

A STUDY OF THE EFFECT OF pH
ON THE DEGRADATION OF WOOD PULP
BY SODIUM HYPOCHLORITE.

By

CYRIL ROMANOVSKY B.Sc.

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INTRODUCTION

GENERAL INTRODUCTION

Cellulose appears in all plants as the fibrous portion of the cell walls. It always exists in association with other substances which are essentially non-cellulosic in character, the nature and quantity of which varies according to the type and age of the plant.

The hairs of the cotton plant are composed of cellulose in an almost pure form and constitutes one of its chief sources. The purification of the raw cotton is a simple process and consists of extracting the encrusted fat, wax and other soluble impurities with organic solvents. A subsequent treatment with dilute alkali followed by washing and a light hypochlorite bleach frees the cellulose from the remaining pectic-like non-cellulosic substances.

Woody plants are also an important source of cellulose, but here it occurs in association with a large amount of impurities, such as lignin and suberin, and the extraction of the pure cellulose is much more complicated. First the pulp is extracted by cooking wood chips with any one of three accepted solutions. A solution of calcium or sodium bisulphite and free sulphurous acid is used in the "sulphite process", the one most extensively employed. The "soda" and "sulphate processes" use, respectively, a solution of sodium hydroxide, and a solution containing in

addition to sodium hydroxide, some sodium sulphide originating from sodium sulphate. The remaining lignin and other coloring matter in the pulp so obtained is then removed by a process of bleaching. The cellulose still contains a few per cent of non-cellulosic carbohydrates, such as xylan and araban, and also a little resin but these may be removed by a final treatment of alkaline refining.

It is with the bleaching stage in the purification of cellulose that the following dissertation is concerned.

The term bleaching signifies the art of destroying the natural color of vegetable and animal products in such a manner as to leave them unimpaired with as white an appearance as possible. In the bleaching of cellulose, an attempt is made to direct the oxidation so as to attack the non-cellulosic constituents without effecting a change in either the physical or chemical aspects of the cellulose itself.

Among the various bleaching agents in use, nature's own elements of sun, wind and rain are the original and mildest of all. The more modern bleaching agents used in the textile industry are of a chemical nature, and their action is generally one of oxidation.

Hydrogen peroxide has found extensive use in the bleaching of delicate fabrics, ivory and hair, and it

is perfectly harmless to both operators and goods. Another mild bleaching agent with powerful bleaching effect is sulphur dioxide; it has been of prime importance in the industrial bleaching of such delicate materials as silk and wool. Chlorine and especially its oxy-compounds are widely employed for bleaching purposes and are used almost without exception in the cellulose industry.

The nature of the impurities and coloring matter found in wood pulp necessitates the use of a powerful oxidising agent in the bleaching treatment. A cheap and effective bleaching agent for use in the cellulose industry has been found in the hypochlorites, those of calcium and sodium being most commonly used.

Due to the similarity in chemical properties between some of the impurities and the cellulose itself, it is difficult to effect their removal without impairing, to some extent, the quality of the finished product. Although the hypochlorites impart extreme brightness to the cellulose, they also cause a breakdown in the cellulose fiber. The action of the hypochlorites upon the cellulose varies according to the hydrogen ion concentration of the bleach liquor, marked changes being manifested between the alkaline, neutral and acidic zones. By virtue of this nature of hypochlorite action, optimum conditions of hydrogen ion concentration, at which the cellulose itself is least modified

by a maximum removal of impurities, could be determined. The product demonstrating a minimum of degradation is obtained when the bleaching operation is carried out in an alkaline medium, the actual pH varying from 8 to 10 depending upon the source and preceding treatment of the pulp, and also upon the ultimate use for which the cellulose is intended. Generally a solution containing 0.5% to 1% active chlorine is employed at temperatures ranging up to 40 degrees C.

THEORETICAL INTRODUCTION

(a.) Structure of Cellulose.

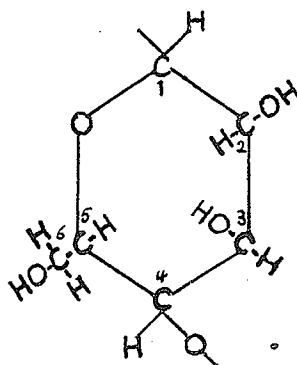
The chemistry of cellulose degradation products is necessarily closely connected with that of cellulose itself, and a consideration of the structure of cellulose is deemed desirable before proceeding to the discussion of some of the degradative modifications that it may undergo.

Cellulose is the fibrous portion of the cell walls of all plants. It may be obtained from any plant by the careful removal of the non-cellulosic constituents which exist in varying amounts and as different substances according to the nature and age of the plant. It appears to the naked eye as a fibrous aggregation, and under the ordinary microscope the fibers are seen to be made up of fibrils which are twisted about one another.

Cellulose has never been isolated as an absolutely pure chemical individual. Although qualitative analyses show samples from every natural source to be made up of carbon, hydrogen and oxygen, there are slight variations in its percentage composition. These variations are believed to be due to either residual impurities or to degradation products of the cellulose formed when undergoing purification. All quantitative analyses indicate an empirical formula of $C_6H_{10}O_5$, and chemical investiga-

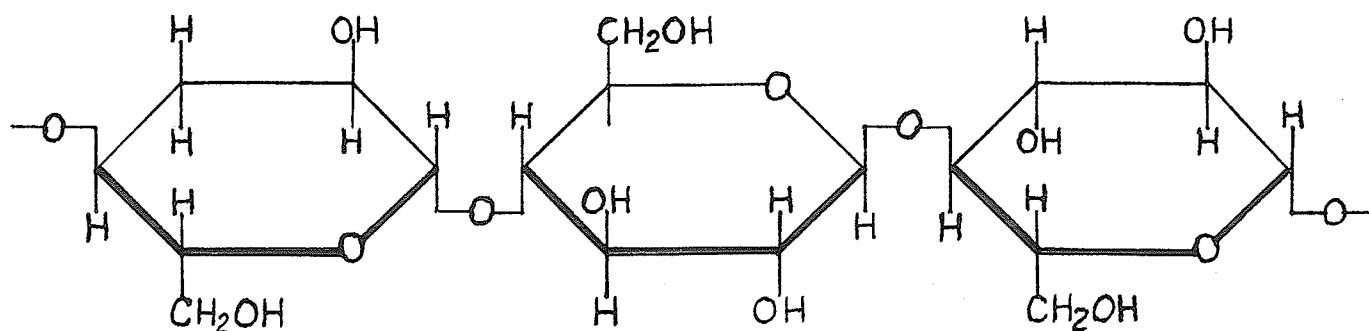
tions as well as X-ray diffraction studies indicate that the twenty-one atoms are arranged as in β -glucose anhydride, (1). (figure 1.)

Figure 1.



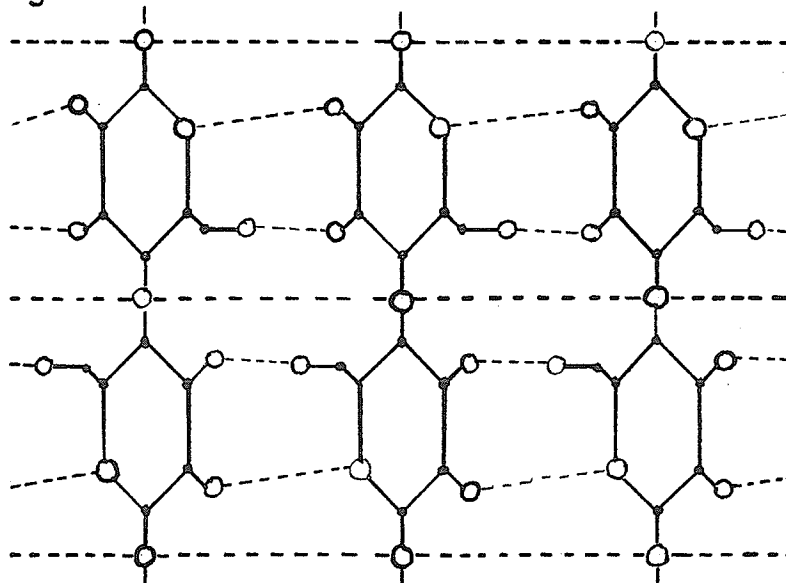
Degradation and hydrolysis after methylation indicate that these glucose residues are joined through their carbon atoms numbered 1 and 4 by oxygen bridges to form a primary valence chain of unascertained length. These so called molecular chains may consist of one hundred to three thousand glucose rings in the native cellulose, and alternate rings are rotated through one hundred and eighty degrees about the chain axis. (figure 2.)

Figure 2.



The fine structure of cellulose as identified by X-ray analysis has revealed the configuration of the chains to be crystalline within very small volumes, but, there is also an indication that the crystalline order is interrupted at undetermined intervals which show some degree of periodicity. It is assumed therefore, that, within the geometrical unit cell, the individual molecular chains are arranged parallel to each other. It is now generally recognized that the bonds between the hydroxy groups are responsible for holding the carbohydrate molecules together in the crystalline state. Hence, it is believed that the secondary valences or polar forces of the hydroxy groups which lie along the sides of the parallel chains align these primary valence chains into "bundles" or crystalline aggregates. (figure 3.)

Figure 3.



These assumptions have been confirmed by chemical analysis and synthesis, and subsequent X-ray studies of the various products formed. They also conform accurately to the chemical behavior of cellulose as a trihydroxy alcohol. It is assumed further that the chain bundles of varying length are of fixed breadth and thickness, and are arranged in hypothetical units, (2). These micelles are supposedly held together by supermolecular forces, and in the native cellulose fibers they are usually oriented parallel to the fiber axis.

There has been much evidence of late to justify the belief that there is yet another unit existing between the micelles and the fibril, and that these units are held together by colloidal rather than valence forces.

Ludtke, (3), was able to discern very small fibrillar sections under the microscope which he called "fusiform bodies". He assumed that one of these bodies, according to its size and the size of the micelles, contained eight micelles united in a row, and that a row of twenty to one hundred of these bodies, held together by a colloidal substance, made up the fibril.

From microscopic investigations of young cotton cell-membranes, in which the relative proportion of cellulose to non-cellulose is small, W.K. Farr, (4), obtained similar results. She observed numbers of

uniform sized ellipsoid particles of cellulose embedded in the inner region of a dense homogeneous colloidal mass. In contrast to the colloidal matter, the cellulose particles were nearly opaque, and their ability to diffract X-rays indicated their crystalline nature. These particles were of similar size and shape to the "fusiform bodies" described by Ludtke,(3). She observed moreover, that the particles were almost invariably oriented in respect to each other, with their long axes parallel to the surface of the protoplast of the cell-membrane. In mature cell-membranes, where the matrix is reduced to a minimum, she found a thin layer of the colloid surrounding the entire fiber. There were thinner layers alternating with the layers of cellulose fibrils in the wall, and she believed that there was even a thinner layer around each individual particle where the colloidal matter took on the role of cementing material.

Farr concluded from her observations that during the process of fiber development in the plant, the fibrils are formed from single rows of cellulose particles arranged end to end, and the fibrils, closely intertwined, form the successive layers of the cell-membrane of the mature fiber.

It is believed that the plant uses the primary valences of simple compounds for synthesising the

disaccharides and the oligosaccharides, stabilizes them by dehydration, and thereafter leaves it to the polar, supermolecular and micellar forces to produce the stable cellulose particles.

The complicated structure of cellulose, both chemically and physically, tends to cause any of the reactions which it undergoes to be heterogeneous in contrast to the lower carbohydrates and most other compounds. Moreover, the uncertainty of the complete structure of cellulose adds to the confusion in determining the direction in which any reaction proceeds.

On the whole, cellulose undergoes the reactions of a trihydroxy alcohol and of the simple sugars. According to the present conception of cellulose structure, all the potential aldehyde groups except the ones at the ends of the molecular chains are involved in the linkings between the individual glucose anhydrides, and hence, cellulose lacks the characteristic reducing powers of most of the sugars and its chief reactions are based on its hydroxyl groups. Cellulose would therefore be expected to act as an aliphatic alcohol forming addition products with alkalies and some complex salts, alcoholates, esters and ethers, and on oxidation, a stepwise conversion of its alcoholic groups into aldehydic or ketonic and into carboxylic groups. Cellulose is also amenable to

hydrolysis as are all other polysaccharides.

Reaction may be by disrupting the linkages holding the glucose units together, or it may be any of the reactions of the hydroxy groups. Tendency for one hydroxy group to react before the others is slight in acid medium, but may assume importance in alkaline reactions, e.g. oxidation. The reaction of cellulose in the fibrous state or any other solid state is governed by the rate of diffusion of reagent to the individual hydroxy groups. This in turn is governed by the peculiarities in structure of the fiber, and the degree of swelling of the cellulose. Increase of volume due to swelling may proceed to a considerable extent without essential loss to the previously orderly arrangement. The greater the extent of swelling, the greater is the rapidity of the reaction; the greater the uniformity of swelling, the greater is the uniformity of the reaction.

(b.) Cellulose Degradative Modifications.

(1.) Hydrolysis.

Hydrolysis of cellulose is brought about in the same way as is the hydrolysis of other polysaccharides, viz., the action of dilute mineral acids. This modification by acids follows a definite course, the nature of the modification being independent of the conditions. The rate of the reaction, however, does depend on the hydrogen ion concentration and temperature. Cellulose, upon hydrolysis, undergoes an irreversible modification which is exhibited by a decrease in its intrinsic strength and by a lowering of the viscosity in cuprammonium solution.

The products of cellulose hydrolysis are known as hydrocellulose, and among them may be found substances which have undergone various stages of modification, ranging from almost untouched macromolecular chains down to monomeric glucose.

In the formation of the hydrocellulose the only conceivable chemical change is a shortening of the long cellulose chains. A physical change also occurs which is manifested by a swelling effect on the cellulose fibers. Under the hydrolysing effect of the acid a number of the oxygen bridges may be ruptured, resulting in a mixture of saccharides with lower molecular weight and pronounced reducing power, due to the liberation of aldehyde groups,

with chains still of considerable length. The chief reason for the variable degree of modification of the products of cellulose hydrolysis, as is also the case in any reaction cellulose may undergo, is that reaction begins on the surface of the fiber and works inward.

The dual nature of the cellulose structure probably also explains the heterogeneity of cellulose reactions as compared to those of the simpler carbohydrates. The pectic-like colloidal matrix which exists in the cellulose fiber is very similar in composition to that of the cellulose itself, and would be expected to produce similar products. The rate of reaction, however, would be faster than that of the cellulose particles as the pectic phase does not exhibit the orderly arrangement, and is not stabilised by the secondary and supermolecular forces with which the cellulose particles are endowed.

Moreover, the colloidal matrix surrounding the fibre would be expected to undergo modification before that of the matrix between the fibrillae, and the latter before the cementing material which holds the cellulose particles together.

Evidence for the above theory has been produced by Compton, (5), in a very convincing manner. He showed that the so-called solution of cellulose in cuprammonium solution was merely a solution of the intercrystalline

cementing material, leaving the crystalline phase dispersed.

(2.) Oxidation.

Oxidation, as is the case among the sugars, is a more complex process than hydrolysis. The course of the reaction depends essentially upon the nature of the oxidising agent, although there is some tendency to the formation of aldehydic oxycellulose in acid solution and of carboxylic oxycellulose in alkaline solution. As is the case in hydrolysis, the reaction is one of degradation, i.e., an irreversible modification occurs with a resulting lowering of viscosity in cuprammonium solution and a decrease in fiber strength.

Oxycellulose, like hydrocellulose, is a mixture of compounds, but whereas the products of hydrolysis are all homologous, oxycellulose generally contains compounds that have undergone different reactions. The first products formed in oxidising solutions are polysaccharides that have undergone various degrees of chain scission, and they exhibit an increase in reducing power. This would serve to indicate that the first reaction is one of hydrolysis; but as glucose is never the end product of cellulose oxidation the initial hydrolysis must be assumed to be followed by oxidative changes.

Actually in the degradation of cellulose by oxidis-

ing agents, the two reactions occur side by side, the products formed containing both aldehyde and carboxyl groups. It is conceivable that oxidation of the hydroxy groups, especially the ones attached to the carbon atoms marked 6, (figure 1), could occur without rupture of the oxygen bridges between the glucose units. Investigations on this possibility have been carried out by Tollens and Vignon, (6), but there has been no definite proof of such a hypothesis, no product of oxidation having been isolated and identified unequivocally approaching the high molecular weight of cellulose itself. The relative degree of the two reactions will depend on the amount and type of the oxidant used, on the time it is allowed to react, on the hydrogen ion concentration of the solution, and also whether colloiddally dispersed or solid cellulose is attacked. Evidence for the belief that the reaction is a surface reaction is forthcoming from the fact that only a relatively few alcohol groups are attacked when solid cellulose is oxidised. When cellulose dispersed in cuprammonium solution is oxidised all the micelles are attacked simultaneously yielding a product which is still colloidal in nature, and hence, still of a high molecular weight and which is also characterised by its high acidity. On the other hand, when solid cellulose is used the number of glucose units that come in contact with the oxidising agent is very

small, only those present on the surface of the fibrillae, and the resulting product exhibits degradation products of a very low molecular nature, ranging from carbon dioxide to saccharic acid, and also a large amount of unattacked cellulose. The amounts of the two types of products would depend largely on the length of time of the reaction.

When cellulose is overbleached, or subjected to the prolonged action of oxidising agents in general, the product develops certain definite chemical properties which were almost altogether absent in the original material. There are many properties associated with oxycellulose many of which appear also in other forms of degraded cellulose. Although some of these properties are hardly characteristic of oxidised cellulose, they may be used in determining the rate and degree of change which has taken place in the cellulose when attacked by oxidising agents.

The chemistry of cellulose is complicated by the fact that the material is capable of continuous modification in various ways, so as to yield an almost infinite number of products whose properties vary within wide limits. On this account, qualitative tests are of little value in the investigation of modified celluloses. A number of quantitative chemical and physical tests, however, are used to study the modification of natural cellulose; their interpretation is as a rule arbitrary and subjective rather than

definite and stoichiometric.

Among the properties of cellulose the following may be cited:

Physically, a breakdown of the fibrous structure occurs resulting in a loss in both weight and strength of the fibers. With prolonged action, the fiber becomes so weak that it falls to a powder on being touched.

Oxidised cellulose is chemically different from the native cellulose in these respects:

(a.) A reducing group is present which is probably aldehydic in nature. This is indicated by its reaction with Schiff's reagent, by the appearance of a yellow color on treatment with alkalies, and by its reduction of Fehling's solution.

The reducing capacity of the oxidised cellulose may be evaluated in several different ways.

The "copper number" determination of Schwalbe,(7), or some modification of it, is the one most generally employed. The method of determination includes the treatment of the oxidised cellulose with a freshly prepared boiling Fehling's solution for a definite period of time, and the subsequent titration of the cuprous oxide thus formed. The number of grams of copper reduced by an amount of air-dry cellulose equal to one hundred grams of cellulose dried at 105° C. gives the copper number of the sample.

Although it is generally acknowledged that the reduction to the cuprous state is due to the presence of aldehyde groups in the degraded cellulose, this method of evaluating the degree of degradation to which the cellulose has been submitted has been widely criticised. Parsons, (8), has criticised its empirical nature and also its failure to differentiate between hydrocellulose and oxycellulose. On oxidation of various carbohydrates by different oxidising agents, Hibbert and Hassan, (9), found the copper numbers for all the oxidised products to be practically the same. Weltzien and Nakamura, (10), attack this method of studying the constitution of cellulose preparations on the basis that it depends on the degree of dispersion in the copper solution, a variable which cannot be stabilised.

Although the copper number, as a means of determining the extent to which oxidised cellulose has been modified, has been attacked on various grounds, it still remains one of the few approximate evaluations open to the investigator. Providing that the variables are standardised as much as possible during the procedure, the results show a fairly high degree of consistency.

Another value used in measuring the degree of attack on cellulose, and based on the reducing power of oxidised cellulose, is the "silver number" which was first intro-

duced by Gotze, (11). It is based on the reaction of a sodium acetate solution of silver nitrate with the oxidisable groups in the cellulose products. The determination consists of boiling the cellulose with the above solution for exactly thirty minutes, dissolving the reduced silver with nitric acid and then titrating the silver nitrate with an ammonium thiocyanate solution. The number of grams of silver reduced by an amount of air-dry cellulose equal to one hundred grams of cellulose dried at 105°C . gives the silver number of the sample.

Bressard, (12), on a study of the Gotze method, pointed out that the cellulose is continuously oxidised by the solution of silver acetate. The action of the original reducing groups of the cellulose is thus reinforced by the formation of degradation products. L. Brissaud, (13), concluded from his experiments on silver numbers that the reaction is due not only to the reducing groups that are pre-existent in the material, but to a far greater extent to those produced by degradation taking place during the course of the reaction.

(b.) The presence of acidic groups. The acidic character of oxycellulose is indicated by its neutralising effect on very dilute alkalies, and is considered to be partly responsible for the solubility of oxidised cellulose in concentrated alkalies.

- (c.) Small amounts of furfuraldehyde are split off when oxycellulose is distilled with dilute hydrochloric acid. Conclusive evidence that this is brought about by oxidation is lacking, however, since it is also characteristic of unoxidised cellulose. The property is generally regarded as an implication of the prior existence of a pentose or pentosan which either existed as such, or in the form of a glycuronic acid derivative which, on hydrolysis, gave rise to a pentose.
- (d.) Oxycellulose is markedly soluble in alkalies not of peptising strength. The solubility of oxycellulose in alkalies is apparently due to the aldehyde and acid constituents of it, these being more or less completely dissolved leaving an unchanged or slightly modified cellulose.

In respect to its solubility in alkalies, cellulose can be divided into three fractions: α -cellulose is the alkali insoluble portion which is similar to, if not identical with, unchanged cellulose. β -cellulose is the alkali soluble portion which is re-precipitated when the solution is acidified. γ -cellulose is the alkali soluble portion which is not re-precipitated by acids. The most degraded substances are assumed to be present in this fraction.

According to Hibbert and Parsons, (14), the solubility of oxidised cellulose in alkali is due not only to

salt formation, and to reactions involving the aldehyde groups, but also to a peptisation of a portion of the un-attacked cellulose. Heuser and Niethammer,(15), regard the alkali adsorption by cellulose and its degradation products as a measure of the degree of depolymerisation. The property has been used extensively in this connection for determining the degree of cellulose degradation.

The procedure consists of treating the sample of cellulose with a 17.5% solution of sodium hydroxide for a definite period of time with accompanying maceration of the mass. Water is then added, and the mixture is filtered. The residue is subsequently washed with water, and then with a weak solution of acetic acid. The salts thus formed and the excess acid, are then washed and the cellulose remaining is placed to dry at 105° C. and weighed.

This portion of the cellulose is called α -cellulose and its percentage weight of the original material is used as an index of the depolymerisation and the degree of oxidation of the hydroxy groups in the oxycellulose.

(e.) Oxycellulose demonstrates a marked affinity for basic dyes.

On this property is based the "methylene blue number" determination which may be used as an indication of the degradation of cellulose attacked by oxidising agents. The procedure consists of immers-

ing a sample of the cellulose into a buffered solution of N/250 methylene blue, and titrating the excess with naphthol yellow S. Brissaud,(16), regards the index as a measure of the non-cellulosic impurities, and states that it is most satisfactory for use with wood pulp and straw.

- (f.) The viscosity of oxidised cellulose in cuprammonium hydroxide solution is comparatively low.

The relative viscosity measurements, as carried out by Hibbert and Parsons,(14), consist of drawing a carefully prepared solution into a water-jacketed 100 c.c. pipette, and noting the time taken to discharge the contents. The time of discharge of a solution of pure cotton cellulose at 25° C. is ascertained, and the relation of this figure to the time of outflow of 100 c.c. of distilled water is taken as the relative viscosity of the cellulose.

- (g.) Ultimate analysis points to the fact that oxycellulose contains more oxygen than does cellulose or even hydrocellulose.

(c.) Survey of Work on Oxidation of Cellulose.

Some of the earliest work on the nature of the reaction of cellulose with oxidising agents was carried out by Hibbert and Parsons,(14), in the year 1925. The oxidising agents chosen for this investigation consisted of potassium, magnesium and barium permanganates in neutral and slightly alkaline solutions, and also chromic acid in 90% acetic acid solution. The experiments were carried out at room temperature and over the oxidising range of 0.01 to 2.00 atomic portions of oxygen per glucose unit.

Their results indicated that the degree of disintegration of the fibers is more pronounced in neutral or slightly alkaline solutions, a fine powder being obtained when 2.00 atomic portions of oxygen was employed. They found that a marked disintegration of the fiber does not appear until after 0.10 atomic portions of oxygen is consumed, although a deterioration in strength is noticeable. With the permanganates, the fiber losses were seen to be practically independent of the nature of the metallic radical and did not vary materially when the concentration of the solution was changed within a small range. Apparently the degree of disintegration of the fiber is not necessarily influenced by the formation of oxidised material, as these investigators proceeded to claim that cellulose when oxidised in acid solutions contained a larger

amount of oxidised material than when oxidised in either neutral or alkaline solutions. The ash, copper number, alkali solubility, pentosan and glycurone constituents were noted to have higher values in the case of cellulose oxidised in acid solution. Little confidence can be placed in the results obtained by these investigators as they appear to further contradict themselves by stating that "the oxidation is accelerated by alkalies and retarded by dilute acids because the former act on the initially oxidised cellulose so as to give a much larger concentration of the oxidisable components". These latter are more readily oxidised, under the conditions, than cellulose itself. They observed that the viscosities of the cuprammonium hydroxide solutions of the various oxidised celluloses were much lower than those of the original cotton.

Further investigations on the action of chromic acid solutions on cellulose were carried out in 1927 by Hibbert and Hassan,(9). They oxidised pure cotton cellulose at 26° C. using an amount of chromic acid equivalent to 2.00 atoms active oxygen per glucose unit in sulphuric acid varying in concentration from 10% to 50%.

Their results, in partial contrast to those obtained by Hibbert and Parsons, (14), showed that an increased acid concentration increased the amount of degradation and decreased the amount of oxidised product.

In 1935 Nakashima and Oinuma, (17), carried out experiments on the oxidation of cellulose using chlorine. Their object was to investigate the relation between the pH of the bleach liquor and the degree of degradation of the cellulose. They lowered the pH gradually by increasing the chlorine content from an initial 1% to 9%.

With decreasing pH they found the ash content of the pulp to increase slightly, the α -cellulose content to remain constant up to 3% chlorine concentration beyond which there was a decrease, and the copper number and bleaching loss to increase gradually. The copper number was seen to be a minimum at 2% chlorine concentration, and the bleaching loss did not exceed 6%. A rise in temperature caused a decrease in the α -cellulose content and an increase in both the copper number and the bleaching loss, and prolonged bleaching was seen to bring about a degradation of the cellulose itself and an increase in copper number. The highest tensile strength of the cellulose was obtained with 2% chlorine concentration.

In 1936 Hisey and Koon, (18), made a study of the bleaching of sulphite pulp in buffered solutions of fixed pH. Electrometric titrations of their bleach liquors indicated that the pH of chlorine-containing solutions is of great importance in determining the activity of the solution as an oxidising agent. They found that the lower the pH, the

more active is the solution as measured by the oxidation potential.

There were indications also that, in bleaches buffered to maintain constant pH conditions, the rate of consumption of chlorine by the pulp is roughly dependent on the oxidation potential, a more rapid reaction being obtained under acid conditions. The strongest pulp under these conditions was obtained at pH 1.7, and pulps bleached at higher pH values were progressively weaker, roughly in proportion to the pH. The sodium hydroxide solubility of the pulp was noted to vary widely with the pH, being low under acid conditions, maximum at neutrality, and low under alkaline conditions. The results obtained by these investigators do not seem reasonable however, as it is inconceivable that the strongest and least modified pulp would be obtained under strongly hydrolysing conditions, and under conditions of maximum oxidation potential.

Birtwell, Clibbens and Ridge,(19), were among the first investigators to use hypochlorites as the oxidant in researches on the nature of cotton cellulose oxidation. They announced, in 1925, that there were two distinct types of oxycellulose, and that the type predominantly produced depended chiefly on the acidity or alkalinity of the hypochlorite solution. When an alkaline solution was used, the type formed showed high methylene blue adsorption, low

copper number, and an abnormal affinity for alkalies. The oxycellulose formed in acid solution, on the other hand, had a high reducing power and showed a substantial decrease in weight on alkaline scouring, whereby it regained most of its original properties. Viscosity in cuprammonium solution, however, revealed changes in the cellulose regardless of the conditions of oxidation or subsequent treatment.

Further work on the oxidation of cellulose by hypochlorites was carried out by Clibbens and Ridge, (20), in 1927. They subjected the cellulose to oxidation in buffered hypochlorite solutions varying in pH from 5 to 10.

Their results indicated that a maximum rate of oxycellulose formation takes place at pH 7, and they claimed that the results obtained were due to a variation of pH alone, and not to any specific effects of the buffered salts. In contrast to this claim, Nabar, Scholefield and Turner, (21), at a later date pointed out that "the buffer substances for the sodium hypochlorite solutions appear each to exercise a special influence upon the potential of the solution, upon the oxygen consumption and upon the fluidity, copper number and carboxyl content of the oxidised cellulose".

Sigurd Kohler in 1932, (22), oxidised cotton cellulose with alkaline sodium hypochlorite of pH 11.2 at 25° C., and obtained a product which showed a relatively low copper number and a great decrease in tearing strength. Using a

neutral solution, he found the resulting product to possess a great increase in reducing capacity and little decrease in strength.

In 1934 Fotiev, (23), treated 100 grams of soft cellulose with two litres of a 5% calcium hypochlorite solution at 30° C.

He found the α -cellulose content to decrease slowly at the start and quicker towards the end, from 88.5% to 85.6%. The copper numbers were noted to rise slowly from 1.6 to 1.7 in the first three hours and then rose sharply to 2.6. The viscosity decreased from 25 to 17 in the first three hours, and at the end of six hours had reached the value of 10.

Brissaud, (24), in 1937, oxidised cellulose in the dark with a neutral solution of Sodium hypochlorite.

He found the copper numbers to increase with increasing oxidation, in contrast to cellulose hydrolysed by acids. A decrease in the percent α -cellulose was noted, while at best only small amounts of gluconic, glucuronic or saccharic acids were formed. The ash content also increased with the degree of oxidation.

Nabar, Scholefield and Turner, (21), in 1937, found that the curve showing the relation between the pH and the oxidation potential of the sodium hypochlorite solution agrees closely in shape with the curves showing the relation of the pH of the solution with:

(1.) net oxygen consumption.

- (2.) cuprammonium fluidity.
- (3.) copper number
- (4.) carboxyl groups of the degraded cellulose.

Neale and Stringfellow, (25), stated, in 1937, that oxy-cellulose prepared in neutral or acid solution reduces the alkaline copper sulphate solution and has little affinity for methylene blue. Prepared in an alkaline medium, there is much less reducing effect on the copper solutions and much greater affinity for methylene blue.

Parsons and Jackson, (26), in 1938, claimed that a pH of 8 to 11, using hypochlorite, tends to repress the degradation of cellulose.

The Mathieson Alkali Works' Research Staff, (27), have conducted exhaustive studies in recent years on hypochlorite bleaching. From their results, they adopted the following standard conditions:

They suggest the use of alkaline hypochlorite solutions at pH's between 8 and 9 and at temperatures not exceeding 40° C. Using these two conditions they carried out experiments with a view to standardising the other variables concerned, the optimum conditions being determined on the basis of such physical properties as brightness, busting strength and tearing strength. They concluded that the standard conditions for consistency should be 5%, the bleaching time 2 hours, and the available chlorine from 0.5% to 1%.

DISCUSSION OF PROBLEM

It is hardly possible to define the impurities in cellulose, especially if the dual nature theory of cellulose structure is to be accepted. Assuming the theory to be correct, it is highly conceivable that the impurities would be so intimately associated with the pectic-like colloidal phase as to render their removal impossible without deleteriously affecting the physical aspects of the cellulose fiber. The chief physical property that would be affected is the tensile strength of the fibers, the property to which cellulose owes its importance in industry.

It is due to the association between the impurities and the cellulose that such drastic methods of bleaching as hypochlorite bleaching have been resorted to in the processing of wood pulp. Industry, especially that portion concerned with the manufacture of rayons, demands a pulp of maximum brightness and fiber strength. The quality of brightness is readily obtained with hypochlorite bleaching, but it is difficult to obtain the extreme brightness required in some celluloses without impairing their strength.

Researches have been conducted on a wide scale by various investigators with a view to the determination of the optimum conditions of hypochlorite bleaching under which a suitably bright cellulose could be obtained which had undergone but little degradation. The results obtained,

however, were generally contradictory and could not be conclusively accepted.

The object of this problem is to investigate the effect of pH and temperature on the bleaching of commercial sulphite wood pulp by an aqueous solution of pure sodium hypochlorite crystals, without the use of buffers to keep the pH constant.

A pH range of 6 to 10 was investigated at 35° C., the pH for each stage being kept constant by the addition of sodium hydroxide solution or hydrochloric acid as required. The effect of temperature was determined by repeating the pH 9 stage at 45° C. The time of the reaction was set at four hours, samples of the treated cellulose being removed at intervals within the time limit for analysis.

The tests employed for the determination of the degree of degradation consisted of copper numbers, silver numbers and α -cellulose content determinations.

EXPERIMENTAL

APPARATUS

Among the apparatus employed in carrying out the various procedures embodied in the research problem were the following instruments:

Beckman pH Meter.

This meter is essentially a potentiometer and galvanometer assembled in such a way as to give direct readings of the pH. The electrodes used in connection with the meter were of the external type of calomel and glass electrodes. These electrodes were connected to the meter by means of a three foot extension of insulated wire enabling their immersion in the reaction vessel contained in the thermostat.

Thermostat.

The thermostat employed was of the cylindrical tank type insulated with asbestos fiber. An immersion heater was used, and the heating current was controlled by means of an electro-magnetic relay in conjunction with a thermo-regulator of the mercury-in glass type. A uniform temperature was maintained by the use of a mechanical stirrer, the variations not exceeding $\pm 0.5^{\circ}$ C.

THE OXIDATION OF CELLULOSE

Reagents and their preparation.

(1.) Cellulose.

The cellulose employed for the reactions was a commercially prepared low resin sulphite pulp.

In order that the maximum surface of the cellulose would be open to reaction, it was broken up into its component fibers by means of/^amechanical egg-beater. This was accomplished by placing fragments of the cellulose sheets in a beaker of water and beating the mass until it became fluffy, with no visible pieces of the original sheets of cellulose remaining. The water was then filtered off as completely as possible and an amount of the moist cellulose equal to 60 grams of cellulose dried at 105° C. was placed in a container in the ice box until required. The cellulose was kept in a cool place to prevent mould from forming.

(2.) Sodium hypochlorite.

As this reagent was desired to be as pure as possible, it was prepared by the method of MacMillan,(28), modified somewhat by Underwood and Mack,(29), as follows:

A 30-35% aqueous solution of sodium hydroxide of grade B quality was added to 40% of its own volume of tertiary butyl alcohol. Through this mixture, kept at 0° C. and mechanically stirred, chlorine gas was slowly passed

until a sample of the aqueous solution became acid, and showed only a slight effervescence upon being treated with neutral hydrogen peroxide solution.

The passage of chlorine gas was discontinued at this point in order to prevent the reaction of free chlorine with the tertiary butyl alcohol to form tertiary butyl chloride. The hypochlorous acid which is being formed throughout the process reacts with the alcohol to give tertiary butyl hypochlorite, a yellow colored liquid layer which rests above the sodium chloride solution.

The upper yellow liquid layer was decanted and washed, first with a 2% solution of sodium hydroxide to remove possible traces of free chlorine, and then with distilled water to dissolve out remaining traces of sodium chloride. To the pure tertiary butyl hypochlorite was then slowly added, accompanied by vigorous stirring, slightly more than the theoretical volume of a 40% aqueous solution of grade A sodium hydroxide to obtain the sodium hypochlorite.

The sodium hypochlorite solution was then separated by decantation from the tertiary butyl alcohol, washed with ethyl ether to remove dissolved alcohol and finally decanted from the ether. The concentrated hypochlorite solution was then cooled to 0° C. and seeded with a few crystals of sodium hypochlorite, formed by supercooling a small portion of the solution with solid carbon dioxide.

The pure crystals of hydrated sodium hypochlorite, $\text{NaClO} \cdot 5\text{H}_2\text{O}$, came out rapidly in long pale lemon-yellow needles. These were filtered off in a coarse fritted glass filter and washed with a little distilled water.

(3.) N/10 sodium arsenite solution.

(4.) N/10 hydrochloric acid.

(5.) N/10 sodium hydroxide.

Procedure.

A stock solution of the sodium hypochlorite was prepared by dissolving the crystals in an excess of distilled water. 2 c.c. of the stock solution were then drawn off, diluted with 25 c.c. cold distilled water, and titrated against the standardised sodium arsenite solution. This analysis was carried out in order to determine the amount of stock solution necessary to make up 1940 c.c. of an 0.75% sodium hypochlorite solution. This amount was drawn off and diluted to a volume of 1600 c.c. with distilled water.

The cellulose mass was then weighed and the amount of water contained by it was determined. It was subsequently warmed to the temperature at which the reaction was to be carried out, and maintained at that temperature.

The pH of the sodium hypochlorite solution, contained in a 4 litre beaker, was determined by inserting the elec-

trodes into it and setting the temperature dial of the meter to the corresponding temperature of the solution. N/10 hydrochloric acid was then added, with mechanical stirring, until the required pH at which the reaction was to take place was attained.

The amount of hydrochloric acid added was noted and sufficient distilled water was added to bring the total volume of the reaction solution, including the water contained in the cellulose, to 1940 c.c.

The solution was then brought to the desired temperature and the container set into the thermostat. The time was noted as the cellulose was being added to the hypochlorite solution, stirring by hand so as to make the mixture of the same consistency throughout. It was impossible to use mechanical stirring in this connection as the cellulose mass would not respond to it.

In this manner a reaction mixture was obtained of 3% cellulose in an 0.75% sodium hypochlorite solution.

The electrodes were then immersed, the temperature dial of the meter adjusted to the corresponding new temperature and the pH of the solution was determined. N/10 sodium hydroxide or hydrochloric acid was added to bring the pH back to that desired, stirring as quickly and thoroughly as possible. The procedure was repeated throughout the reaction so as to maintain a constancy of the pH

of the reaction mixture.

At the end of five minutes of reaction 2 c.c. of the hypochlorite solution were drawn off, added to 25 c.c. cold distilled water, and titrated against the sodium arsenite solution. The concentration of the hypochlorite was thus determined, and enough of the stock solution was added to the reaction mixture, with steady stirring, to bring the solution back to its original concentration. This procedure was also repeated as often as time permitted throughout the reaction.

At the end of fifteen minutes of reaction the container was removed from the thermostat and one third of its contents poured off into ice-cold water. The reaction mixture was then returned to the thermostat for further reaction to take place. The sample removed was immediately filtered through a coarse fritted glass filter and washed with 300 c.c. of water containing a trace of sodium bisulphite to remove any remaining hypochlorite, and the salts formed were removed by further washing with 2 litres of water. The cellulose was then removed from the filter, marked, and placed in the icebox until the end of the reaction. The above procedure was repeated at the end of one hour of reaction, one half of the remaining cellulose being removed, and at the end of four hours when the remaining mixture was similarly treated.

At the end of the reaction the three samples of oxidised cellulose were pressed in a hydraulic press using 5000 pounds pressure per square inch in order to remove excess water, and then rasped with a clean knife into fibers. The fibrous cellulose was placed into white envelopes, sealed and marked, and then placed in the ice box until required.

The above procedure was carried out at pH 10, 9, 8, 7.5, 7 and 6 at 35° C., and pH 9 was also repeated at a temperature of 45° C.

In this manner samples of cellulose were obtained which had been reacted upon by the same percentage concentration of sodium hypochlorite at different pH's and for different intervals of time. The effect of time, pH and temperature on the oxidation of cellulose by sodium hypochlorite could thus be determined.

During the oxidation processes it became increasingly difficult to control the pH, hypochlorite concentration and consistency of the mixture as the pH desired was lowered from 10 to 6. This was due to an increasing decomposition of the sodium hypochlorite itself in the solutions at lower pH. Decomposition products possessing pungent odors could be detected emanating from the reaction mixture at all pH's, and below pH 8 the quantity was so large as to make it very difficult to work over

the reaction vessel. On account of the increasing decomposition of the hypochlorite and, hence, increasing tendency of the pH of the reaction solution to decrease, the quantities of sodium hypochlorite and sodium hydroxide solutions that had to be added, in order to maintain the required hypochlorite concentration and pH, became increasingly large as the pH zones of the reaction mixture were lowered from 10 to 6. The frequency with which these additions had to be made also became greater as the desired pH was lowered. The high cellulose consistency of the mixture prevented the use of mechanical stirring and stirring could only be done by hand. As much of the writer's time was taken up with other stages in the procedure it was difficult, if at all possible, to keep the pH and hypochlorite concentration consistent throughout the reaction solution and at all times during the procedure.

DETERMINATION OF THE COPPER NUMBER

Reagents and their preparation.

(1.) Copper sulphate solution.

138.6 grams of crystallised copper sulphate were dissolved in distilled water and diluted to a volume of 2 litres, and filtered through glass wool.

(2.) Alkaline tartrate solution.

692 grams of Rochelle salt and 200 grams of sodium hydroxide pellets were dissolved in distilled water and diluted to a volume of 2 litres, and filtered through glass wool.

(3.) Fuller's earth suspension.

20 grams of kaolin were suspended in sufficient distilled water to make up 2 litres.

(4.) Ferric sulphate solution.

100 grams of ferric sulphate were dissolved in 1 litre of distilled water and 220 c.c. concentrated sulphuric acid were added. The solution was then boiled for two to three minutes and diluted to 2 litres.

(5.) 5% sulphuric acid solution.

(6.) N/10 potassium permanganate.

Procedure.

Approximately 2.1 grams of the air-dry cellulose were carefully weighed in a glass stoppered bottle. In

another glass stoppered bottle about 1.5 grams of the same cellulose were weighed and placed in a constant temperature oven at 105° C. until it was completely dry and no further decrease in weight was to be observed.

In this manner the oven-dry weight of the first sample could be determined without subjecting it to any possible degradation caused by heat.

The air-dry cellulose contained in the stoppered bottle was transferred to a 2 litre round-bottom flask and 250 c.c. of boiling distilled water were added. The flask was then connected to a Liebig condenser through which a mechanically driven stirrer was passed; the stirrer was started in motion and heat was applied to the flask.

As soon as boiling began the apparatus was disconnected and a freshly prepared mixture of 50 c.c. boiling copper sulphate and 50 c.c. boiling alkaline tartrate were added. The containers of the Fehling's solution were then rinsed with 50 c.c. of distilled boiling water and this was also added to the contents of the flask. The apparatus was again assembled, stirrer set in motion to prevent bumping and heat was applied. The time was noted when boiling was first observed and the mixture was allowed to boil for exactly fifteen minutes.

At the end of this time 250 c.c. of cold water were

added, to prevent further reaction from taking place, and also 50 c.c. of the kaolin suspension. The cellulose was then filtered through a 17 G₃ Jena fritted glass filter, never allowing the residue to become dry, and then washed with 1000 c.c. of boiling distilled water. The filtrate was discarded and the suction flask washed.

To the residue contained in the filter were added 100 c.c. of the ferric sulphate solution which was first used to dissolve any cuprous oxide remaining on the stirrer and in the flask. After a brief moment, to allow solution of the cuprous oxide held by the cellulose fibers to take place, suction was applied and the flask and residue in the filter were washed with 500 c.c. of 5% sulphuric acid.

The filtrate was then transferred to a 1 litre beaker and titrated with potassium permanganate. This gave an indication of the amount of ferric iron reduced to the ferrous state and hence the amount of copper reduced by the cellulose. From this could be determined the copper number of the oxidised cellulose by the following formula:

$$\frac{\text{c.c. N/10 KMnO}_4 \times \text{Factor} \times 0.006357 \times 100}{\text{grams oven-dry cellulose}} = \text{Copper number.}$$

This procedure was repeated in duplicate for all the different samples of oxidised cellulose prepared, and was also carried out with the original cellulose in order to make comparisons possible.

DETERMINATION OF THE SILVER NUMBER

Reagents and their preparation.

(1.) Silver acetate solution.

60 grams of silver nitrate crystals were dissolved in distilled water and 14 grams of sodium acetate were added. Dilute ammonium hydroxide was then added until the precipitate was completely dissolved, and the solution was diluted to a volume of 2 litres.

(2.) 25% nitric acid solution.

(3.) N/10 ammonium thiocyanate solution.

(4.) Ferric indicator.

Procedure.

0.53 grams of the air-dry cellulose were accurately weighed in a glass stoppered bottle and its oven-dry weight determined as in the previous case.

The cellulose was transferred to a 500 c.c. round bottom flask and 50 c.c. of the silver acetate were added. The flask was connected to a Liebig condenser through which was passed a mechanically driven stirrer and heat was applied. When boiling was first observed the time was noted and boiling was continued for exactly thirty minutes.

At the end of the boiling period 100 c.c. of cold water were added to prevent further reaction from taking place. The contents of the flask were then filtered through

a 17 G₃ Jena fritted glass filter, the stirrer and flask rinsed and the washings used to wash the residue in the filter until the filtrate showed no further signs of containing any silver.

The filtrate was then discarded and the suction flask washed. The reduced silver in the residue in the filter was then dissolved with 75 c.c. of 25% nitric acid which had first been used to dissolve any of the remaining silver on the stirrer and in the flask. The flask and residue in the filter were washed with cold distilled water until all traces of silver nitrate were removed.

The filtrate was subsequently transferred to a porcelain basin, 5 c.c. of the ferric indicator added and titrated against the ammonium thiocyanate solution.

From the number of c.c. thiocyanate solution required to titrate the silver, the silver number of the oxidised cellulose could be determined by the following formula:

$$\frac{\text{c.c. N/10 NH}_4\text{CNS X Factor X 0.010788 X 100}}{\text{grams oven-dry cellulose}} = \text{Silver number.}$$

As in the case of the copper number determinations the above procedure was repeated in duplicate for all the samples of oxidised cellulose and also for the original cellulose.

DETERMINATION OF THE α -CELLULOSE CONTENT

Reagents and their preparation.

(1.) 17.5% sodium hydroxide solution.

430 grams of sodium hydroxide sticks were dissolved in an equal weight of distilled water and allowed to stand for ten days to allow time for the sodium carbonate and other impurities to settle. The clear supernatant liquor was then decanted and diluted with carbonate-free distilled water until its density at 20° C. had become 1.192.

(2.) 7% sodium hydroxide solution.

150 grams of sodium hydroxide sticks were similarly treated, the final density of the solution being 1.076 at 20° C.

(3.) 10% acetic acid solution.

Procedure.

Approximately 3.2 grams of the air-dry cellulose were accurately weighed and its oven-dry weight determined as in the two previous instances.

The weighed cellulose was transferred to a mortar of 400 c.c. capacity and 35 c.c. of the 17.5% sodium hydroxide were added. This was allowed to stand for five minutes. At the end of this period the contents were macerated with a pestle for a period of ten minutes during which time 40 c.c. of the 17.5% sodium hydroxide were added in 10 c.c. portions.

The mercerised cellulose was allowed to stand for ex-

actly thirty minutes when 250 c.c. of distilled water at room temperature were added with thorough mixing. The contents of the mortar were then filtered through a 50 c.c. Gooch crucible, matted with glass fibers, which had been previously weighed. As much as possible of the sodium hydroxide was allowed to filter through without applying suction, and when suction was applied it was done gently until a good sized mat had formed at the base of the crucible. The filtrate was then passed through the filter a second time and the remaining cellulose was filtered.

The cellulose was then washed with 100 c.c. of the 7% sodium hydroxide and further with 750 c.c. of distilled water at room temperature. 40 c.c. of the 10% acetic acid were then added to the residue and allowed to stand for two minutes after which time suction was applied. The residue was then washed with water until the filtrate showed no further traces of acid. The crucible and its contents was placed in the constant temperature oven at 105° C. until it reached a constant weight. The weight of the residue was taken as the α -cellulose content and the percent contained by the oxy-cellulose was thus determined.

For each degree above or below 22° C. at which the procedure was carried out 0.1% was added^{to} or subtracted from the α -cellulose value.

This procedure was carried out in duplicate for each sample of oxidised cellulose and also for the original cellulose.

RESULTSOriginal sulphite pulp.

		<u>Mean value</u>
Copper number:	1.51 1.57	1.54
Silver number:	8.55 8.64	8.60
% α -cellulose:	89.39 89.57	89.48

Sulphite pulp treated with hypochlorite at 35° C.

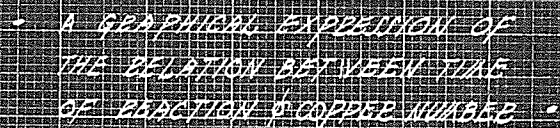
	<u>Time</u>					
<u>At pH 10</u>	$\frac{1}{4}$ hour	mean	1 hour	mean	4 hours	mean
Cu No.	1.05 1.03	1.04	0.95 0.86	0.91	0.80 0.81	0.81
Ag No.	7.96 7.86	7.91	7.70 7.82	7.76	9.31 9.17	9.24
% α -C.	87.94 88.20	88.07	84.83 85.54	85.18	81.12 81.34	81.23
<u>At pH 9</u>						
Cu No.	1.21 1.23	1.22	1.56 1.59	1.58	2.62 2.68	2.64
Ag No.	8.27 8.19	8.23	9.21 9.06	9.14	11.40 11.18	11.29
% α -C.	87.40 86.65	87.03	72.45 72.85	72.65	67.66 67.16	67.41

<u>At pH 8</u>	$\frac{1}{2}$ hour	mean	1 hour	mean	4 hours	mean
Cu No.	3.84 4.00	3.92	7.57 7.69	7.63	14.50 14.80	14.65
Ag No.	11.02 10.61	10.32	11.71 11.41	11.56	15.10 15.97	15.54
% α -C.	72.02 71.30	71.66	42.62 43.05	42.84	33.29 33.54	33.42
<u>At pH 7.5</u>						
CU No.	6.42 6.46	6.44	18.19 18.40	18.30	25.33 25.53	25.44
Ag. No.	10.68 10.42	10.55	15.15 14.85	15.00	38.30 36.80	37.55
% α -C.	52.76 53.43	53.11	18.32 17.64	17.98	0.77 0.84	0.81
<u>At pH 7.</u>						
Cu No.	10.80 11.10	10.95	31.37 31.63	31.50	18.75 18.37	18.56
Ag No.	13.32 14.01	13.67	14.65 14.93	14.79	27.52 27.12	27.32
% α -C.	35.66 35.01	35.34	11.08 ---	11.08	0.00 0.00	0.00
<u>At pH 6</u>						
Cu No.	5.53 5.57	5.55	31.94 32.63	32.29	55.25 ---	55.25
Ag No.	13.83 14.04	13.94	18.00 17.41	17.71	50.50 ---	50.50
% α -C.	53.81 53.76	53.79	15.94 16.68	16.31	1.95 ---	1.95

Sulphite pulp treated with hypochlorite at 45° C.

<u>At pH 9</u>	<u>Time</u>					
	$\frac{1}{4}$ hour	mean	1 hour	mean	4 hours	mean
Cu No.	1.38		1.94		3.04	
	1.72	1.55	2.09	2.02	2.95	3.00
Ag No.	8.14		8.39		12.43	
	8.07	8.11	8.27	8.33	11.80	12.12
%α -C.	85.25		74.21		45.45	
	84.33	84.79	74.95	74.58	46.25	45.85

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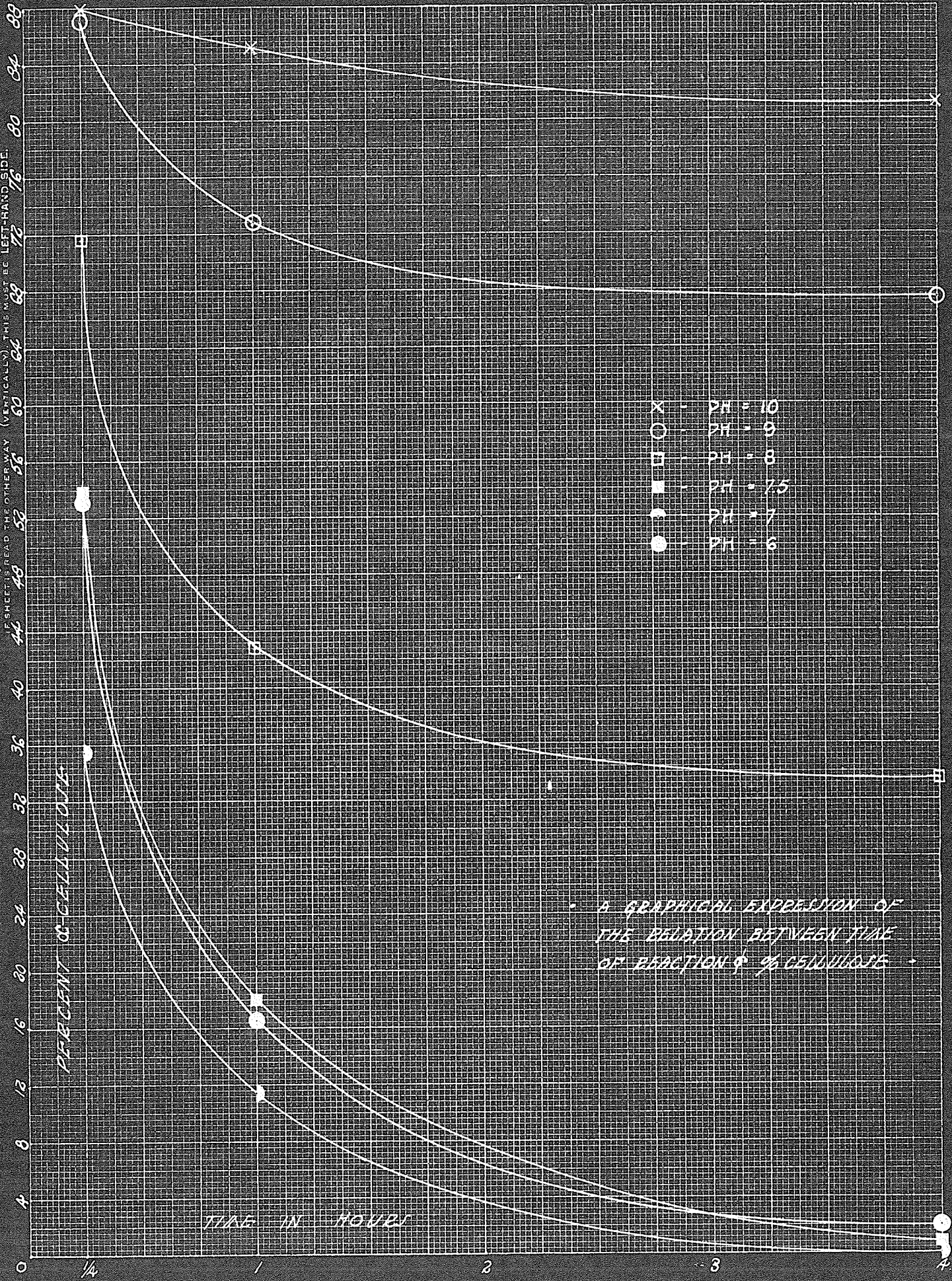
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PERCENT OF CELLULOSE

TIME IN HOURS

- X - $\text{pH} = 10$
- O - $\text{pH} = 9$
- - $\text{pH} = 8$
- - $\text{pH} = 7.5$
- - $\text{pH} = 7$
- - $\text{pH} = 6$

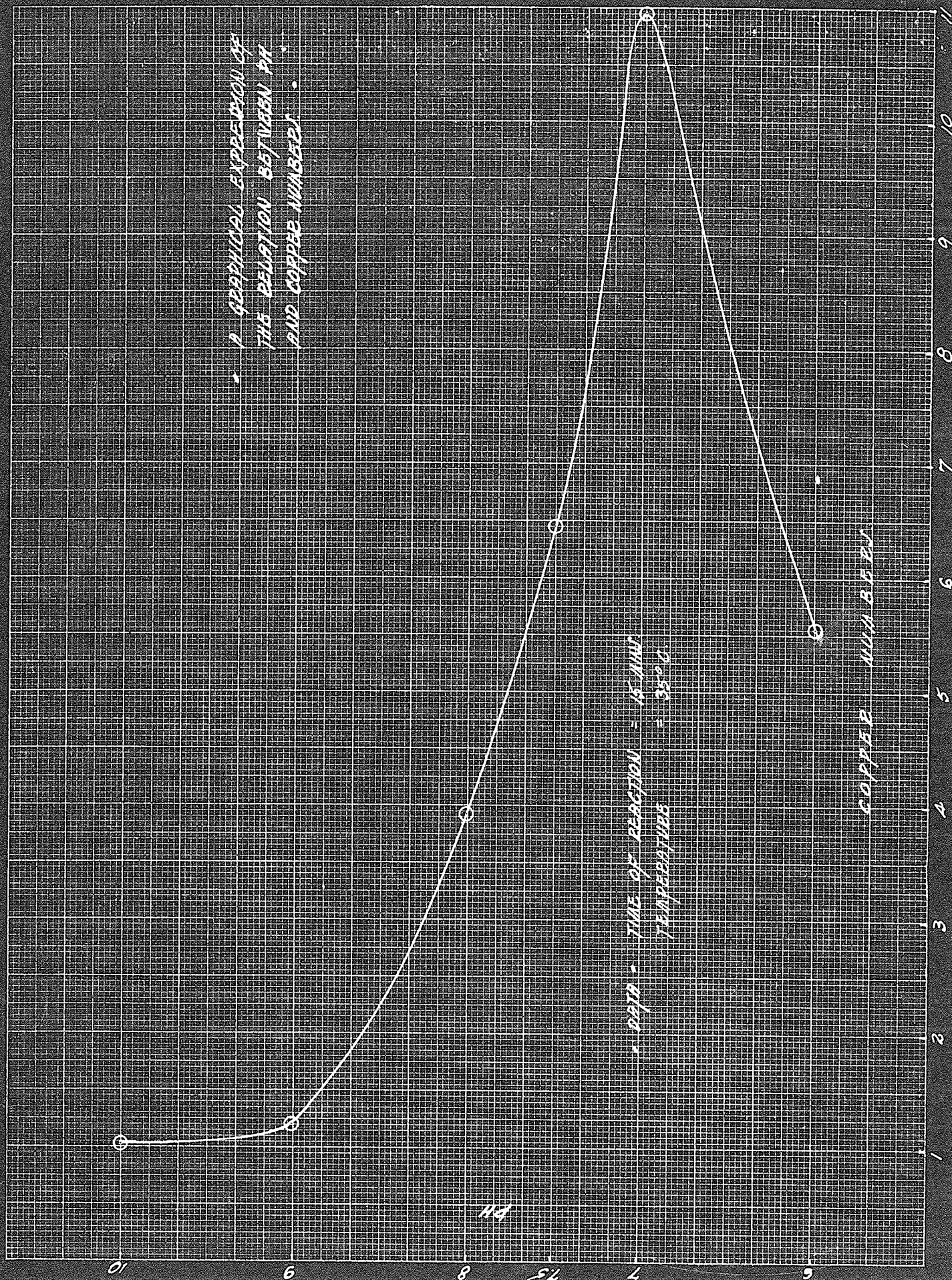
A GRAPHICAL EXPRESSION OF THE RELATION BETWEEN TIME OF REACTION & % CELLULOSE



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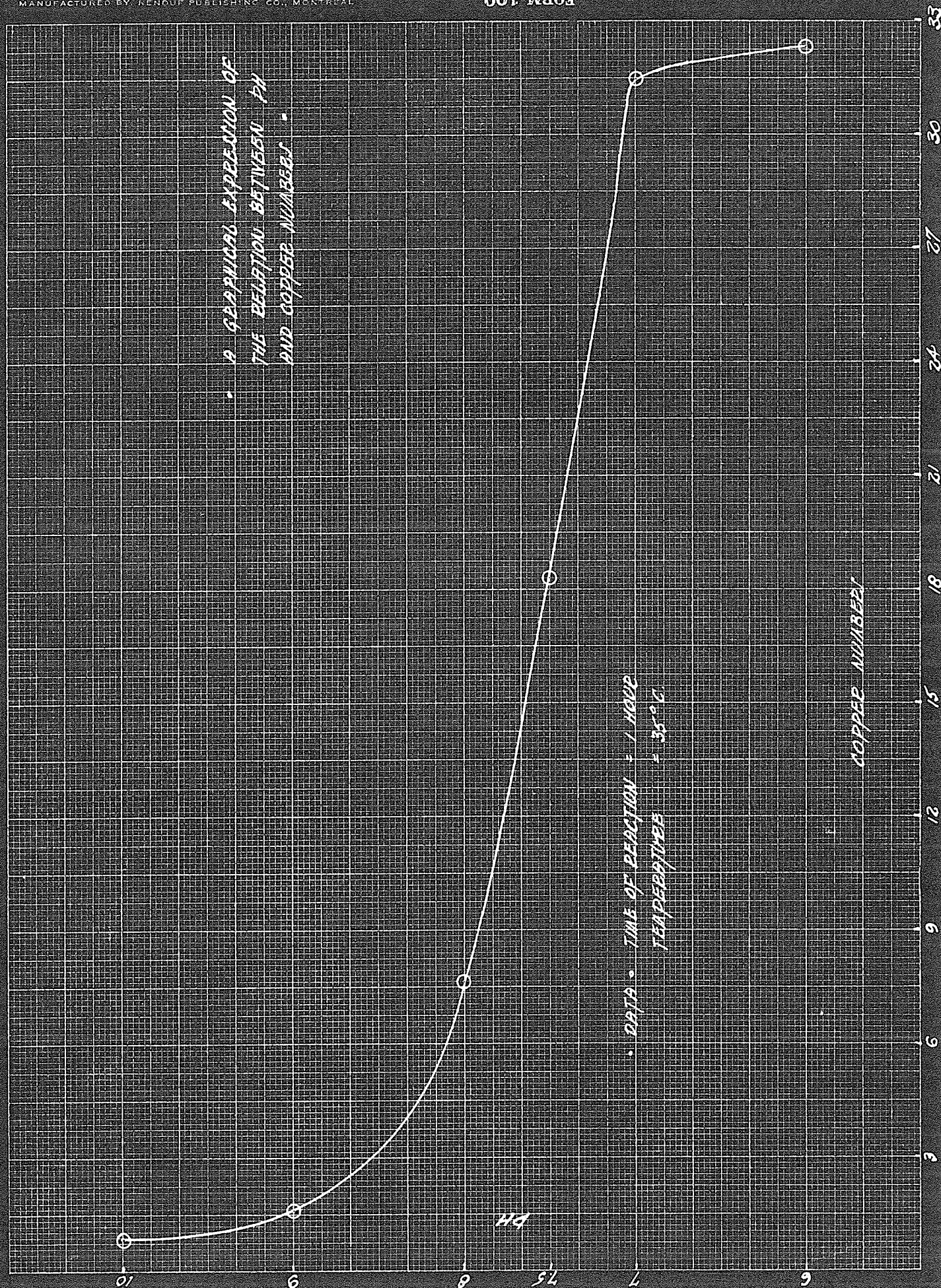
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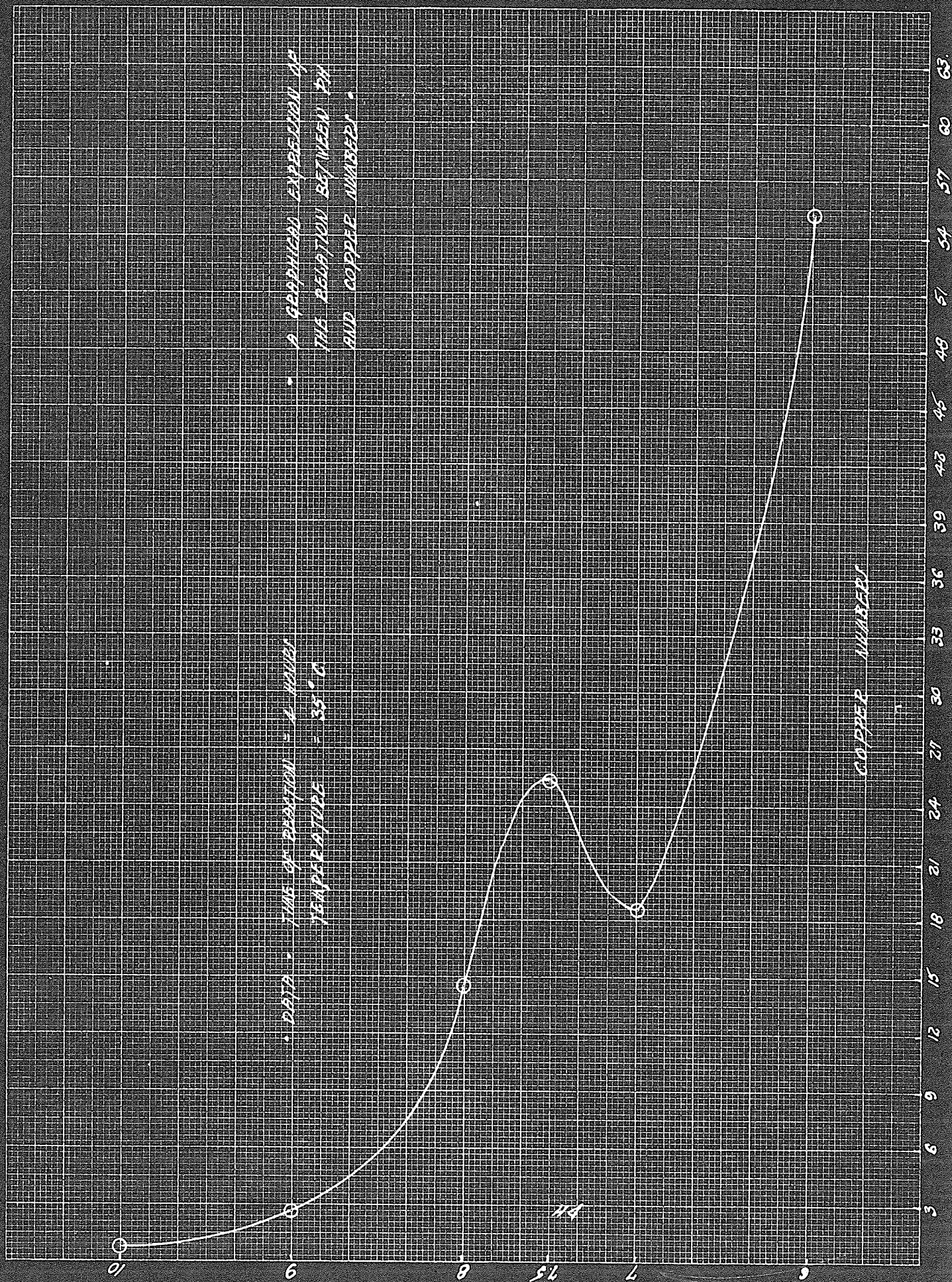
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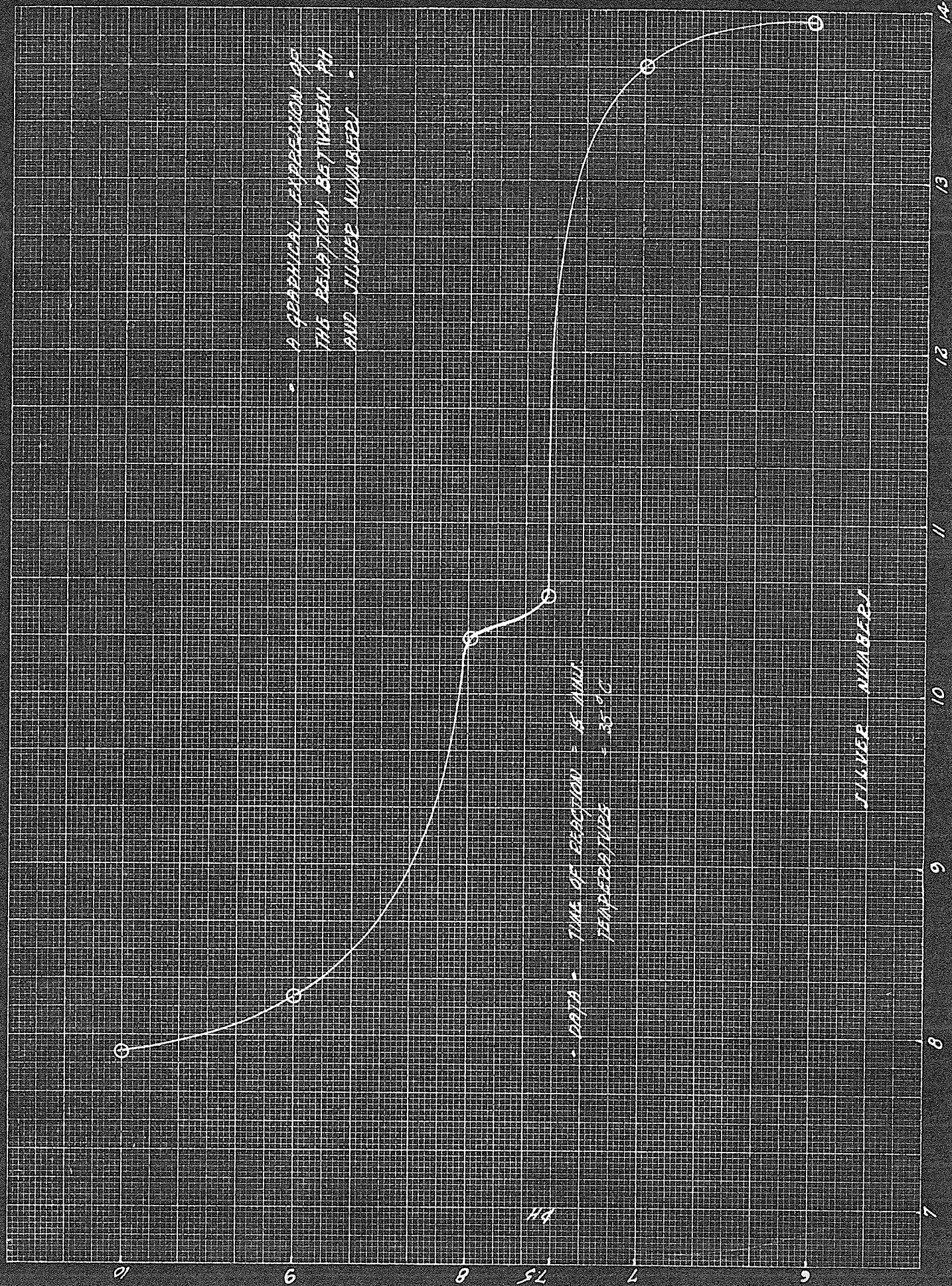
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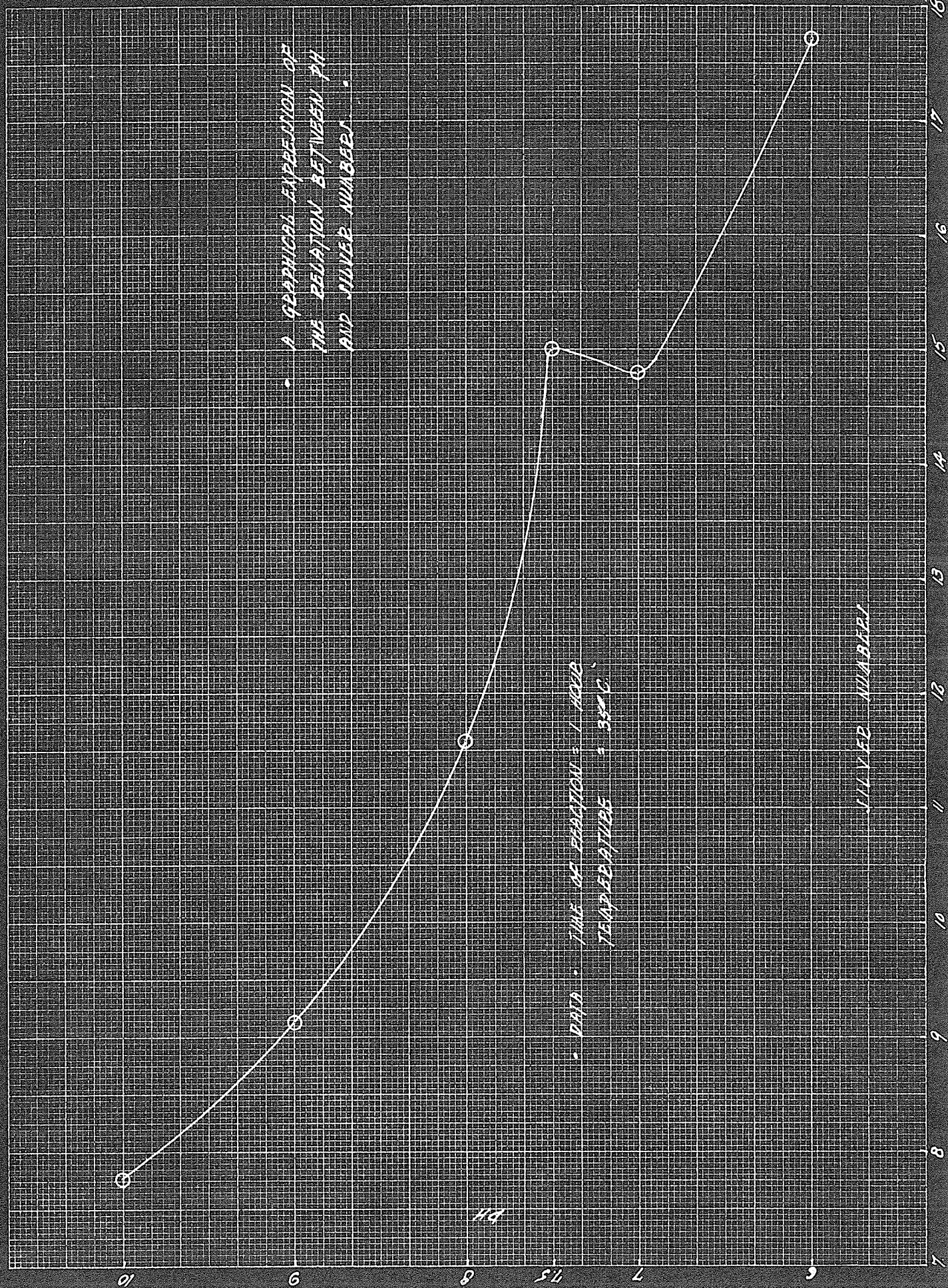


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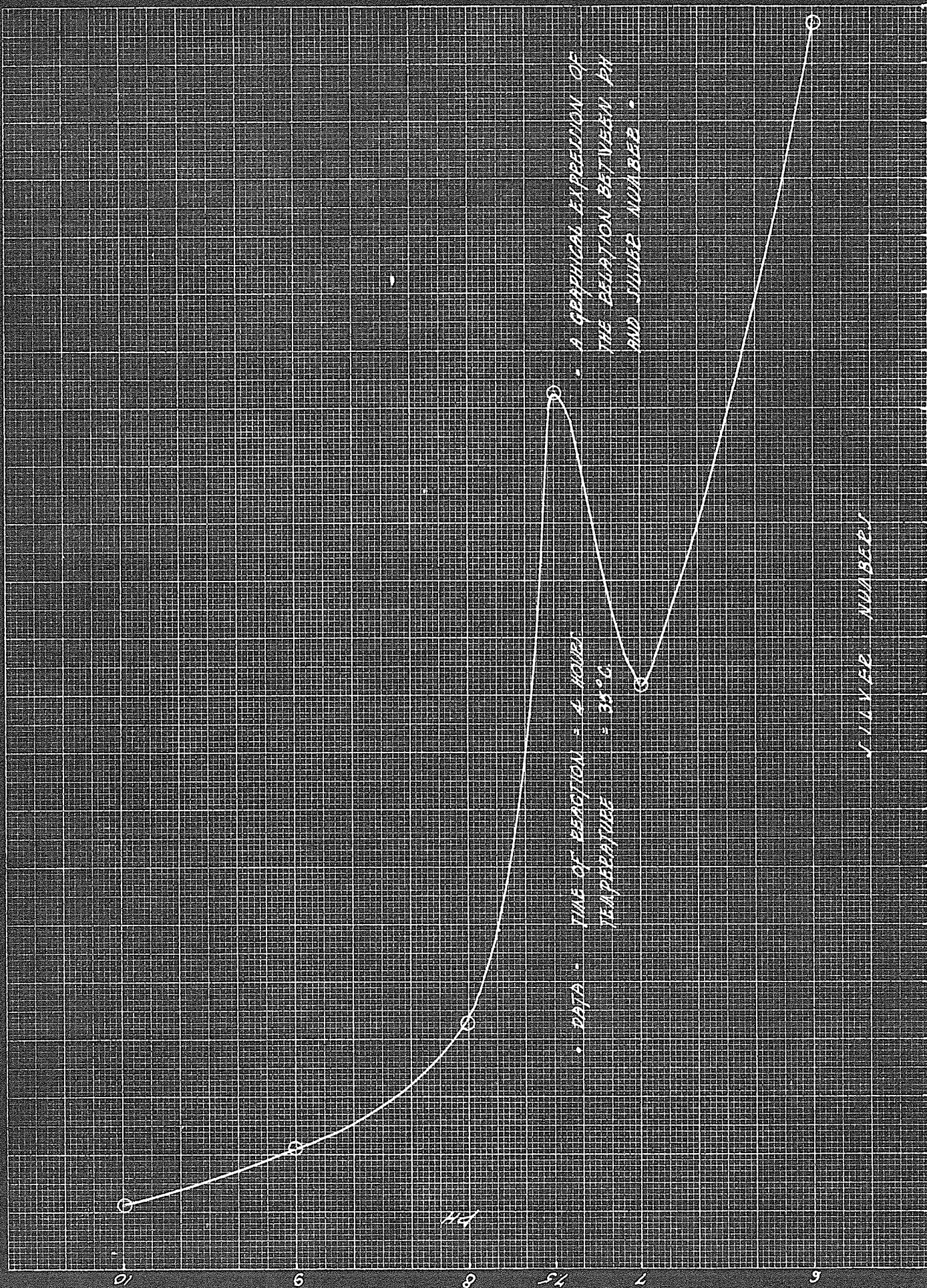
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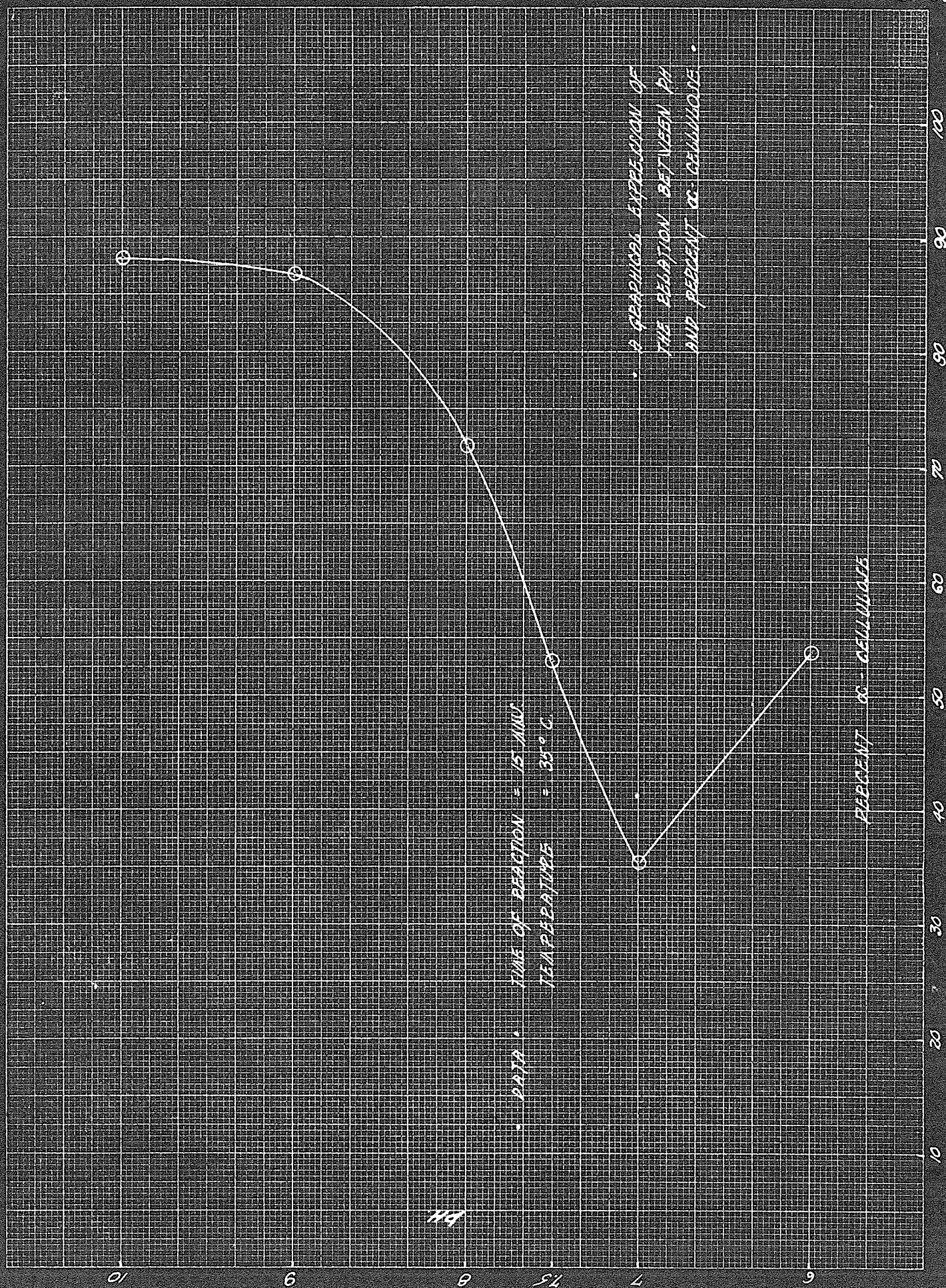
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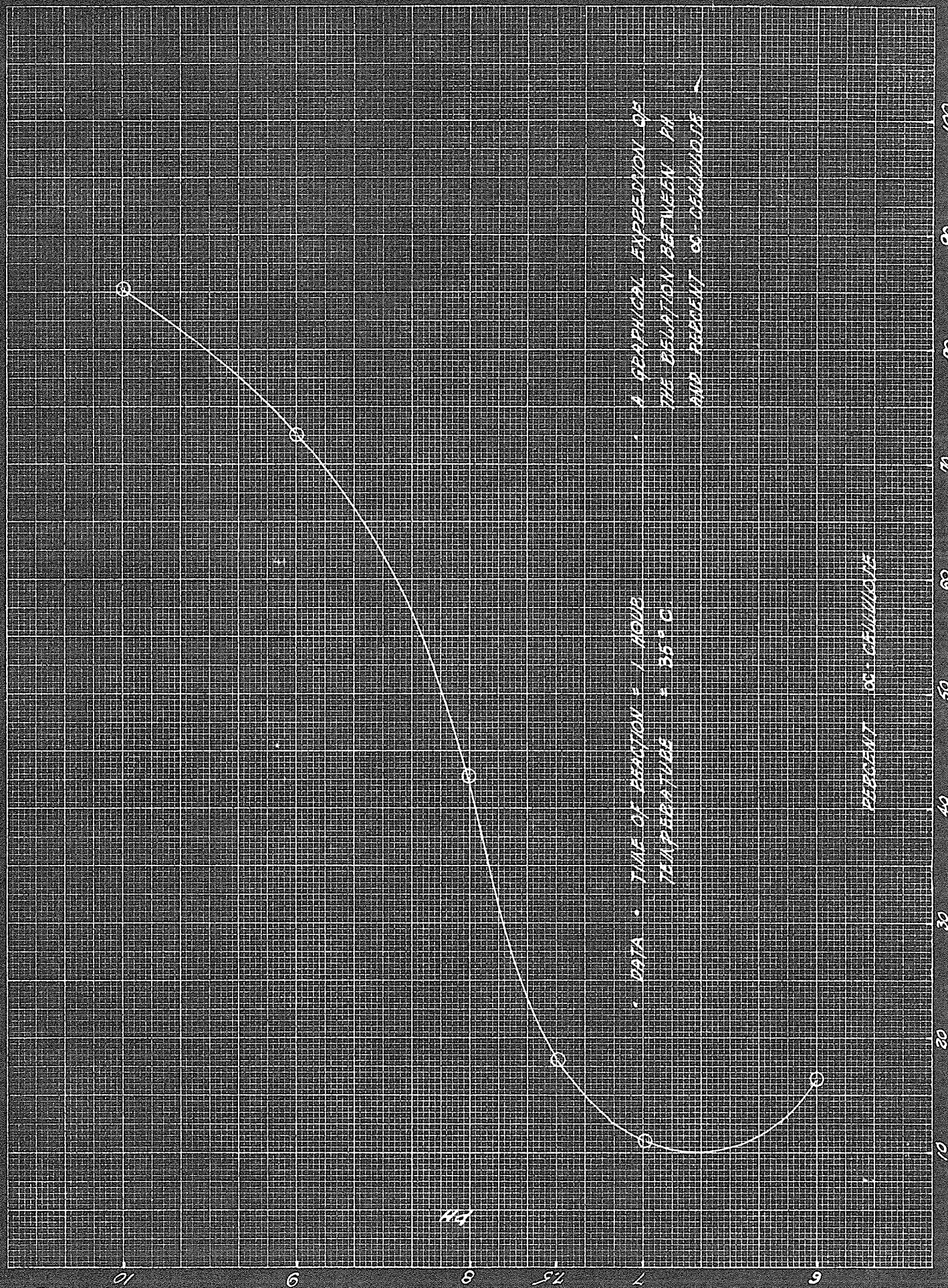
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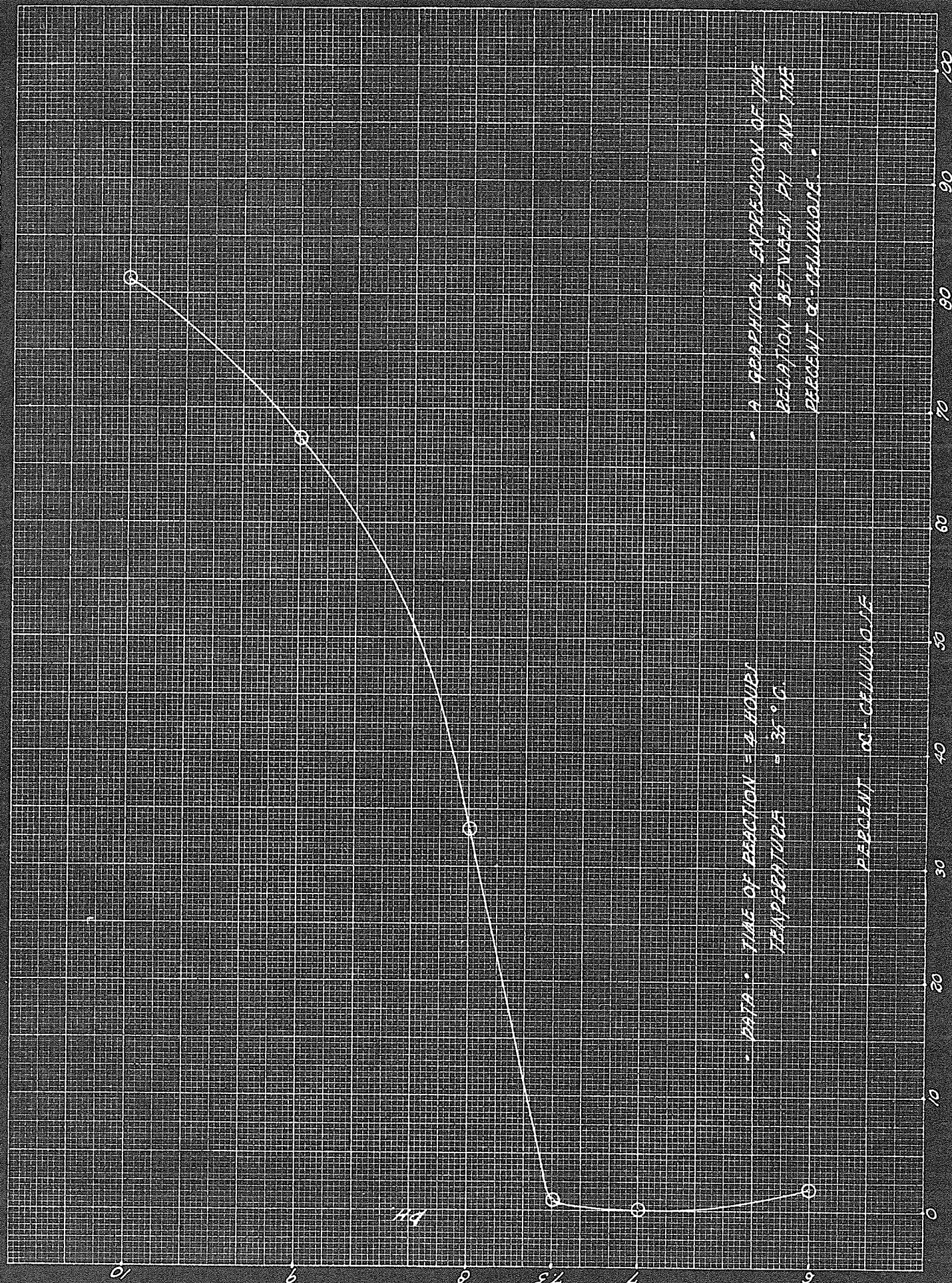


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Discussion of Results

The copper numbers and α -cellulose determinations appear to present a fair indication of the degree of degradation to which the cellulose had been subjected, at least under alkaline conditions of oxidation and when the bleaching period was short. On the other hand, there was difficulty in obtaining consistent results with the silver numbers and their interpretation in the light of cellulose modification failed to indicate the true relationship between the pH and cellulose degradation. This is evident from the fact that there are double inflexions in the curves representing the relation of silver numbers to pH. Theoretically there should be good agreement between the silver numbers and the copper numbers as both are assumed to be a measure of the reducing capacity of the cellulose; but, since this was not the case, practically, no definite interpretations can be drawn from their values.

The cellulose oxidised at pH 10 showed a decrease in the copper number over that of the original cellulose, and a further decrease was brought about with bleaching time. In contrast to this indication of purification, there was a decrease in the α -cellulose content indicating a rupture of oxygen bridges in the cellulose macromolecule. Such degradation would necessarily release aldehyde groups increasing the reducing power with a consequent increase in the

copper numbers. As the copper numbers were seen to decrease rather than increase it must be assumed that the aldehyde groups that were present in the original cellulose, and those formed during the reaction were oxidised further to non-reducing acidic groups.

The cellulose oxidised at pH's 9,8 and 7.5 demonstrated an increase in the copper numbers with a corresponding decrease in their α -cellulose contents. At these pH values therefor, oxidation with hypochlorite effected a breakdown of the cellulose molecules liberating reducing groups which were not oxidised further to acidic groups as at pH 10, or if such secondary oxidation did take place, its rate was greatly exceeded by the rate of the primary reaction.

The copper numbers of the cellulose oxidised under neutral conditions first showed a large increase and then, after the oxidation had proceeded for a longer period of time, the oxycellulose demonstrated weaker reducing power. On the other hand, the solubility of the oxycellulose increased proportionately with time until it became completely soluble in the sodium hydroxide. These facts compel the assumption that hypochlorite oxidation, at pH 7, is manifested by a rapid breakdown of the cellulose chain molecule releasing reducing groups which are dominant as such for the first two or three hours of reaction but which are subsequently further oxidised with the effect of rendering the final sample

sample of oxycellulose less reducing.

In the acid zone the copper numbers again increase with a corresponding decrease in the α -cellulose content. In contrast to the alkaline and neutral oxidations, degradation begins slowly and then becomes much more pronounced with time. In contrast to the results obtained with neutral oxidation, the copper numbers increase from the beginning to the end of the reaction; this is to be expected as it is not conceivable that the aldehyde groups first formed would tend to become acidic in an acid medium. On the whole there is less degradation at pH 6 than in neutral oxidation.

α -cellulose determinations, compared to copper number and silver number evaluations, depend to a far greater extent upon the physical properties of the oxycellulose than upon its chemical properties. The α -cellulose values are therefore to be accepted as the most valid indications of the physical degradation of the cellulose.

From the preceding graphs, prepared from the results, it is evident that degradation of the cellulose as indicated by the α -cellulose content is greatest when the hypochlorite oxidation is carried out at pH 7. The copper numbers can also be assumed to indicate the relation of pH to degradation especially if the degradation is not allowed to proceed too far. This is evident from the fact that the copper numbers also reach a maximum at pH 7, except for the

four hour samples. The silver numbers do not show any such maxima, even when the reaction is only allowed to take place for a few minutes. There does, however, appear to be an inflexion in the curves, representing their relation to pH, around the neutral point. Silver numbers, therefor, are taken to be least representative, among the three analytical methods employed, of the degree to which cellulose has been modified by hypochlorite oxidation.

The effect of temperature on hypochlorite oxidation of cellulose is great, an increase of 10° C. on cellulose treated at pH 9 brings about a large increase in the sodium hydroxide solubility of the four hour sample. For the first hour of reaction, however, the increase in temperature does not affect the α -cellulose content of the cellulose to any great extent. Temperature increase causes an increase in the copper numbers which is almost as great in the early stages of the reaction as after the oxidation has proceeded for four hours. There is an decrease in the silver numbers with an increase in temperature for the first few hours of reaction, but thereafter cellulose oxidised at 45° C. has greater reducing power, as demonstrated by the silver number, than that treated at 35° C. An increase of 10° C. in the temperature at which the cellulose was oxidised at pH 9 produced a 31.98% decrease in the α -cellulose content, a 13.63% increase in the copper number and an increase of

7.35 % in the silver number of the four hour sample.

It was very difficult to filter the oxidised cellulose from the hypochlorite solution for both the four hour sample and one hour sample of pH 8 and 7.5 respectively. The filtered cellulose in these cases appeared to be sticky. Degradation had advanced to such a degree in the four hour sample of pH 7.5 and in the one and four hour samples of pH 7 and 6 that the degraded cellulose had to be separated in a centrifuge. The products had become increasingly like starch in appearance, and the mass separating out at the bottom of the centrifuge vessels formed an almost transparent mould.

It is for the above reason that analyses, especially the α -cellulose content determinations, were very difficult to perform. In the case of the one hour sample of pH 7 the

α -cellulose analyses had to be carried out several times before a result could be obtained, and there was not enough cellulose to complete a second trial. In the four hour sample treated at pH 6 there was only sufficient oxycellulose remaining to enable one trial for each of the three analyses.

CONCLUSION

Hypochlorite oxidation produces various effects upon the structure of cellulose depending upon the pH of the solution. The reaction is accompanied by a degradation of the cellulose which occurs, more or less, under all conditions of alkalinity, neutrality and acidity. Cleavage of the cellulose macromolecules results in a liberation of reducing groups which tend to be further oxidised, in alkaline and neutral media, to non-reducing groups. This secondary reaction tends to be slight but becomes significant when only a few aldehydic groups are present in the oxycellulose as at pH 10, or when the rate of the primary oxidation is lower than that of the secondary oxidation, as at pH7.

The α -cellulose content of the oxidised cellulose affords the truest indication of the extent of degradation to which the cellulose has been subjected, as its value depends upon the degree of chain scission. The copper number evaluation depends upon the number of reducing groups present in the oxycellulose, but since a secondary oxidation also occurs, in alkaline and neutral media, which tends to counteract the reducing capacity of the oxycellulose, it can only be accepted as an arbitrary interpretation of the extent of degradation. The silver number evaluation depends upon similar properties in the oxidised product as does the copper number, and affords an even more

indefinite picture of the degree of degradation to which the cellulose has been subjected during hypochlorite oxidation.

Maximum oxycellulose formation, as identified by the α -cellulose content and copper numbers of the products occurs at the neutral point. The rate and extent of oxycellulose formation varies with the temperature, an increase in temperature causing an increase in degradation.

In the hypochlorite oxidation of cellulose there is least degradation of the cellulose itself when the reaction takes place under alkaline conditions and at temperatures below 35° C. The results of this problem, moreover, suggest that the commercial bleaching of cellulose materials should take place at pH's varying from 9 to 10.

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