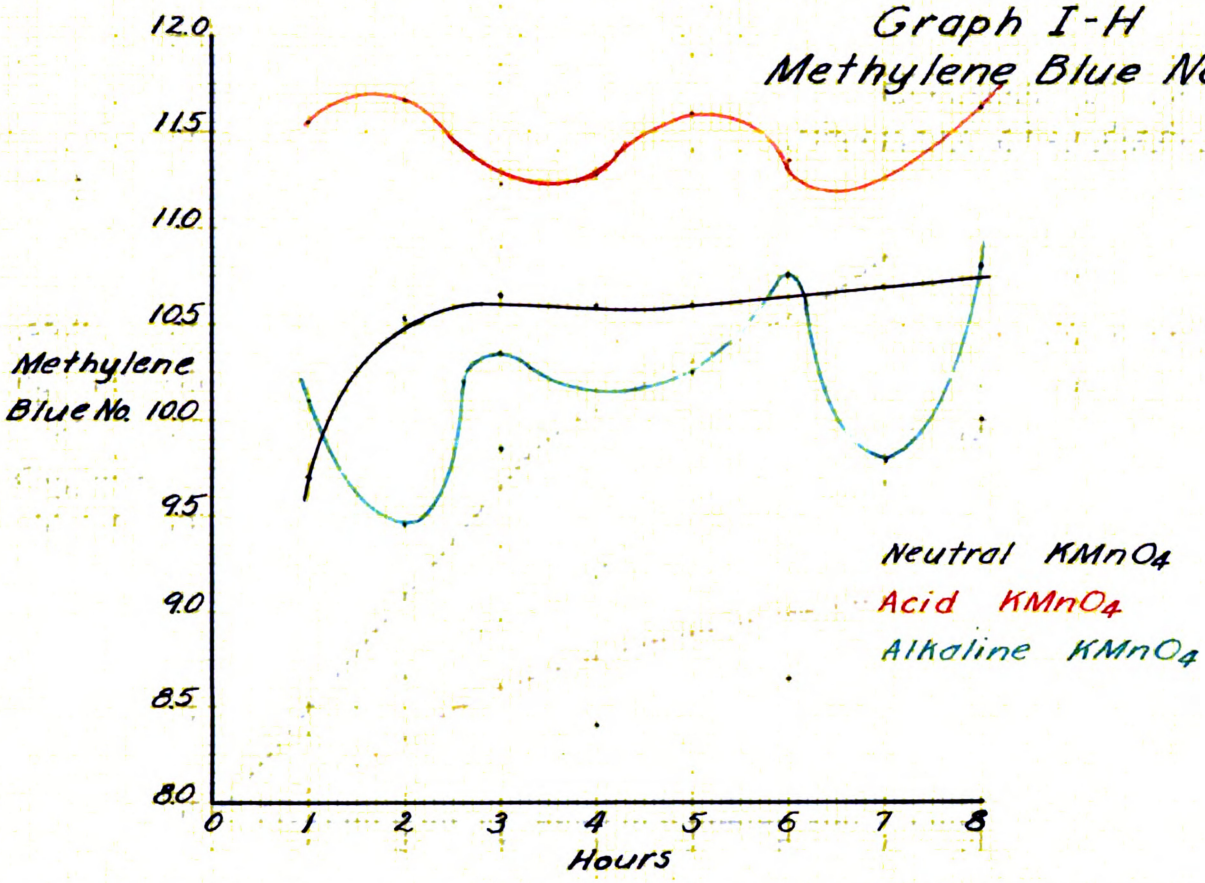


Graph I-G

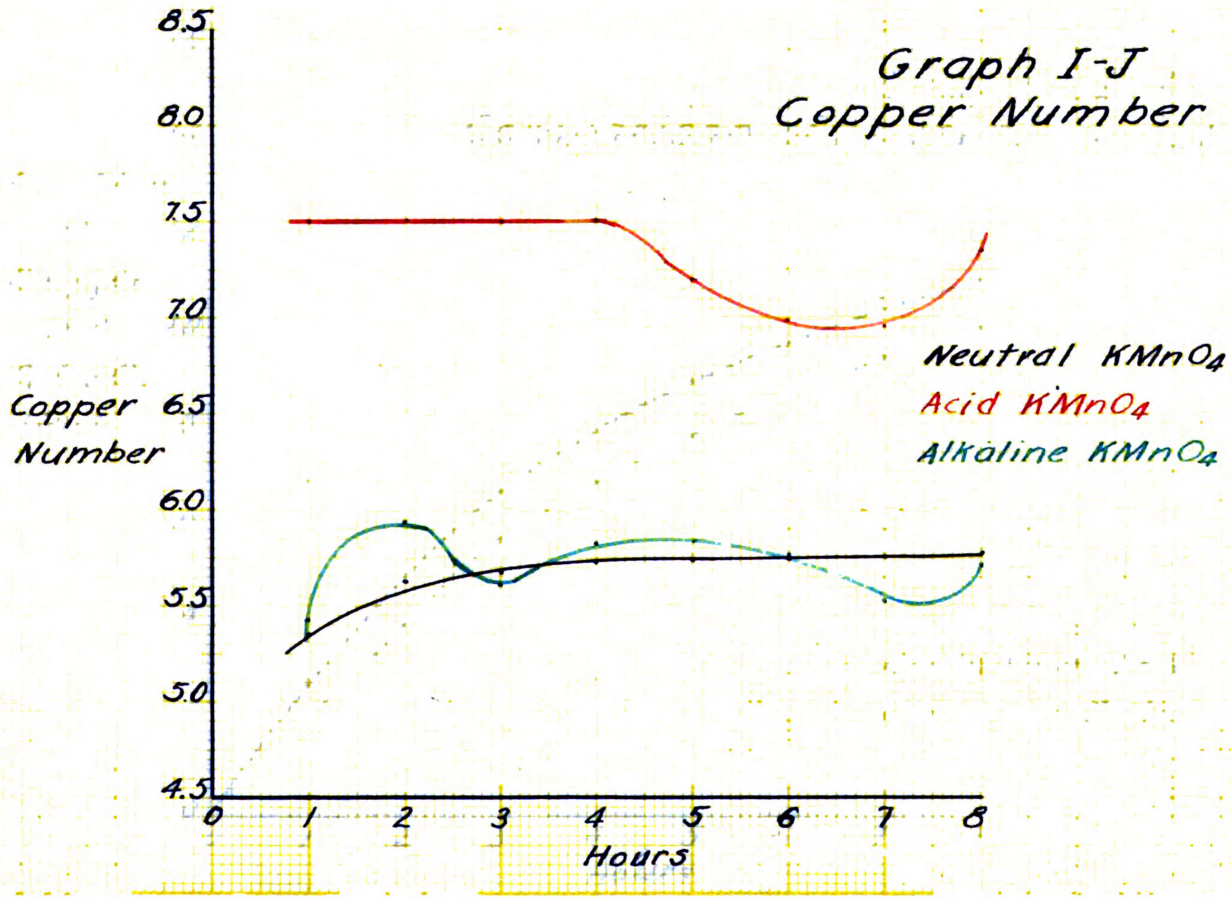
Alkali Solubility

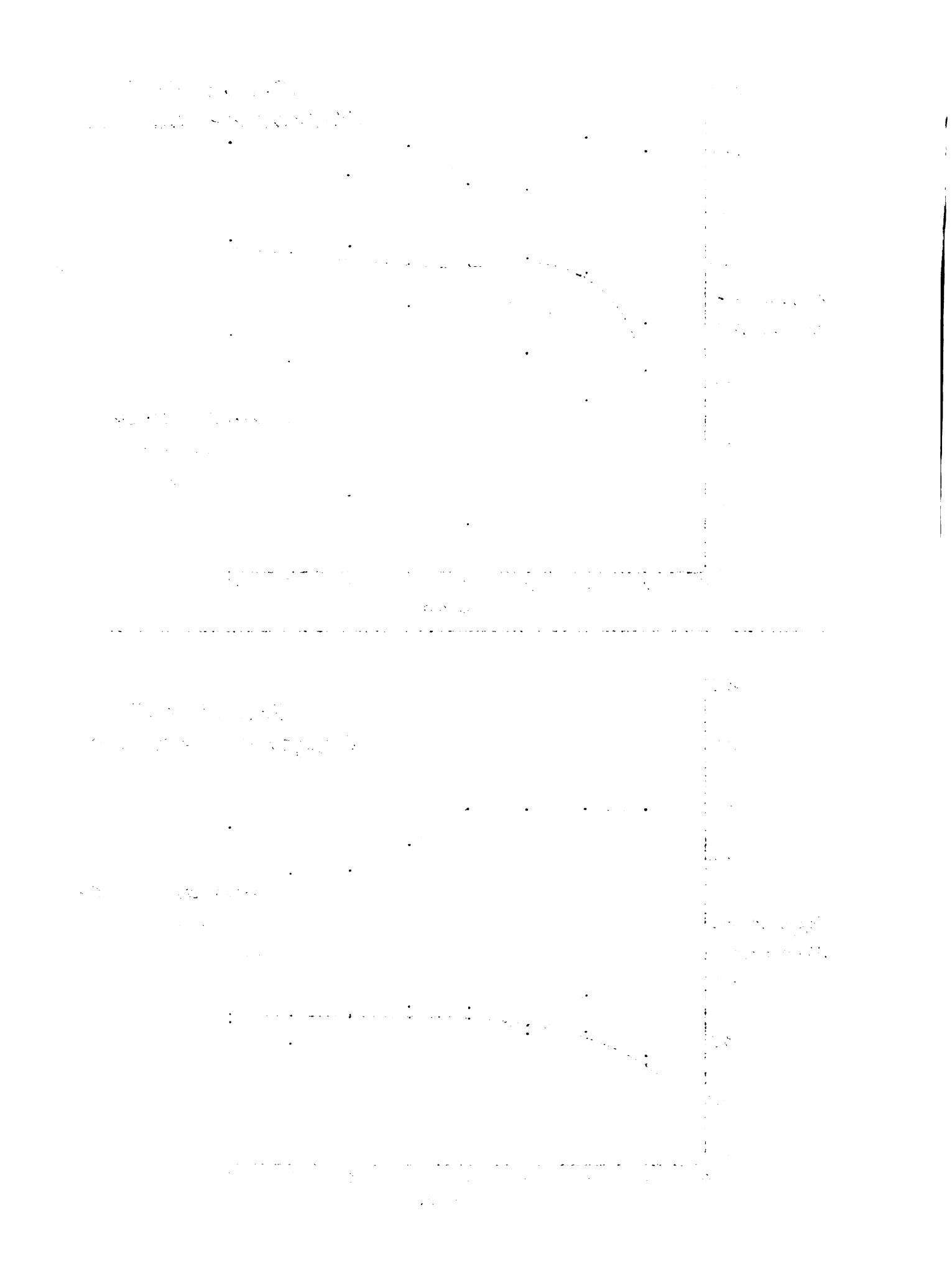


Graph I-H
Methylene Blue No.

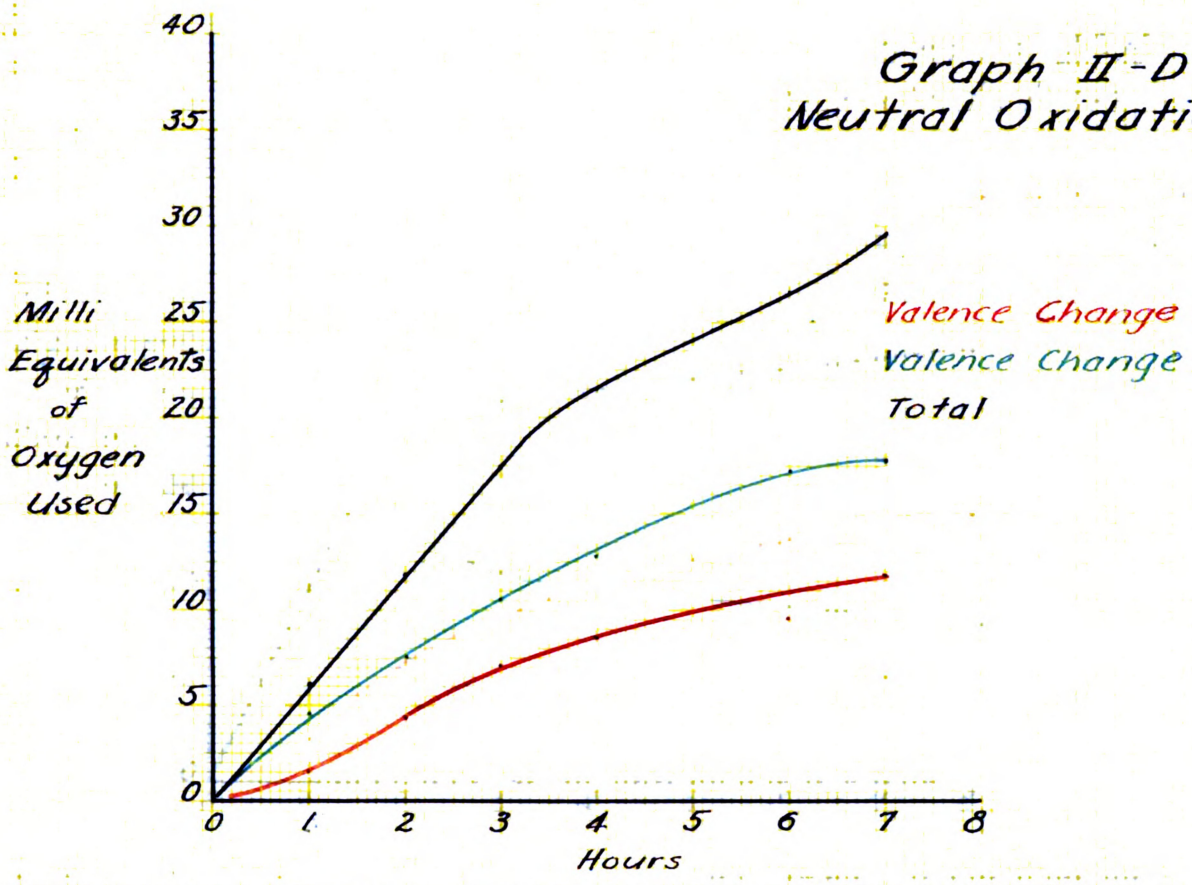


Graph I-J
Copper Number

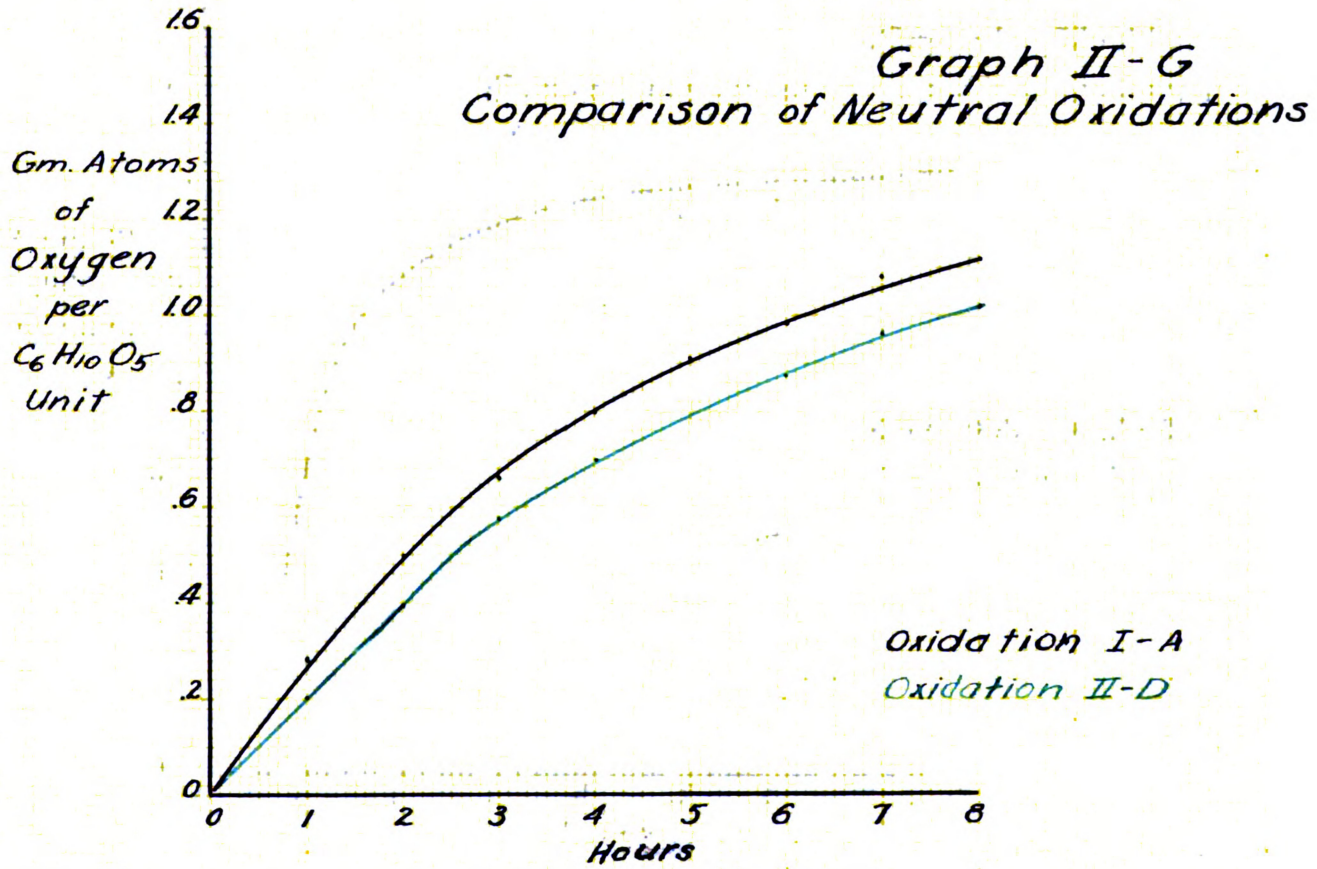


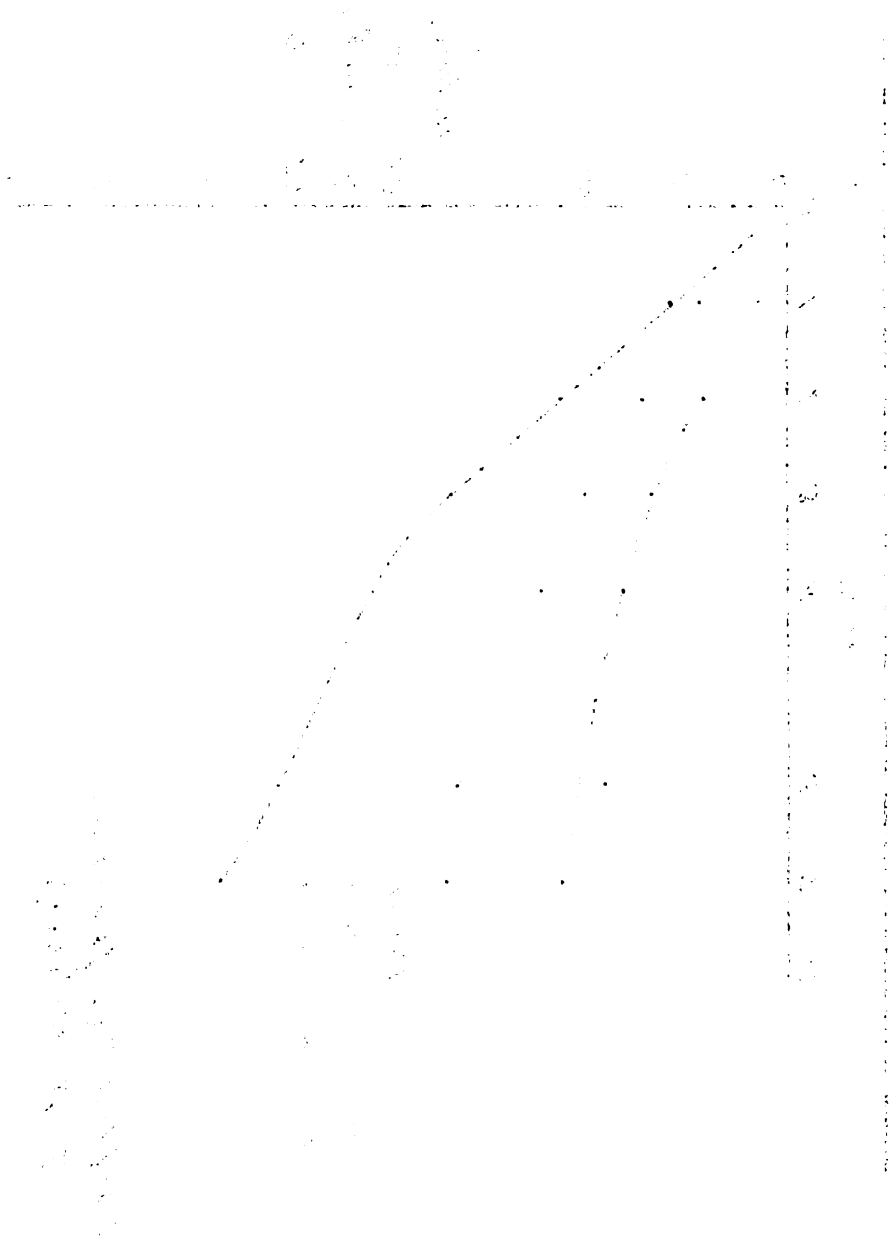


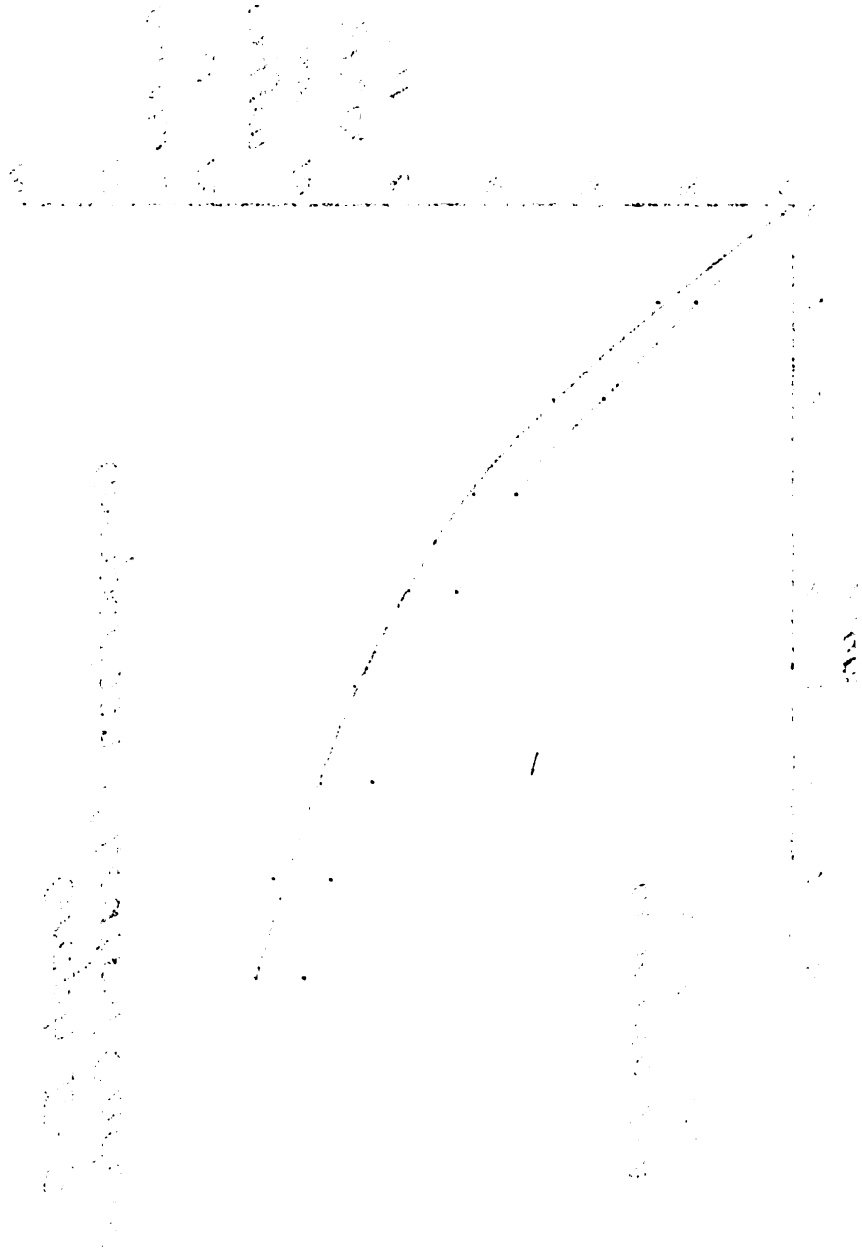
Graph II-D
Neutral Oxidation



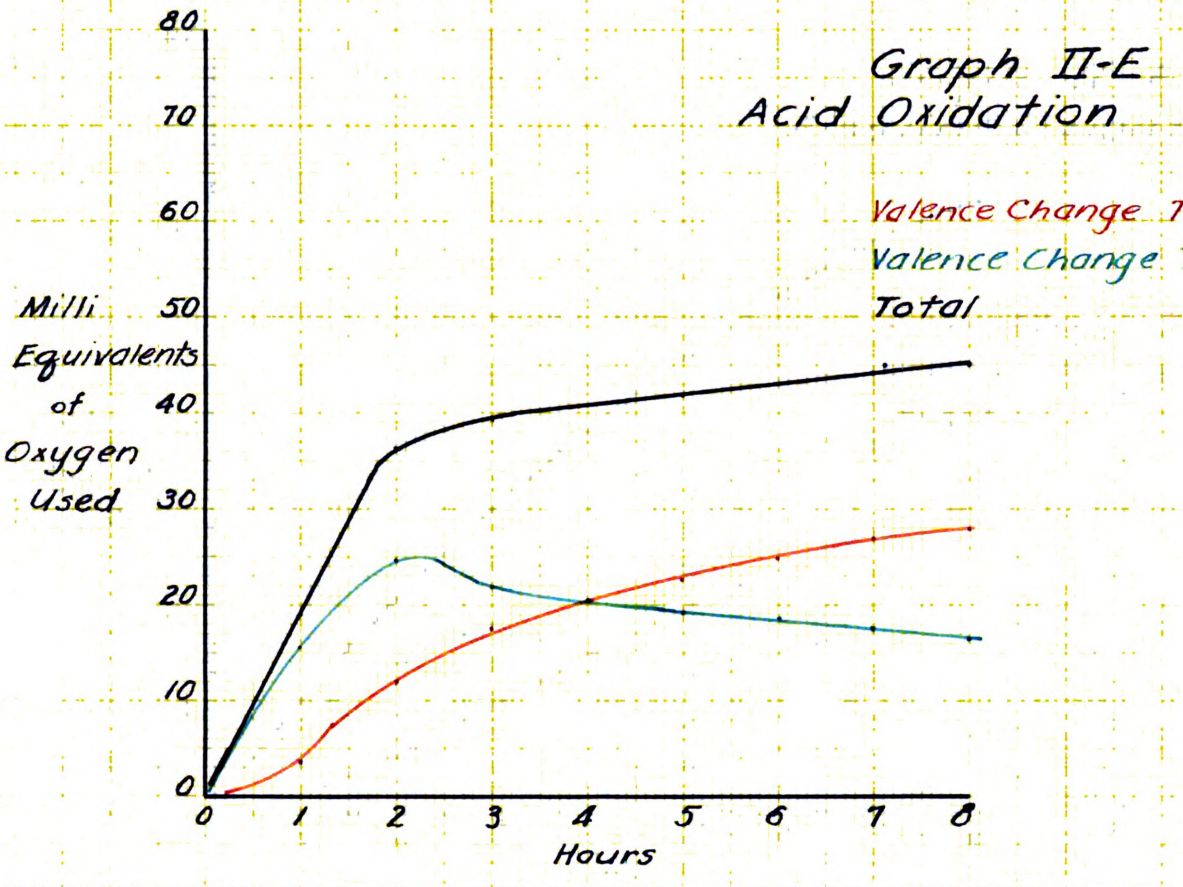
Graph II-G
Comparison of Neutral Oxidations



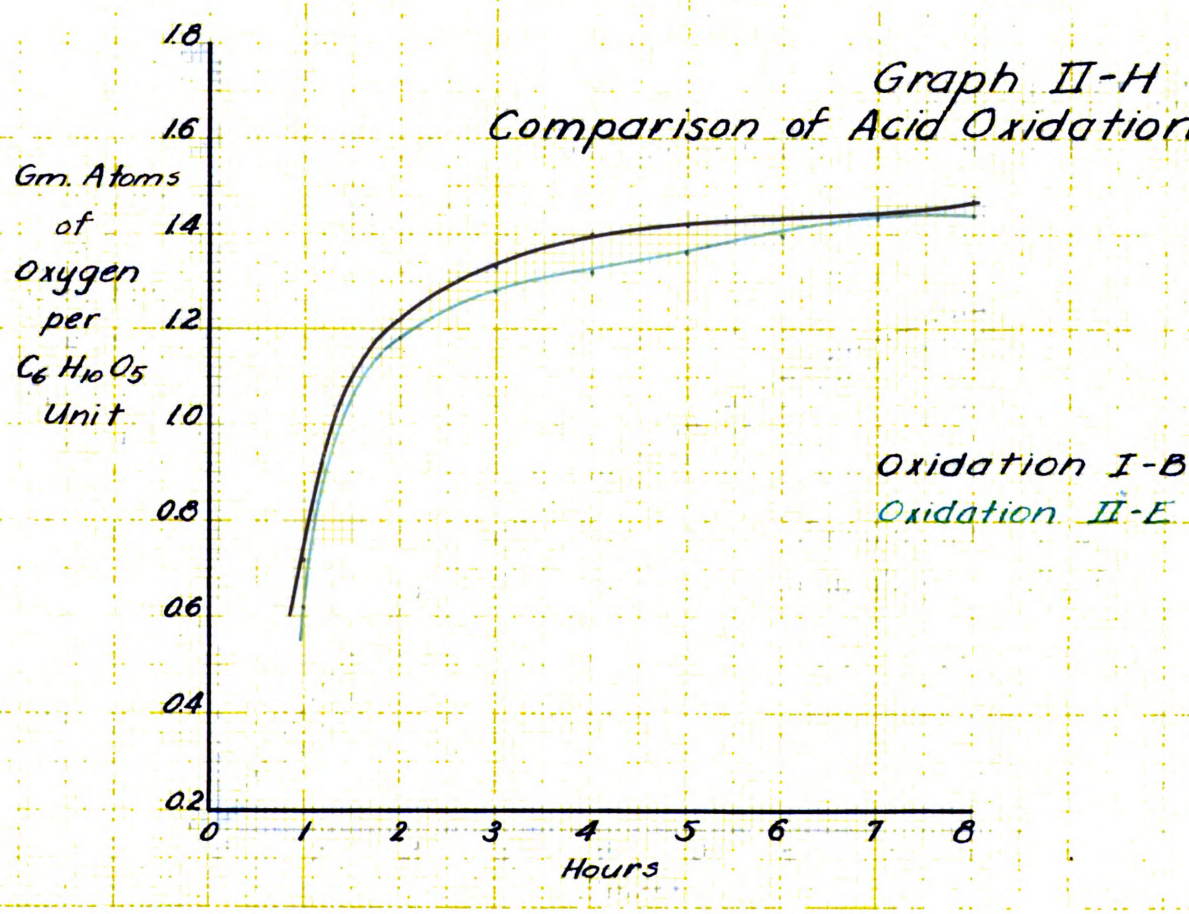


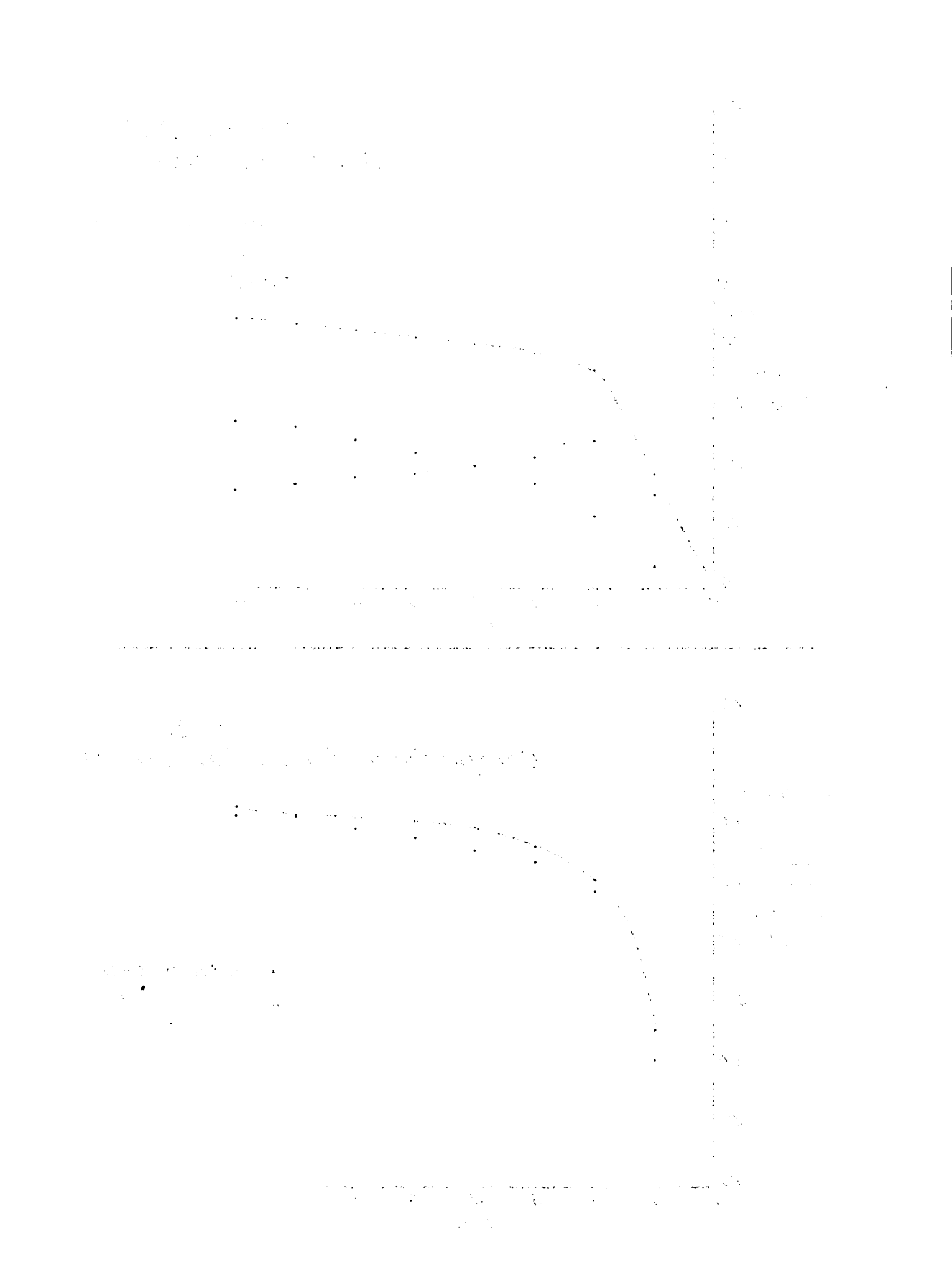


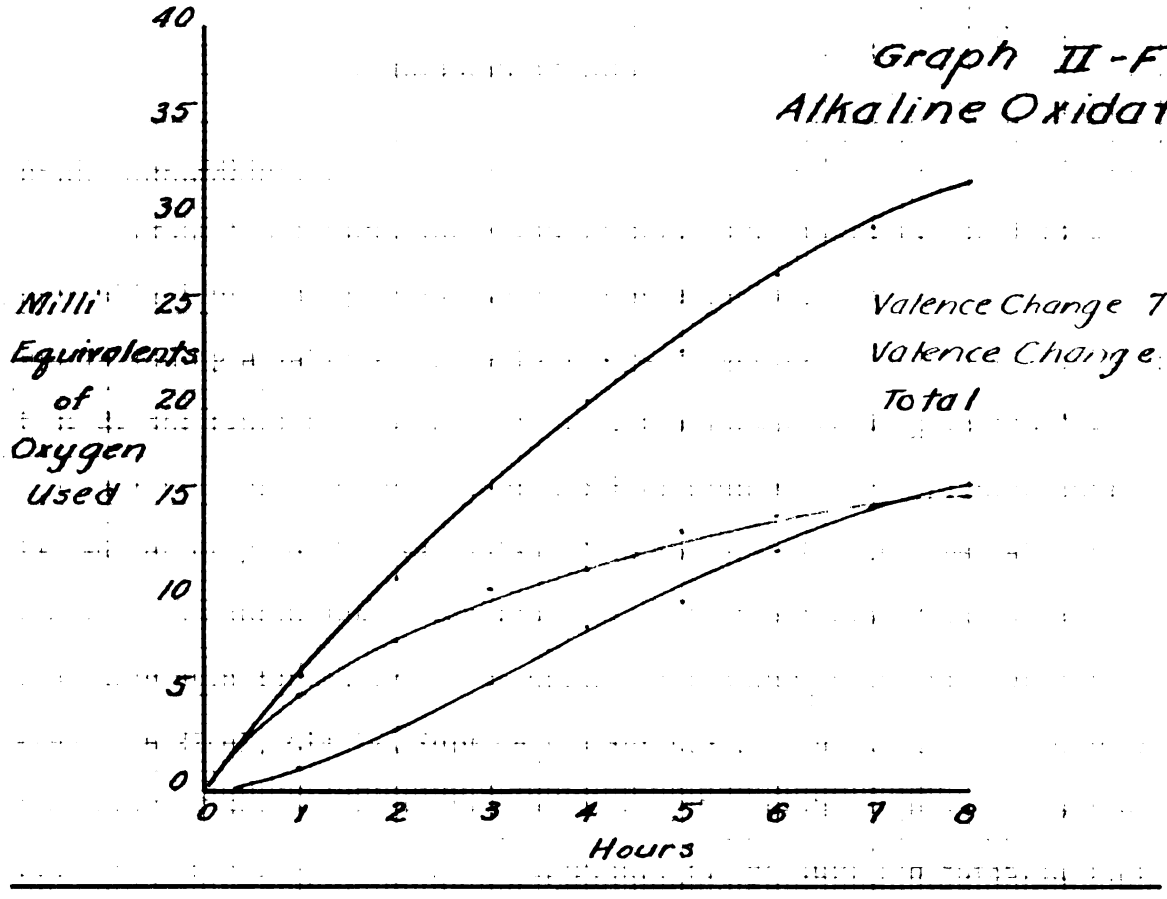
Graph II-E
Acid Oxidation

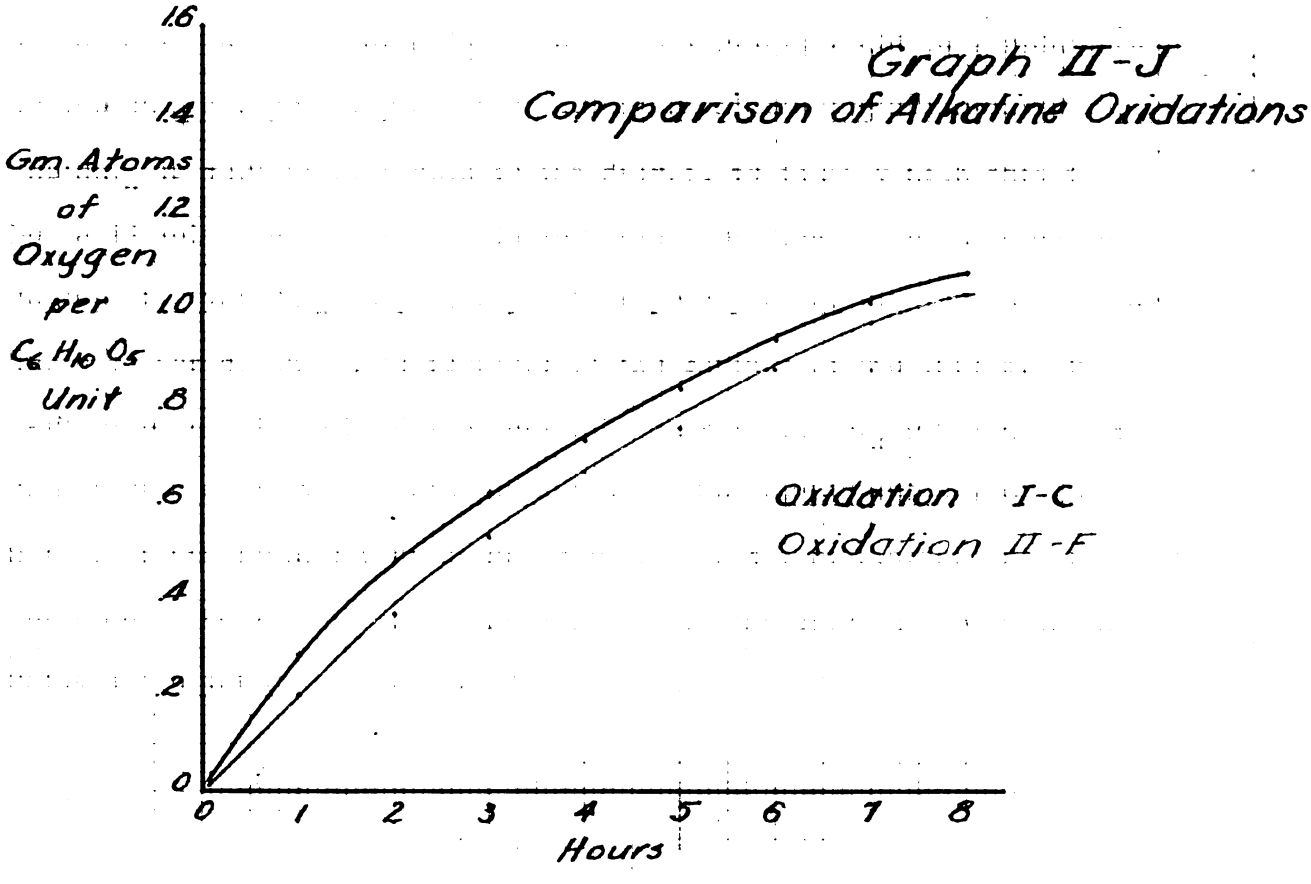


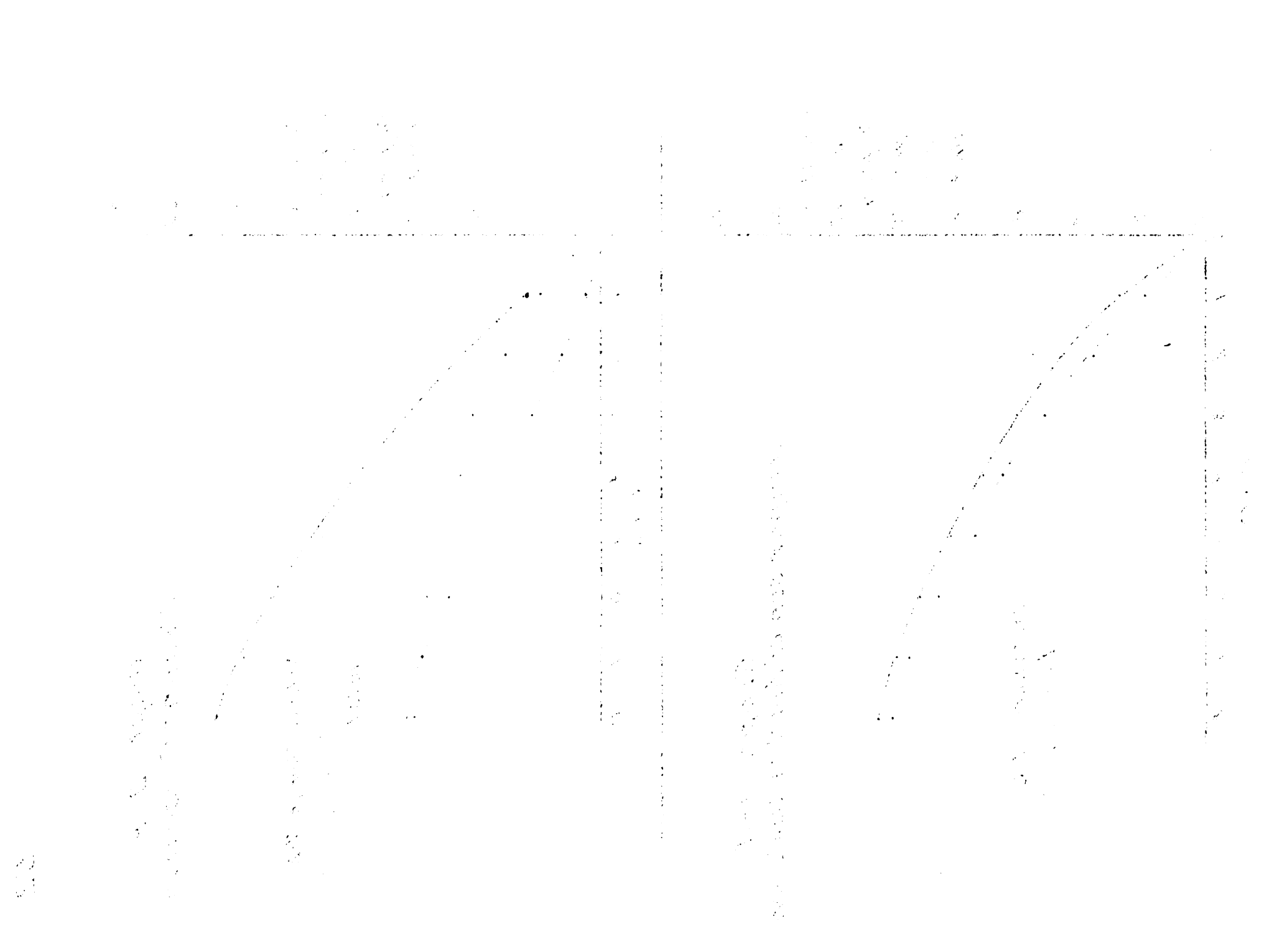
Graph II-H
Comparison of Acid Oxidations






Graph II-F
Alkaline Oxidation
Milli Equivalents of Oxygen Used
40
35
30
25
20
15
10
5
0
0 1 2 3 4 5 6 7 8
Hours
Valence Change 7-2
Valence Change 7-4
Total


Graph II-J
Comparison of Alkaline Oxidations
Gm. Atoms of Oxygen per C6 H10 O5 Unit
1.6
1.4
1.2
1.0
.8
.6
.4
.2
0
0 1 2 3 4 5 6 7 8
Hours
Oxidation I-C
Oxidation II-F



Discussion of Data

A. Neutral Oxidation

During the neutral oxidation of cellulose oxygen was used at a gradually diminishing rate. As would be expected, more of the oxygen was formed by a valence change in the permanganate from 7 to 4 than from 7 to 2, the final figures showing that the amount used up in the 7 - 4 change was nearly double that of the 7 -2 change. Since permanganate is reduced only to the tetravalent form in neutral solutions, all of the divalent manganese which was present at the close of oxidation must have been formed by the reduction of the MnO_2 which is precipitated in a finely divided form on the surface of the fabric. The acidic character of the oxidized residue probably has much to do with the reduction of the MnO_2. It is not difficult to picture the reaction that would take place between an organic residue rich in carboxyl groups and an adsorbed layer of MnO_2. The obvious result would be a reduction of the MnO_2 and probably a decarboxyllation of the organic material. The MnO_2 is very tightly held by the fabric, so tightly held that a hot acid solution of oxalic acid requires from five to ten minutes to remove it. The MnO_2 is probably either precipitated within the micellar units of the cellulose or adsorbed on the surface of the fabric, or perhaps both. It is hardly conceivable that moist MnO_2 would have the same effect without intimate contact with the fabric, and the acidic nature of the residue also seems to be one of the requisites of the reaction. The effects of the MnO_2 upon the character of the oxidized residue are discussed under acid oxidation.

The pH of the oxidizing solution showed a gradual increase as the oxidation proceeded. Since the $KMnO_4$ was the only soluble substance originally present, the pH of the solution would be dependent on it. Theoretically it would hydrolyze into KOH and $HMnO_4$, and it probably does to a slight entent. The effect of the oxidation would be equivalent to completely hydrolyzing the permanganate and removing the $HMnO_4$ because most of the MnO_4 radicles are destroyed during the oxidation. This effect would produce an appreciable increase in pH. During the oxidation some of the originally insoluble cellulose is oxidized to soluble organic acids which would tend to minimize the increase in pH. The percent loss in weight during oxidation also showed a gradual increase as the oxidation proceeded.

The analysis of the residues was not as informative as it might have been because the methods of analysis were more applicable to earlier stages of degradation than were represented in the present work.

The alkali solubility showed a large increase in the first hour of oxidation, and from then on a gradual increase. The copper number also showed a large increase in the first hour and then a gradual increase, the increment being constant after the third hour of oxidation. This constant increase in copper number indicates that the formation of reducing groups in neutral media is cumulative, or that they are formed at a slightly faster rate than they are destroyed. It is difficult to explain how reducing groups can exist in such a powerful oxidizing medium. The logical explanations for this are that they exist in some portion of the molecule which is not accessible to the oxidizing solu-

tion, or that there are other chemical groups present which are more readily oxidized. It is easier to picture the condition of the cellulosic fiber when it is remembered that there are two oxidizing agents present and that the MnO_2 might serve several purposes. For instance, it might form a coating over a partially oxidized bit of residue and thus protect it from the more powerful oxidant, $KMnO_4$. However, at the same time the MnO_2 might be oxidizing the residue, but its oxidizing effect would be much slower because it could react only at the solid to solid interface.

The methylene blue numbers in the present work were abnormally high because the original method had to be modified. Instead of using the 2.5 gram samples of the original method, 5 gram samples were used because of the small amount of material which was available for the analyses. For 2.5 grams of unoxidized cellulose a methylene blue number of .99 was obtained, and for a .5 gram sample a methylene blue number of 1.61 was obtained. This data shows that the decrease in sample weight caused the methylene blue number to be 1.6 times greater than the normal value. A proportionate increase in all of the methylene blue number which were determined in this work would be expected.

The methylene blue numbers determined on the residues obtained from the neutral oxidation showed a large increase in the first hour of treatment, a much smaller increase in the second and third hours and a marked irregularity beyond that time. This data indicates that the methylene blue number is a sensitive test only during the initial stages of oxidation.

B. Acid Oxidation

Because of the chemical nature of the $KMnO_4$, much more oxygen was used up during the acid oxidations. In neutral and alkaline media $KMnO_4$ is normally quantitatively reduced to MnO_2, and in strongly acid media it is completely reduced to divalent manganese. However, in the present work the oxidizing solution was only .1N with respect to acid and .3N with respect to $KMnO_4$, so a complete reduction of the oxidant was not possible. The effect of the acid was shown in the large amount of oxygen which was used up during the first two hours of oxidation. By the end of the second hour all of the $KMnO_4$ had disappeared from the solution and from the third hour onward oxygen disappeared from the system at a constant rate. All oxidation which took place after the second hour resulted from the reduction of MnO_2. As would be expected, the solid MnO_2 was very irregular in its oxidizing effect, and this irregularity was reflected in every measurement made during the oxidation process and every analysis of the residues.

The percent loss in weight during oxidation showed the large expected increases during the first two hours of treatment and was irregular, but fairly constant for the remainder of the oxidation period. This constancy shows that the effect of the MnO_2 was not powerful enough to convert the insoluble cellulose and oxycellulose to soluble degradation products.

The pH increased at a constant rate throughout the entire oxidation. The greater increases which might have been expected in the first two hours of oxidation were not obtained because the pH scale is

logarithmic and is more sensitive to small changes in H-ion concentration as the middle of the scale is approached. The apparent cause of the increase in pH is the neutralization of the acid by the potassium and manganese as the $KMnO_4$ and MnO_2 are reduced.

The alkali solubility of the residues showed very high values. There was a large increase during the first hour of oxidation, a small increase during the second hour and from that point onward the results showed a marked irregularity.

The copper numbers also showed very high values, no doubt due to the hydrolytic effect of the acid. There was a large increase during the first hour of oxidation and that value was maintained until the end of the fourth hour. During the remainder of the oxidation period the copper number gradually decreased at a constant rate. Since most of the acid and $KMnO_4$ disappeared during the first hour no appreciable increase in copper number would be expected after that time. The oxidizing effect of the MnO_2 in the later hours was to slowly destroy the reducing groups (aldehyde), thus lowering the copper number.

The methylene blue numbers also showed very high values. The value that was obtained at the end of the first hour remained fairly constant throughout the oxidation. Evidently the MnO_2 has no effect on the chemical groupings which cause an absorption of methylene blue.

C. Alkaline Oxidation

The initial pH of the alkaline $KMnO_4$ solution was slightly higher than the initial pH of the neutral solution, and the function of the oxidant was very similar in each oxidation. As in the neutral oxi-

dation, the oxygen disappeared at a gradually diminishing rate throughout the reaction, and the total oxygen used was nearly equal in both cases. In the alkaline oxidation the permanganate was reduced to MnO_2 quite rapidly during the first hour, and at a constantly decreasing rate for the remainder of the oxidation period. In contrast to this the permanganate was reduced to divalent manganese very slowly during the first hour, and at a constantly increasing rate from that time onward. At the end of the seventh hour of oxidation the amount of oxygen produced by a 7-2 valence change was equal to that produced by a 7-4 change, and at the end of the eighth hour had exceeded it. This indicates that the MnO_2 disappears more rapidly from an alkaline solution than from a neutral solution because in the neutral oxidation the amount of oxygen produced by both valence changes increased at the same rate after the first hour of treatment. In both neutral and alkaline media the reduction of permanganate to divalent manganese is a two-step process and must go through the MnO_2 stage. Therefore, any manganous ions which were present in the solution were formed by a reduction of MnO_2, and any increase in the rate at which they are formed means that a concurrent increase in the rate of MnO_2-reduction is also taking place.

The percent loss in weight of the cellulose showed the usual large increases during the first and second hours of oxidation, and a small constant increase for each succeeding hour.

The pH varied very little during the alkaline oxidation. The original pH was maintained until the fourth hour, when a slight lower-

ing occurred. During the last two hours of oxidation there was a slight increase in pH, and the final value was exactly equal to the original value. The buffering effect of the $NaHCO_3$ was probably responsible for the maintenance of a relatively constant pH in the system.

The alkali solubility of the residues obtained from the alkaline oxidation gave a variation in results that was very similar to the variation obtained from the acid oxidation. The values were irregular; in some cases an increase in oxidation (one hour period) caused an unexpected drop in alkali solubility, but the next sample would show the expected increase again. This is further evidence that MnO_2 is the active oxidant in the alkaline system during the later hours of oxidation.

The results from the copper number also showed irregularities, but nevertheless were quite similar to the results obtained from the analysis of the residues from the neutral oxidation. There was the characteristic large increase for the first hour of oxidation, a small increase for the second hour and a fairly constant set of values for the other six samples.

The methylene blue numbers were also quite irregular, but a constant value was indicated after the first hour sample.

D. Comparisons

In part II of the present work a set of oxidations which were very similar to those of part I were carried out. The same weight of cellulose obtained from the same source was oxidized at the same

temperature by similar oxidizing solutions for the same lengths of time. In spite of this reproduction of conditions the results showed that in every case more oxygen was used during oxidation in Part I than in Part II. However, each pair of corresponding lines on each graph (II-G, Hand-J) representing gram atoms of oxygen plotted against time showed exactly the same shapes, thus indicating that the oxygen was used at the same rate in each corresponding pair of oxidizing systems. The reason for the apparent higher values of oxygen used in Part I lies in the fact that different methods of analysis were used in each experiment. In Part I the excess oxalic acid was titrated directly and quite an appreciable error in the positive direction was caused by the soluble cellulosic degradation products which were present in the solution. Some of these soluble organic products were oxidized by the permanganate in the backtitration, and made it appear that more than the actual amount of oxalic acid was present, and this in turn gave the false impression that less oxidizing agent remained at the close of the oxidation period and that more had been used during the oxidation than had actually been used. The method of analysis used in Part II gave a negative error, and thus instead of compensating for each other the errors caused a noticeable difference in the results. In Part II the excess oxalic acid was determined by precipitating calcium oxalate, filtering and dissolving it, and finally titrating the oxalic acid. Here the error would be much smaller, but nevertheless would lead to a slightly low result. In the acid oxidations there was less variation between the two sets of data than in the neutral and alkaline, and in the later hours of

oxidation the values approached each other. There is no apparent reason for the better agreement of results in the case of the acid oxidation. However, the similarity in the rates of oxidation in each pair of experiments clearly indicates that the oxidation of cellulose under identical conditions is reproducible.

In contrasting the three types of oxidation it is very noticeable that only in the case of the neutral oxidation did the different measurements show the consistent increases that would be expected in such a progressive reaction. The probably reason for this is that no other chemical agent was present to complicate and interfere in the normal oxidation process. However, in most of their effects the neutral and alkaline systems were very similar. The cause of this can be traced back to their initial pH's which were in the same range.

The acid system showed a much larger disappearance of oxygen during the first three hours than the other two systems did. During this time all of the $KMnO_4$ disappeared from the acid solution and from that time on the oxygen disappeared very slowly as the MnO_2 was gradually reduced. The neutral and alkaline solutions suffered a loss in available oxygen at nearly the same rate throughout the entire oxidation period with the neutral solution showing slightly higher values. In spite of the fact that the oxygen disappeared at the same rate from both systems, the character of the oxidation process and the residues was quite irregular in the case of the alkaline oxidation. The acid oxidation showed a 75.3% disappearance of available oxygen, while in the neutral system it was 56.7% and in the alkaline 55.7%.

The changes in pH during oxidation were very similar in the neutral and acid oxidations. Both showed a gradual but steady increase, while the alkaline reaction produced a nearly constant pH. The reason for the failure of the alkaline system to show an increase was undoubtedly the presence of the $NaHCO_3$, which would react with any KOH that might be formed during the oxidation and would prevent an increase in pH.

Upon comparing the percent loss in weight of the cellulose during oxidation, it is found that the neutral and alkaline systems produced nearly the same effect except that in every case the values were slightly higher for the latter. The acid solution gave much higher values than the other two during the first three hours, but it showed no increase after that time. At the end of the fifth hour the increasing values of the alkaline solution had equalled and surpassed that of the acid solution, and the following hour saw the value of the neutral solution surpass the acid solution. The explanation of this data is fairly evident. The high percent loss in weight of the cellulose during the first three hours of the acid oxidation was a result of the large amount of oxygen which was consumed during that time. Much of the cellulose was probably oxidized to carbon dioxide, and during the first two hours a partial hydrolysis might have accompanied the oxidation with the formation of soluble hydrolytic products. Since oxidized cellulosic residues are soluble in alkali, it was expected that there would be a larger percent loss in weight during the alkaline oxidation. The neutral system was slightly alkaline

at the end of the oxidation period and showed the intermediate value which was expected. The organic acids that were formed during the oxidation were soluble in the alkaline oxidizing medium, partially soluble in the neutral medium and difficultly soluble in the acid medium. By the same reasoning the alkali solubilities were expected to show a reversed order of the three systems because some of the oxidized residue was soluble in the neutral solution and a still larger percent was soluble in the alkaline solution.

The results on the alkali solubilities of the residues fulfilled this expectation. The residues from the acid oxidation gave values which were one and one-half times higher than those from the other two types of oxidation, and the final values for the neutral were slightly higher than those of the alkaline. The values from the alkaline and acid oxidations gave curves that were quite similar, and in both cases the values were irregular, but the final samples showed higher values than the initial samples. The results from the residues obtained by neutral oxidation again showed the characteristic constant rate of increase from hour to hour. The alkaline and neutral oxidations again gave samples which showed numerically similar results.

The results from the determination of methylene blue numbers were much like those from the alkali solubility determination. The residues from the acid oxidation gave much higher values than the others. However, the values were very irregular and there was no marked increase or decrease in the various samples. Once again the values for the residues from the alkaline and neutral oxidations were in the same range

with the latter type showing noticeably higher numbers. The neutral samples again showed the gradual increase from hour to hour, and the alkaline samples showed irregular values.

The results from the copper number determinations substantiated the data that was obtained from the other analyses of the residues. The acid-treated samples gave values which were half again as large as those from the other oxidations. And once again the samples from the alkaline and neutral systems gave values which were nearly equal, with the former showing their usual irregularity and the latter showing their gradual increase.

It is easy to see why the residues after the third hour of acid oxidation should give irregular results, because the oxidation from that time onward was a result of the reduction of MnO_2 at the interface between the MnO_2 and the cellulosic material. The cause of the irregularity in the case of the alkaline oxidation is not so easily explained, because permanganate was present in the system throughout the oxidation. The only difference between the neutral oxidation, whose residues showed gradual increases in every analysis, and the alkaline oxidation was the accumulation of the MnO_2 in the former system and its gradual disappearance in the latter system. This clearly indicates that the permanganate was the active oxidant in the neutral oxidation and that the MnO_2 was responsible for a great deal of the degradation which took place in the alkaline system. It is known that sugars are very susceptible to oxidation in alkaline solutions, so it seems possible that the MnO_2 would have a greater oxidizing effect in the alkaline solution because of the greater susceptibility to oxidation of the cellulosic

material. Pure cellulose is very stable toward alkalis, but degraded cellulose does not possess this property. The cellulosic material in contact with the MnO_2 would certainly be partially oxidized and would have lost its stability toward alkalis. This is suggested as a possible explanation for the marked disappearance of MnO_2 during the alkaline oxidation and for the very noticeable irregularities in the results from the analysis of the residues.

SUMMARY

1. The oxidation of cellulose by $KMnO_4$ under carefully controlled conditions is reproducible.

2. The rate of oxidation of cellulose by $KMnO_4$ is very similar in neutral and alkaline solutions.

3. The pH of neutral and acid $KMnO_4$ solutions increases steadily during the oxidation of cellulose while the pH of an alkaline solution remains constant.

4. When in very close contact with partially degraded cellulose, moist MnO_2 exerts an oxidizing effect. The MnO_2 is reduced more readily in an alkaline solution than it is in a neutral solution. The oxidizing effect of the MnO_2 is not powerful enough to convert appreciable amounts of insoluble cellulosic products to soluble products. The MnO_2 oxidation has the effect of lowering the reducing power of the oxidized residues.

5. Copper number and methylene blue number are sensitive tests for extent of oxidation only during the initial stages of oxidation.

6. The alkali solubility is a good index of the extent of oxidation in the later stages.

Bibliography

1. Haworth and Machemer	J. Chem. Soc.		2372	(1932)
2. Thomas	J. Soc. Chem. Ind.	52	80-86	(1933)
3. Cross, Bevan and Beadle	Berichte	26	2527	(1893)
4. Knecht and Thompson	J. Soc. Dyers and Colourists	38	132-6	(1922)
5. Knecht and Egan	J. Soc. Dyers and Colourists	39	67	(1923)
6. Lewis, S. J.	J. Soc. Dyers and Colourists	40	29-40	(1924)
7. Hibbert and Parsons	J. Soc. Chem. Ind.	44	473-85	(1925)
8. Kalb and Falkenhausen	Berichte	60-B	2514-20	(1927)
9. Hibbert & Hassan	J. Soc. Chem. Ind.	46	407-411	(1927)
10. Miss Elaine Alvord	Masters Thesis Michigan State College			
11. Miss Louise Drake	Bachelors Thesis Michigan State College			
12. Murray, Staud and Gray	J. Am. Chem. Soc.	52	1508-19	(1930)
13. Sommer and Markert	Monatschr Textile Ind.	46	132-3 173-5	(1931)
14. Doree and Healey	J. Soc. Dyers and Colourists	49	290-5	(1933)
15. T. Brissaud	Mem. Poudres	27	195-213	(1937)
16. Birtwell, Clibbens and Ridge	J. Textile Institute	16	13-52	(1925)
17. Clibbens and Geake	J. Textile Institute	15		(1924)
18. Heyes	J. Soc. Chem. Ind.	47	90-92	(1928)
19. Birtwell, Clibbens and Ridge	J. Textile Institute	14	297-313	(1923)

20. Doree	"Methods of Cellulose Chemistry"		p.24-25	(1933)
21. Neale and Stringfellow	Trans. Faraday Soc.	33	881-9	(1937)
22. Clibbens and Geake	J. Textile Institute	17	127-9	(1926)