

CELLULOSE XANTHATE:
CHEMISTRY, MANUFACTURE, AND
POSSIBILITIES FOR USE IN ORE FLOTATION

by

FRANKLIN JAMES DEWDY, M. S.
University of Montana

A Thesis

Submitted to the Faculty of the
Department of Chemistry and Chemical Engineering
in Partial Fulfillment of the Requirements for the
Degree of Chemical Engineer

VIRGINIA POLYTECHNIC INSTITUTE
BLACKSBURG, VIRGINIA
June 1, 1934

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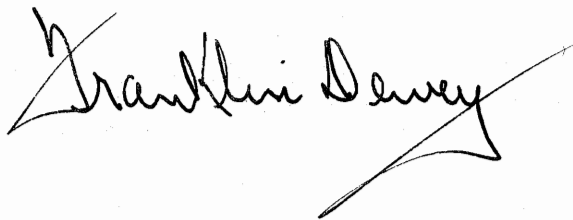
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A handwritten signature in cursive script, reading "Franklin Dewey". The signature is written in dark ink and is crossed out with a single diagonal line from the top left to the bottom right.

PREFACE

The work of this thesis has really been concerned with two fields: that of ore dressing, in which the behaviour of cellulose xanthate in ore flotation has been investigated; and that of cellulose chemistry, in which the problem of manufacture of cellulose xanthate suitable for flotation purposes has been considered.

Evidence is furnished by the thesis that, contrary to the popular belief that the chemists' knowledge is incomplete and inadequate only in the outlying fields dealing with the structure of matter, there are still borderlands of which little is definitely known, even in industrial chemistry. Though ore flotation and processes depending on cellulose chemistry are important in modern industry, our knowledge of them is largely empirical, and our theories and theoretical methods are wholly inadequate to explain or deal with them. This is not because there has been a lack of research, however, but because unusual difficulties are encountered in experimental work. To the reader of this thesis, such a fact must become evident.

In view of the double aspect of the problem and the impossibility of dealing with either part of it, as a known quantity, it has been deemed advisable to consider the work in two divisions as much as possible, and to strictly relate them only in the introduction

and in the conclusions. Also, because of the complexity of the problem it has been considered necessary to review the theoretical knowledge of cellulose xanthate and to give a brief discussion of the methods and pitfalls commonly encountered in flotation research. This was done because ~~of~~ the knowledge of the two fields involved would be necessary to anyone endeavouring to continue the research of this thesis on the same comprehensive basis on which it was started. It is suggested, however, that further work be limited to one of the two phases.

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I. INTRODUCTION

The modern theory of ore flotation, based on the results of many researches, says that the floatability of a mineral depends primarily upon the condition of its surface, upon its avidity or repellantcy toward water. Gaudin (1) says that for a mineral to float it must repel water and thus tend to go into the air phase, and he further believes that collector molecules act by attaching themselves to the mineral surface with an orientation such as to present their non-polar groups outward in a water repellant film. This view, once highly disputed, is now generally accepted. Wark and Cox (2) and their co-workers have made use of the bubble machine (3) in an attempt to quantify the action of collectors, and they have been able to show that the effectiveness of a collector is dependent on the length of the hydrocarbon chain of the molecule. They have shown that the same contact angle always results from treatment of any mineral with excess of any collector having a particular non-polar radical. In actual flotation practice, it is found that some collectors are better for some minerals than for others, but this does not necessarily nullify the work with the bubble machine, though it must be used to modify the conclusions reached from that method.

Even if one accepts the hypothesis of the non-polar

coating, there remains the problem of how this coating is formed. Taggart and his co-workers have done some work on this (4), and others have proposed theories to explain it, notably Holman (5), Ostwald (5), and Gaudin (1b). The latter believes that the collectors, in a majority of cases at least, react with the mineral surface chemically. By working with pure minerals and pure collectors, and investigating the compounds actually formed on the minerals, Gaudin's co-workers have shown this to be positively the case, and have found that both polar and coordinate valences must play a part in these surface reactions to produce non-polar films (6). The action of xanthates has been investigated quite extensively, and so far as they are concerned, one seems justified in concluding that their action is positively one of reaction with the mineral surface to form the metallic derivatives of the xanthate, and other compounds as well (7) (8) (9). Research has also shown that the action of conditioning agents and of toxic salts is certainly largely one of surface compound formation, and the marked effect of pH on the flotation has been explained to a considerable extent upon a basis of its effect on the chemical reactions involved (1 c).

Just as a non-polar organic radical is used in collector molecules to make the mineral surface water-repellant, it seems conceivable to use a polar radical to make the mineral

water-avid and thus prevent its flotation. Gaudin (1 d) has suggested the use of organic depressors for this. He proposes that organic molecules containing polar groups, such as oxygens or hydroxyls, may find such a use in flotation if they are combined with radicals, such as amines or xanthates, that will enable them to become attached to the mineral surface. This seems logical for if the flotation theory is correct such molecules should orient themselves with their polar groups away from the mineral, this tending to make the mineral water-avid and to reduce its floatability.

So far as is known, no such depressor has yet been in practice, though such depressor molecules have been prepared and futile attempts made to use them as collectors. A xanthate prepared from a glycol has thus been investigated (10), and Taggart has attempted the use of organic sulfides bearing hydroxyl groups on the ends of the hydrocarbon chains. In every case it has been noted that the collecting power of such molecules is nil.

Cellulose xanthate was suggested as a collecting agent before the theory of flotation was placed on a satisfactory basis, when it was thought that xanthates acted as collectors because of some peculiar property of the xanthate group which was independent of the rest of the molecule. No doubt many attempts have been made to use the substance as a col-

lecting agent (11). Gaudin reports (12) that he did some research on this with "discouraging results." The only attempt to look at the matter from a theoretical standpoint, in the light of our present knowledge, was given in a recent report by Ruemele (13), who says that the substance is not a suitable collector for two reasons: it contains polar groups; and it is too easily hydrolyzed.

It appears that no attempt has been made to use cellulose in a depressor molecule, and that it has not even been suggested for that purpose. However it has characteristics which would make it admirably suited for that use. For each C6 unit of the cellulose there are five oxygen atoms; and one of these were taken up in the reaction with the mineral, there would still be five others to exert their action as water-avid groups. Of all polybasic alcohols available cellulose appears to be the most suited for the purpose, and, besides having the proper structural characteristics, it is plentiful and cheap.

Only one use of cellulose has been proposed in connection with ore flotation and gained any practical application, and that has been in quite a different way from that proposed here. E. W. Wilkinson proposed using the products of destructive distillation of wood for collecting and frothing purposes (14). The process is obsolete.

It might be possible to couple many different groups to

the cellulose in order to make it mineral-avid, notably the amine and thiocarbonate groups. Of these, the latter appears the more practical, because the cellulose xanthate so formed is already well known. Like other xanthates it forms insoluble derivatives with metal salts, but whereas the alkyl xanthates of heavy metals are very water repellent, the corresponding derivatives of the cellulose xanthate seem to have an affinity for water. They attract it and precipitate as highly hydrated floccules, which is what one would expect from a knowledge of the polar nature of the cellulose.

The problem is not as simple as the foregoing make it appear, however. The cellulose xanthate is not as stable as other xanthates. Further, in its preparation and during its decomposition, compounds are formed, particularly inorganic sulfur compounds, which might exert an action of their own such as to nullify the effect of the cellulose xanthate. This necessitates study of the preparation of the xanthate to determine if it can be made into a pure stable product, and if not, if it can be used in flotation at all. It would be desirable to investigate the flotation properties of the pure substance and then the effect of the decomposition impurities.

Heretofore, work on the manufacture of xanthate has been in connection with its use for rayon production, and the preparation of xanthate for that purpose is largely on an empirical basis. Much research of a theoretical nature has been

done, but it has been difficult to establish any facts with certainty, and consequently our knowledge of the theoretical cellulose xanthate or xanthates is far from being complete or satisfactory. The first part of the following discussion concerns itself with this inadequate knowledge of the cellulose xanthate and with the experimental work that was done in connection with attempts at the preparation of a pure stable xanthate for flotation purposes. The second part is concerned with actual flotation work.

II. THE CHEMISTRY AND PROPERTIES OF CELLULOSE KANTHATE

The Structure of Cellulose

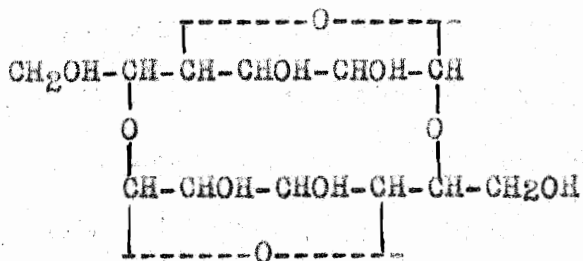
It has long been known that the empirical formula of cellulose can be represented by $C_6H_{10}O_5$, but the exact structural formula is a matter of great doubt even today. Researches into the structure have aimed at the determination of the bonding and configuration of the elements of the C_6 units, and at the determination of the number of C_6 units in a molecule and the bonding between the units. Numerous theories have been proposed for the exact structure, but many of them have been discarded because of their failure to meet certain requirements of the reactions of cellulose. Only the most acceptable of the present formulae will be discussed here. A full discussion of the many proposed types will be found in textbooks of cellulose and organic chemistry, and particularly in that of Heuser (15).

Researches have disclosed many informative facts about the cellulose molecule. Partial hydrolysis converts it into cellobiose, which is taken today as having two C_6 groups per molecule. Further hydrolysis takes the cellulose to glucose, which has the structure $CHO.4HCOH.H_2COH$. Cellulose must then be related to these two compounds. It does not ordinarily give the typical aldehyde reactions, as does glucose, but under proper conditions these will take place with reluctance, and from this and other data

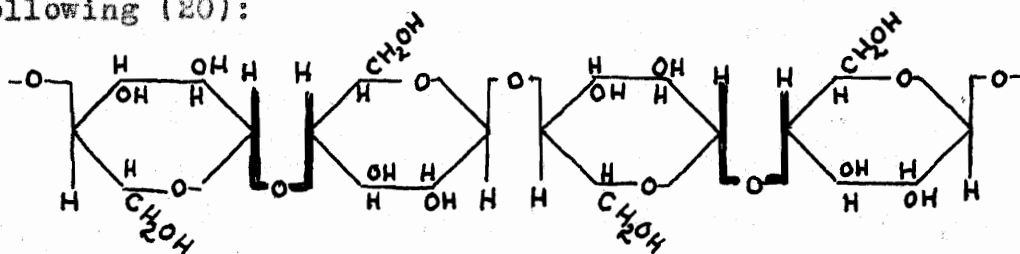
it is deduced that one oxygen is in an alkylene oxide ring form which can be changed over to the aldehyde form.

Esterification reactions indicate that there are approximately three alcoholic hydroxyl groups per C_6 unit. All though it has been found that a full three molecules of acid usually cannot be reacted, this may be due to equilibrium effects and it is generally supposed that there are three OH groups per C_6 residue. It has been shown that there are one primary alcoholic group and two secondary ones (16).

Research into the bonding between C_6 units has not been so fruitful. Some workers have maintained that each C_6 unit is complete in itself and that the cellulose is made up of such units, joined by secondary valences. Such formulae would not account for the behavior of the cellulose on hydrolysis and have fallen into disrepute. Most workers are now agreed that there are a number of C_6 units joined together by oxygen bridges, and the empirical formula becomes $(C_6H_{10}O_5)_x$. The determination of the value of x has not been done directly. Herzog (17) and Karrer(18) were of the opinion that it should have the value two, and gave the cellulose formula as:



They base their formula on the fact that the formula of cellobiose contains two C_6 units. Irvine and Hirst (19) have proposed a formula which is identical except for the value of x , which they let equal three, limiting the possible yield of cellobiose to 70%. Other values of x , even up to high numbers, have been suggested. The x ray data of Herzog indicate that only values of 1, 2, 4 or higher multiple of two are permissible, however. The workers referred to above all proposed their formulae at a time when it had not yet been shown that the amylene ring is the proper oxide ring for the glucose residue. More recent formulae take this into account and give the amylene ring. It is also common practice now to give the formula a hexagonal ring form, as in the following (20):



Here some of the oxygen bridges linkages are indicated as

being stronger than others to explain the two hydrolysis products: cellobiose and glucose.

The fact that not quite three of the hydroxyl groups take part in esterification reactions may be considered some basis for the assumption that the molecule may be more complicated than the above discussion would suggest. One such formula given by Gray (21) suggests the combination of four C₆ units, three containing the amylenoxide ring, and one the butyleneoxide ring. It is proposed that the OH adjacent to the latter should show properties different from the other.

General Methods for Preparation of Cellulose Xanthate

In the rayon industry the manufacture of the cellulose xanthate is carried out according to empirical methods evolved after much experimentation to determine the best conditions to give the most satisfactory xanthate for rayon production. The exact conditions vary from plant to plant, but the general procedure is always the same. Cellulose in the form of wood pulp or cotton linters is treated with NaOH solution of 17-18% at a definite temperature and for a given length of time. The soaked cellulose is then pressed in a hydraulic press so as to remove the excess solution--generally to a weight of about three times the weight of the original pulp. This leaves approximately 2NaOH per C₆H₁₀O₅. This soda-cellulose is then shredded in a suitable apparatus until a certain state of disintegration is acquired, and is put in containers and allowed to age at a constant temperature. The aging is not necessary for xanthate production, but is done in the rayon industry so that the final solution of the xanthate will have the proper characteristics for spinning. The viscosity of the pulp is decreased by the aging. The aged soda-cellulose crumbs are treated with pure CS₂ in a quantity ranging from 16% to 47% of the weight of the pulp, at a controlled temperature and for a definite length of time. In this xanthating process the crumbs take on a yellow-orange color. After xanthating, the material may be dissolved in NaOH solution or in water. The sol-

ubility in the former is greater and the solution may be made as concentrated as a cellulose content of 9%, with NaOH of 5-8%. This solution in NaOH is the viscose solution. It undergoes changes on standing and may be aged until its characteristics are proper for spinning.

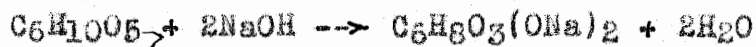
Details on this process are available in many places (22).

Soda-Cellulose

The action of NaOH on cellulose was first observed by Mercer (15 b), from whence comes the term mercerization for the process of treating cotton with NaOH so as to improve certain of its physical characteristics. The exact nature of the action of the caustic has been the subject of much discussion and research.

It is generally accepted today that the action of the caustic is not purely a physical one, but that some sort of bonding exists between the cellulose and the caustic molecules. There ^{is} doubt as to whether this is merely addition of the caustic, or actual reaction of the double decomposition type, and also as to how many molecules of the caustic combine with each cellulose molecule.

Cross and Bevan, the discoverers of viscose, considered that two molecules of NaOH were necessary for the viscose reaction (23). Ost, Westhoff, and Gesner (24) are of the opinion that at least two moles of NaOH per C₆ unit must be present, and Wolffenstein and Oeser (25) held likewise and further proposed information of an alcoholate:



Meunier (26) is of a similar opinion, but differs in that he considers the molecule (C₆H₁₀O₅)_x.

Gladstone (27), Karrer (18b), and Heuser and Schuster (28a) think exactly the reverse; that two C_6 units are bound to only one NaOH. They also propose only addition of the caustic.

Rassow and Wadewitz (29a) originally held for the formula $C_6H_{10}O_5 \cdot NaOH$, but also presumed the power of forming an alcoholate. They have later given up this view (29b) and are of the opinion that the composition of the soda-cellulose depends on the characteristics of the original material.

Vieweg (30a) at first confirmed the formula of Heuser and Schuster, but has later adopted the structure $(C_6H_{16}O_5)_3 \cdot NaOH$.

Possibly the most enlightening data are those of Hussey and Scherer (31a), who allowed sodium metal in liquid-ammonia to react on cellulose. They found that, per C_6 unit, one H was easily replaceable, two less easily so, and a third difficultly replaceable. They never succeeded in replacing a full three atoms of H, however, in which their results are similar to those obtained in esterification reactions referred to previously. Lacking further data, it may be concluded that it is possible to prepare mono-, di-, and tri-alcoholates of the cellulose.

Which alcoholate, if any, is produced in making

soda-cellulose would be difficult to determine. Very probably there is an equilibrium which is affected by many factors as Rasso and Wadewitz have said. In the presence of the water of 18% NaOH solution, it is not likely that the alcoholate formation could progress very far, unless the water is also removed from the system, as by adsorption by the cellulose.

Using the x ray it has been shown that NaOH of strength below 13% will not mercerize, as it does not change the space lattice of the cellulose (32).

For preparation of a soda-cellulose satisfactory for xanthating, a minimum concentration of NaOH solution of about 16% is usable. With more dilute a solution, even very long soaking results in a product which xanthates only very slightly (33). However, Cross and Dore'e (34a) found that cellulose treated with 9% NaOH and pressed to a weight of 2 to 3 times that of the pulp, reacted with CS₂, but apparently with the formation of insoluble xanthates. The degree of xanthation was very low, but the physical properties of the cellulose were changed greatly.

Use of comparatively high concentrations, according to Karrer (18c), results in a product of the same composition regardless of the concentrations, or time of treatment. This indicates that a chemical reaction

takes place in the process, probably just as it does in the sodium liquid-ammonia system, but with the formation of a lower alcoholate.

The use of too concentrated alkali results in degradation of the cellulose (15a). Even in the ordinary treatment this must take place to some extent, particularly in the aging, for, as Rassow and Wadewitz (29) have shown, fresh soda-cellulose dried under toluene is light colored while the aged material is brown colored (33a).

It has not been explained why the more dilute caustic should fail to produce the alcoholate suitable for xanthation. It is generally accepted, however, that the NaOH also has a physical effect on the cellulose, and that during the aging process it tends to break down the cellulose micelles as evidenced by decrease of the viscosity of the pulp. It may be that the OH groups are not exposed for reaction with the NaOH before this dispersion occurs, and that the 16% caustic is necessary to bring the dispersion about. If this were so, one would expect that the alcoholate formation would not be sufficiently advanced to permit good xanthation until the soda-cellulose had been aged, even though 18% caustic were used (judging from viscosity changes). However, the aging of the crumbs

seems to have little or no effect on the xanthation (35).

During the aging, it is probable that the oxygen of the air is also important in breaking down the micelles.

The Xanthation

Cross and Bevan (23a) formulated the production of cellulose xanthate as taking place the same as the formation of the xanthate of any alcohol:



It is apparent that the composition of the cellulose xanthate must depend on that of the soda cellulose. Hypothetically it should be possible to put a xanthate group on each of the OH groups of one C₆ unit. Thus far, evidence has been against the practical accomplishment of this, though Scherer and Simmons have obtained some evidence that it may be possible to form di- and tri-xanthates by action of CS₂ on Na-cellulose prepared in liquid NH₃ (36).

The amount of CS₂ used commercially varies from 47% down to 16% of the weight of the cellulose. The 47% allows one CS₂ per C₆ unit. The xanthation takes place at between 25 and 30 degrees C° usually, and is accompanied by side reactions to form thiocarbonates and sulfides of sodium which color the cellulose xanthate product. If xanthation is carried beyond a certain point the color of the material becomes darker and the mass becomes sticky, just as though addition of water were made. These side reactions necessitate that

even when 47% CS₂ is taken, the product can not contain, on an average, one CS₂ per C₆. However, even with the 16% CS₂ the product is soluble in NaOH solution and is suitable for rayon production (37). Indeed, it is common practice to use a low amount of the CS₂.

Anhydrous soda cellulose will not react with CS₂. This has been reported by various workers, (42b) (35).

In making alkyl xanthates it has been found that a low temperature is favorable to the production of a pure product, as it slows up side reactions far more than it does the main reaction to form xanthate. In the case of cellulose xanthate this must also be important, but the effect is not so marked because the formation of cellulose xanthate is also slowed considerably by a decrease in temperature. Because of this temperature effect the result of some workers (38), who have attempted to relate the degree of xanthation to various factors and have neglected temperature, must be discounted. There is evidence that a lower temperature than that generally used may be optimum. Numa (39) says that 15°C is the best xanthation temperature.

The solution of cellulose xanthate in dilute

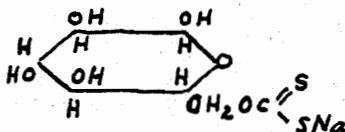
NaOH is not a true solution, but must be regarded as a water dispersion of colloidal particles. Also, it is not a stable system, but undergoes quite rapid change. There is a constant decrease in the content of CS₂ bound as xanthate, and ~~is~~ after complete dispersion has once been reached, there is a constant increase in viscosity until the solution finally gels. There are two distinct theories regarding this decomposition.

Rapid change of the cellulose xanthate, complicated with a lack of good analytical methods for analyzing it in the presence of the impurities it contains (see Analytical Methods), have caused difficulty in determining its composition, so that many theories of this have been advanced, and many round-about ways devised to give evidence for them.

The discoverers of viscose prepared a starch xanthate to which they assigned the formula: $C_6H_7O_2(OH)_2(OCS_2Na)$. They found that solutions of this xanthate remained fluid and did not coagulate, but that they decomposed to give off CS₂ and Na in a manner similar to the cellulose xanthate. They analyzed the solution at different times and on a basis of their analyses proposed formulae giving xanthates with varying numbers of C₆ units per CS₂, changing with time. Their formulae

hardly seemed justified, for such a solution might more logically be considered as containing mixtures of the simple starch xanthate and free starch.

More recently, a glucose xanthate has been purified (40) and the formula assigned to it:



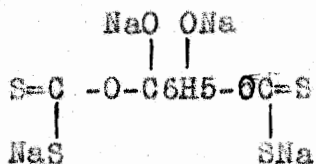
It is to be noted that the xanthate is here put on the primary hydroxyl group, and if this is correct, one might expect a similar condition with cellulose xanthate (13).

The question of whether a xanthate radical can be attached to more than one of the hydroxyls ~~does react~~, has been dealt with.

Berl and Bitter (41) have found that a mono-methyl cellulose can be xanthated, whereas the dimethyl cellulose cannot be. Leiser (42) has prepared a mono-methyl dicellulose of the composition $(C_6H_{10}O_5)(C_6H_9O_4)OCH_3$, and has found that it apparently does not go into the viscose reaction. He further converted the dicellulose compound into glucose and monomethyl glucose and found the latter to form the 2-methylglucose phenylhydrazone, from which he concluded that it is the secondary hydroxyl on the second carbon that reacts in the formation of the viscose xanthate. This is not what one would expect

judging from the glucose xanthate given above.

In view of the fact that a sodium tri-alcoholate can be prepared from the cellulose, it also is surprising that only one of the hydroxyls should appear to enter into viscose reaction. Wolffenstein and Oeser (25b) questioned whether more than one CS₂ could be attached to a C₆ residue, and by taking the cellulose tri-acetate over to a xanthate they obtained a product for which analyses indicated approximately the formula:



Here it would appear that five hydroxyl groups reacted, which is not explainable. This dixanthate differs from the usual xanthate in color, appearance, and particularly in stability, for it splits H₂S with remarkable ease. Also, if treated with more CS₂ it changes to the usual mono-xanthate. The dixanthate can also be prepared from nitrocellulose.

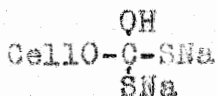
It has been suggested that in the ordinary viscose xanthate preparation more than one CS₂ may react with each C₆ residue. Geiger (43) has proposed this in his formulation of a dynamic equilibrium regarding the degree of xanthation. Others have held the idea

that mono-, di-, and tri-xanthates may be formed. So far as we know, our present methods of analysis would not permit us to so distinguish between such xanthates.

It is assumed by most workers that the xanthate undergoes no change on being dissolved, and that the formula of the cellulose xanthate is the same type as for other xanthates:

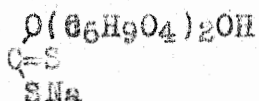


Rassow and Aehnelt (29c) do not agree with this, but believe that either the H₂O or the NaOH, depending on the solvent medium, adds to the xanthate and the double bond to the sulfur is opened up:



Though the authors of this scheme defend it strongly it has not been accepted by others. The theory will be referred to again in connection with precipitation by salts and treatment with acids. However, in connection with this it might again be pointed out that the solution of the xanthate in H₂O is light yellow in color, while that in NaOH solution (even though excess CS₂ be removed before solution) is a dark brown. Formation of a different structure in NaOH solution might help explain this, if one also assumes that the Na₂CS₃ likewise forms as addition compound in the presence of NaOH.

Though many have assumed the formation of the xanthate with one CS_2 for each C_6 residuw, no one has succeeded in isolating and analyzing such a product. However, claim has been made for the isolation of compounds corresponding to two or more C_6 residues per CS_2 . These may have been only mixtures of cellulose and a higher xanthate, as will be later shown, but nevertheless formulae for the xanthate have been written based on these analyses. Bernhardt (44), Frenke (45), Atsuki and Mitarbeiter (46), and Heuser and Schuster (28a) have formulated as the product of xanthation:



If this is assumed, then one must also accept as a fact that the great excess of NaOH used over that necessary to form this hypothetical compound acts merely to physically disrupt the cellulose micelle. Moore has succeeded, however, in isolating the alcoholate which would thus necessarily be formed; that is, one with two C_6 residues and one NaOH. Also, it must be remarked that this is not in accord with the facts that either a freshly prepared or a well aged soda cellulose may be xanthated with the same amount of CS_2 , while the latter should contain more separate molecules from the micelles and require more CS_2

Most workers are in agreement that the degree of xanthation depends on the time and the amount of CS_2 used, and also on the temperature of xanthation. Different compounds have been hypothesized for the different degrees of xanthation (33b), but these seem hardly justified. This and the question of the number of C_6 units present in each xanthate molecule are better discussed in another connection.

Properties of the Xanthate Solution and Changes it

Undergoes

The solutions of cellulose xanthate must be regarded as colloidal solutions rather than true solutions, according to general opinion (33a). The behavior of the viscosity of the viscose solution tends to support this, although the viscosity seems to obey a law of its own (33c). In a dilute caustic solution the solubility of the xanthate is equivalent to about 9% of cellulose, but in pure distilled water it is much lower than this, probably about a third.

The aging of a water solution of the xanthate has not been investigated as widely as that of the viscose or caustic solution. During the experimental work it was observed that the water solution begins to decompose immediately, and if left at room temperature will gell in less than 24 hours. The gelled product is soft and tends to be flocculent and easily broken apart. During the decomposition an odor of H_2S is evident at all times, but no other odor, as of CS_2 , is discernible. The solution is at first yellow, but on standing for considerable time it becomes colorless.

The aging of the viscose solution is well known. The viscosity of the fresh solution at first falls, presumably while the dispersing process is still under way,

and then it rises constantly until the solution gells. The gelled material is quite firm and rubbery and cannot be torn apart nearly so readily as that from the water solution. During the entire decomposition the solution remains quite dark brown in color, and when gelation occurs a reddish brown liquor separates. Odorous gases are given off during this time, and odors of gases other than H_2S are evident.

The original view for the decomposition of the xanthate, and it is still widely held, is that the xanthates originally present in the solution tend to polymerize with breaking off of CS_2 groups, so that xanthates higher in content of C_6 residues are constantly forming. As these lower xanthates are formed their solubility decreases until finally a point is reached at which they tend to precipitate and the gelation takes place. This is presumably aided by the fact that the decomposition is accompanied by formation of inorganic salts, which would help the precipitation, as will be discussed later (see Precipitation by Salts). Such a theory has been proposed by Cross and Bevan (23c), Ost and Mitarbeiter (47), Rassow and Wadewitze (29a), Heuser and Schuster (28a), Bernhardt (44a), and others. The theory is based upon the physical behaviour of the viscose solution, and upon

analyses of xanthate precipitated from solution, or determined in the solution directly. The first criticism of this comes from the fact that the analyses never indicated exact compositions, and also that even if the analyses did indicate such definite formulae they would have to be discounted as the methods are not satisfactory. A second and more striking criticism leads to the second theory.

Pure cellulose may be treated with cellulose xanthate solution and be dispersed, according to Frenkel (45a). This conclusion has also been reached by others, who have then concluded that the xanthate in the viscose solution decomposes to give cellulose which is kept dispersed by the remaining xanthate until the latter has fallen to such a low content that the solution must gell. It would be desirable to find a method to separate such dispersed cellulose from the xanthate, but none has been devised. Nevertheless, this newer theory must be regarded as having much the sounder basis of fact. It does not propose any particular composition for the xanthate which is the dispersing agent and this may be taken to be anything from a cellulose trixanthate to a polycellulose xanthate, taking more definite information.

If this latter theory is adopted it must still

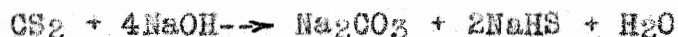
be considered that the xanthate decompose from a highly xanthated to a lower xanthated state, however. Otherwise one could not explain the effect of age of the viscose on precipitation by salts. If only one xanthate and cellulose were present, it should either be possible to salt out the xanthate regardless of age of the solution, or it should be possible to salt out the cellulose independently of the xanthate, and this has not been accomplished.

Inorganic Compounds Associated With Cellulose Xanthate

With the cellulose xanthate are inorganic compounds which result from two types of reactions; side reactions occurring during the xanthation; and consecutive reactions such as the decomposition reactions of the xanthate.

It has been previously mentioned that the xanthated crumbs are a yellow orange color, the water solution of xanthate a yellow color, and the viscose solution brown. Purified cellulose xanthate, which will be discussed later, is very light colored and gives a colorless solution. The color of the product of xanthation must thus be due to impurities.

As has been pointed out, there may be an excess of NaOH present over that necessary to form the alcoholate of cellulose, but in any case, due to the water present, there must be an equilibrium between sodium attached to the cellulose and that present as NaOH solution. NaOH reacts with CS₂ to form thiocarbonates. Ragg (48a) has investigated these reactions in connection with the decomposition of viscose, and they have previously been formulated by others, as by Berzelius (49):



and by Leuchs (50):

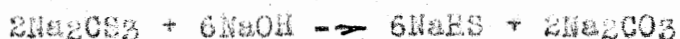


Kita and Tomihisa (51) propose that two moles of NaOH react with approximately one of CS₂, and that sufficient H₂S is formed so that about 60% Na₂CS₃, 40% Na₂CO₃, and no free Na₂S results.

Any Na₂S formed during the xanthation would immediately react with CS₂ to give the trithiocarbonate.

Geiger (43a) has, in connection with his equations for degree of xanthation, given equations for the extent of the reaction of NaOH and CS₂; his products are the same as those in the second equation of Berzelius.

Eggert (52) says the trithiocarbonate reacts with NaOH:



There is one theory which differs remarkable from those given above. This is the theory of Bernhardt (46a) (23b), who hypothesizes the formation of carbonyl sulfide:



This last reaction takes place immediately and prevents the giving off of an H₂S odor during the xanthation, according to Bernhardt.

It would be impossible to say that any one of these

schemes is correct to the exclusion of the others. The thiocarbonates have been somewhat neglected by all classes of chemists, and methods for determining the exact course of the reactions are not available. Perhaps all of the formulated reactions take place to some extent.

The important thing is that considerable CS₂ is used up by reactions other than that to form xanthate, and that impurities thus result. The formation of these impurities is greatly lessened by a decrease in temperature, and at a temperature below 0°C the reactions between water, NaOH, and CS₂ go on very slowly. No one has explained why a sticky xanthate results from too long a xanthation time at the ordinary temperature used. This might be due to extensive reaction between CS₂ and NaOH with liberation of H₂O which tends to dissolve the xanthate and render it sticky. At a low temperature such reactions could be slowed and not enough water liberated to give a sticky product. Also reaction of the cellulose sodium alcoholate should cause constant shift of the reaction between NaOH and cellulose with consequent liberation of water.

The decomposition of the xanthate has previously been discussed in one connection. The mechanism

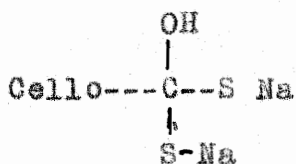
of the decomposition and the nature of the inorganic products of the decomposition will now be considered.

The statement is made (33d) that the cellulose xanthate is the result of the combination of a strong base (NaOH) and a weak acid (cellulose-dithiocarbonic acid), and that decomposition thus takes place readily because of extensive hydrolysis with production of the free acid, which is unstable.

This is open to question. It would be interesting to find out the pH of a solution of pure (NaOH free) cellulose xanthate. Unfortunately such a solution has probably never been prepared, as it is difficult to keep such a solution without decomposition and it is also exceedingly difficult to free the xanthate from excess NaOH. However, one may draw an analogy to the alkyl xanthates. It was long held that these alkyl xanthates are combinations of weak alkyl-dithiocarbonic acids and a strong base, NaOH. However, these xanthates can be purified and brought to such a state that they are free from inorganic impurities and brought to such a state that they are colorless and odorless and analyze over 99% pure. In such a state they do not change the pH of distilled water perceptibly (7b). One questions if such compounds could be made from a weak acid, and by analogy one

questions whether the cellulose xanthic acid can be as weak as is generally supposed. More evidence on this score comes from the fact that the decomposition of the xanthate, even in the presence of excess NaOH, results in the formation of brown compounds, presumably sodium thiocarbonates, which are neutral to phenolphthalein (55a).

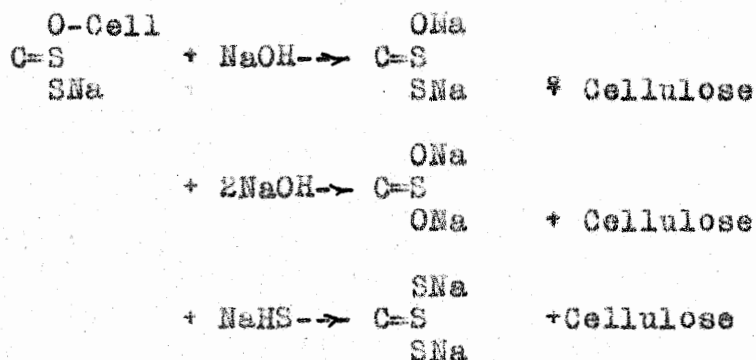
Such analogies are dangerous, however, and other evidence must not be overlooked. Evidence for the idea of the weak acid comes from the fact that strong NaOH solutions of the xanthate are much more stable than water solutions. However, even the water solution contains free NaOH. Data have been given to show that a purified xanthate is more stable in water solution than is an impure one, and this makes one wonder if the small amount of NaOH may not increase decomposition, and a great amount decrease it. This idea may be more valid if one accepts the scheme of Rassow and Aehnelt (29c), whereby the addition compound with NaOH is formed:



Dilute alkali might not cause addition, whereas in a more concentrated solution the NaOH would add. This

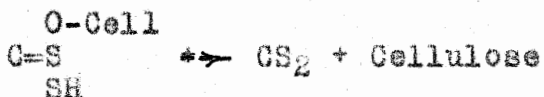
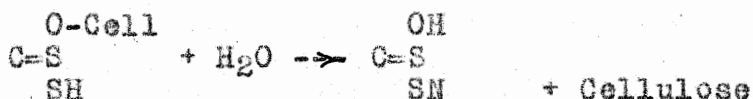
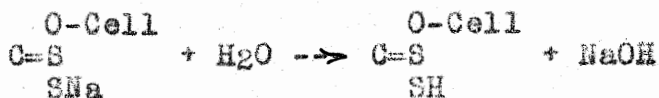
decomposition would be favored in water solution, but the formation of the addition compound would take place better in concentrated caustic solution, which is contradictory. The authors of the theory also propose that water may be added just as caustic. If this took place the vibrations within the molecule would not be decreased as much as by addition of the caustic, and decomposition would take place faster.

Other theories for the decomposition have considered the idea of saponification and hydrolysis. Ragg (48c) gives the following equations:

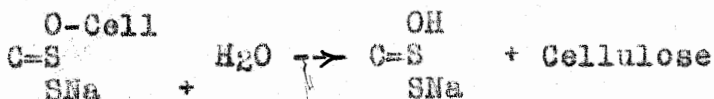


From this one might expect a more rapid decomposition in caustic solution than in pure water, which is contradictory to known facts.

Ost and Mitarbeiter (47a), and Rassow and Wadewitz, held for the formation of the weak xanthaic acid as a first step in decomposition:

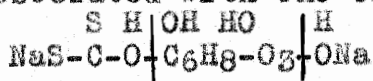


Cross and Bevan (23), and Heuser and Schuster (28) believe it takes place:



They, of course, as has been previously pointed out, believe in the formation of lower xanthates by polymerization, but they think the decomposition for elimination of each xanthate group, takes place as formulated above.

Wolffenstein and Oeser (25) base their decomposition formulation on their idea that one mole of NaOH is associated with one of xanthate:



They added NaOH to alcohol for the precipitation of the xanthate in various decomposition phases, and advance this as evidence for the above splitting out of NaOH.

It has been said that the addition of CS₂ to a xanthate (33c), slows decomposition and such an addition has been proposed by Vitale (57) to increase the stability of xanthate

solutions (59), and to stop the decomposition.

One thing seems sure: there is a decrease in the CS₂ content with time, and the decrease of xanthate CS₂ is greater than of total CS₂. Tanemura (54) gives the following data:

Time-days	Total CS ₂ %	Xanthate CS ₂ %
0	1.85	1.33
1	1.79	1.33
3	1.91	1.26
6	1.52	0.90
9	1.57	---
10	1.61	0.70
12	1.45	0.75

These data are certainly only valid as expressing a trend. They cannot be exact, as in some cases the discrepancies are entirely illogical, and they give evidence of the difficulty of analyzing viscose, and indicate the manner in which all such analyses should be taken.

Bernhardt (44) has found that in the course of the aging, xanthate CS₂ decreases constantly, thiocarbonate CS₂ increases sharply, free CS₂, which is present only in traces, declines a very little, total H₂S and CO₂ act similarly, and COS, always present in small amounts, increases. The statistical effect is that CS₂ constantly decreases.

Wyss (55) has obtained similar data and used them to plot curves (33f).

Kita and Tomahisa (51) have found that free NaOH in viscose decreases until it reaches a zero value.

Herzog and Gaebel (56) declare that the CO₂ of

the air has no measurable effect on the decomposition of the viscose, but Heuser (15c) seems to disagree with this and says that the CO_2 of the air decomposes the xanthate in stages.

Heuser and Schuster have given curves to show that the stability of the xanthate increases as the thiocarbonate content decreases (33g). Particularly is the effect noticeable in the case of caustic solutions, according to their data. No satisfactory explanation of this has been offered, though these authors seem to think that the thiocarbonate may tend to salt the xanthate out of solution (52), though why this should cause decomposition is not explained. It would appear that the reverse should be theoretically the case.

Even in the face of all the theories and evidence presented above it is difficult to find an acceptable theory for decomposition of the xanthate. Possibly decomposition takes place in several ways.

Direct saponification of the cellulose from the sodium cellulose xanthate must be objected to because it should take place more readily in caustic than in water solution.

Objection can be raised to the idea of formation of the free cellulose xanthic acid by hydrolysis, on

the basis that the acid may be too strong for hydrolysis to take place readily in this way. However, there must be some hydrolysis even in the case of very stable salts, and if one considers that hydrolysis thus takes place to only a very slight extent, but that the free acid formed is exceedingly unstable and tends to break down immediately, one can see why decomposition should take place and why it should be decreased in NaOH solutions. The decompositions would result in formation of insoluble cellulose, which would tend to make the decomposition proceed.

One may go further and hypothesize direct breaking out of the CS_2 from the free acid. CS_2 is itself a very unstable compound, even decomposing under the influence of light, and in a compound such as a xanthate its stability may not be entirely changed, particularly in a xanthic acid. It is known that the xanthic acids are unstable, in the case of the alkyl as well as the cellulose compounds.

An entirely different idea for the decomposition may be built up by using the addition compounds of Rasso and Aehnelt. It may be presumed that water adds and that the hydrogen then tends to shift with breaking out of the cellulose. In a strong caustic solution the NaOH would add, and there would be only

half as many hydrogens to shift and the stability would increase, as a consequence. This would not explain the apparent greater stability of purified xanthate in water solution. There are also other difficulties, but on the whole the addition idea has much to commend it, and it permits formulation of a mechanism for the decomposition. It is not likely that cellulose should ionize from any compound yet one would almost necessarily consider such a process as taking place if the other decomposition theories were adopted.

Possibly use of different methods of attack will sometime give an insight into this. The Ramann spectra might be used, for instance, in an attempt to determine if the double bond to the sulfur is broken in xanthate solutions.

Intimately connected with this matter of natural decomposition is the matter of accelerated decomposition.

Decomposition by Acids

Accelerated decomposition is made use of in the rayon industry when a thread of viscose syrup is spun into a bath of sulfuric acid (with other components) which decomposes the xanthate and regenerates cellulose in the form of a thread.

Fresh viscose is not decomposed as rapidly as is aged viscose, though strong mineral acids will decompose even fresh viscose almost instantly. If weaker acid is used a time effect becomes somewhat evident and the older viscose is seen to decompose more rapidly. With weak organic acids the decomposition is slowed considerably, but nevertheless takes place constantly. Faust (58) investigated the effect of acids on fresh and 4 day old viscose solutions, and obtained the following data:

Acid--1 N.	% xanthate in viscose after the decomposing time given in seconds					
	3	(4)	7	12	18	(18)
acetic	6.7	6.5	6.6	6.4	6.0	5.5
Phosphoric	6.3	6.0	6.2	6.0	5.7	5.2
oxalic	5.4	5.4	5.2	4.8	4.5	4.3
HCl	5.2	4.0	4.9	4.5	4.2	3.3
H ₂ SO ₄	5.1	3.8	4.8	4.3	4.1	3.2
H ₂ SO ₄ with 5% Na naphthaline sulfuric acid.	5.2	4.7	4.9	4.6	4.3	3.8

This table illustrates quite well the statements

enunciated above.

The experimental work indicated that there is tendency to underrate the decomposing effect of weak acids. Fresh cellulose xanthate was put into water solution and dilute acetic acid added until it was just acid to litmus. The solution decomposed with apparently complete regeneration of the cellulose in about two hours. This was repeated several times with like results. This fact has direct bearing on the analytical methods which have been used for the analysis of cellulose xanthate, and also on data for the composition of pure xanthate. These will be discussed later. Suffice it to say here that in the decomposition of the xanthate by acids an odor of H_2S is always very prominent, and that it should be noted that the concentration of H_2S in the solution, in the case of acetic, must be appreciable, and that such sulfide as would be there would give a titration value with iodine. If from each molecule of xanthate two sulfide ions resulted, then the decomposition of one xanthate would give products indicating four moles, by the iodine titration.

Precipitation of Xanthate by Salts

Many salts which are not capable of forming insoluble xanthate derivatives tend to precipitate the xanthate from solution, according to the researches of Hassow and Aehnelt (29b). They have found the order of precipitating power to be:

Al_2SO_4	1N	pH	3.2
ZnSO_4	.1N		6.1
$\text{Al}(\text{Ac})_3$	sat.		5.0
MeAc	1N		9
Na_2SO_3	1N		9

The precipitation power, according to them, decreases with decreasing acidity of the salt solution. The di- and trivalent ions seem to have the most effect, but that the effect of pH must be important is seen in the fact that ^{the sulfate} of aluminum has a greater precipitation power than the acetate. This has been given in the patent of Leuchs(59). It is also deduced from these facts that the viscose consists of negatively charged colloidal particles and that precipitation follows the well known rule of colloid chemistry--that precipitating power increases with increasing charge or valence of opposite sign. The position of ZnSO_4 in the above table (above $\text{Al}(\text{Ac})_3$) seems to be an exception to the rule.

Aged cellulose xanthate is more easily precipitated

by means of salts than is the fresh material. This is made use of in the NH_4Cl control method in the viscose industry where an ammonium chloride number is used to trace the aging of the viscose and determine the correct spinning time (60). Fresh material will not be precipitated at all, either by NH_4Cl or NaCl . However, if HAc is added to the salt solution precipitation is possible. This may be due to: greater ease of precipitation in an acid solution; decomposition of compounds tending to hold the xanthate in solution; or decomposition of the xanthate itself, with formation of lower xanthates more easily precipitated. The latter view seems the most logical to the author, after observing the effect of the acid on the precipitation. When the acid salt solution is added to the viscose, quantities of H_2S are liberated. It might also be mentioned again that it is possible that the gelation of viscose solutions may be aided by the presence of salts formed in the decomposition of the xanthate; for instance, trithiocarbonates.

Solubility of the Xanthate in Organic Solvents

One might expect that the xanthate would be soluble in some of the more polar organic solvents, such as the alcohols, or in acetone. However, in this respect the cellulose xanthate does not resemble the alkyl xanthates.

The latter can be dissolved in acetone, and use is made of this in their purification, whereby the xanthate is dissolved in the acetone and filtered away from insoluble inorganic material, then precipitated by the addition of some highly nonpolar solvent such as petroleum ether. This is not applicable to cellulose xanthate, for it does not dissolve in any organic solvent, contrary to expectations.

This insolubility of the xanthate may be made use of in drying or in freeing it from impurities that are soluble in such solvents, however.

In the experimental work it was observed that the cellulose xanthate is decomposed by acetone, and this confirms the observations of others. This is a marked anomaly to the behaviour of alkyl xanthates in acetone, and at present no explanation can be offered for it.

Metallic Derivatives of the Xanthate

Formation of metallic derivatives of cellulose xanthate follows a course much the same as the formation from other xanthates. However, some notable peculiarities are evidenced. Though the derivatives seem to be exceedingly insoluble in water, and in some cases more so than the derivatives of alkyl xanthates, they all have a marked affinity for water and form flocculent, apparently hydrated, precipitates, whereas the alkyl metallic xanthates all exhibit a marked tendency to repel water. Whereas zinc ethyl xanthate is quite soluble (the amyl compound is insoluble) and the barium and calcium alkyl xanthates are also soluble, the corresponding salts of cellulose xanthate appear to be quite insoluble, in spite of the anomalous affinity for water.

Incomplete investigation may lead to the erroneous belief that the cellulose metallic xanthates may differ from alkyl derivatives in color, as the impure cellulose xanthate gives highly colored precipitates. However, the color is due to thiocarbonates present which form colored salts with the metals (61). Purified xanthate (to be discussed later) gives precipitates which appear to follow the same color laws as for other xanthates. Thus, impure xanthate precipitates a carmine-red lead

derivative, but pure xanthate precipitates a white derivative. Formation of the copper salt appears to first give the cupric compound, a chocolate brown substance, but this gradually changes in the course of a few minutes to the cuprous compound, yellow colored. This change from cupric to cuprous does not take place with the rapidity evidenced by the alkyl compounds (7c).

Investigation of the derivatives of alkyl xanthates has not been complete, but it appears that the ferric derivative is the more stable, (62). With the cellulose compound this may not be so; addition of a ferric salt to cellulose xanthate solution first forms a dark brown precipitate, but this gradually lightens to buff colored indicating change of decomposition. No analyses were made. However, formation of both derivatives has been reported by Leiser (42c). This possible difference in behaviour of the alkyl and the cellulose xanthates should be worth investigating on a quantitative basis. Lotze (33h) says that a ferric salt has not been prepared.

The formation of the metallic derivatives has been investigated by Seidel (62). They were also studied in the experimental work and the colors of metallic derivatives were used as a test for purity.

The colors of the precipitates from pure and impure xanthate solutions:

Metallic derivative	With impure xanthate	Purified xanthate
Zinc	yellowish	white
Lead	carmine red	white
Barium	yellowish	white
Copper	purple brown	brown changing to yellow
Bismuth	red brown	???
Iron	dark brown changing to light brown	dark brown changing to buff
Nickel	cherry red	yellow
Cobalt	red-brown	light pink
Manganese	white	white--quite sol.
Chromium	(greenish??)	light--quite sol.
Mercury	yellow	yellow??

The Nickel derivative is soluble in ammonia. The copper compound is insoluble in ammonia but soluble in KCN.

The Zn derivative is soluble in NaOH. The Hg derivative forms a complex with one mole of HgCl₂.

On standing in contact with the mother liquor, the metallic derivatives appear to slowly decompose and change over into the sulfides (color). In some cases this change takes place very slowly.

It may be broadly stated that the stability of the metallic derivatives is a function of the previous history of the xanthate used in their preparation. The lead and iron salts appear to be least stable and the nickel most stable, but these data are not given as results of exact investigation. The copper derivatives are quite stable even in the presence of mineral acid (53) and other metallic derivatives are also amazingly stable under such conditions.

Copper alkyl xanthates are soluble in a solution of CuCl_2 in ethyl alcohol (62) (7). The cellulose derivatives seem to be likewise soluble. It can be reprecipitated from such a solution by water dilution, and it is suggested that this may be made use of in determining the exact composition of the cellulose xanthate. It seems conceivable that by careful treatment with acid the copper cellulose xanthate might be freed from thiocarbonates, and other such impurities.

Some attempts were made to do this, but it was never accomplished. It is nevertheless a possibility, however, and if the xanthate could be so purified it could be dissolved away from cellulose and copper sulfide by means of the alcoholic CuCl_2 solution, [&] sodium sulfur, and carbon and hydrogen, ^{determined} if desired. A cuprous salt would best be used in preparing the copper

xanthate, because if the cupric salt were used, only half of the xanthate would go to copper xanthate, and because of the reducing ions present, this might not be represented by the quantitative equation usually given where represents any xanthate radical and XX is the dixanthogen form:



Cellulose Dixanthogen

Cellulose dixanthogen is an oxidation product of the xanthate and is represented by two molecules of xanthate coupled together through sulfur atoms:

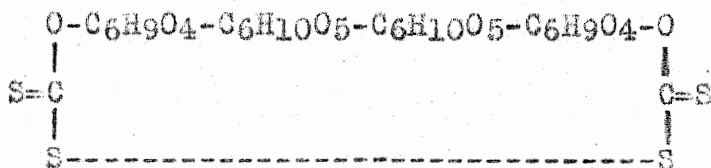


If xanthates with various numbers of C₆ units per CS₂ exist, it should be possible to prepare corresponding dixanthogens. However, the proof of existence of such molecules is accomplished with more difficulty than even the proof of the composition of the xanthates.

The formation of the dixanthogen is best carried out by oxidation of the xanthate with iodine. Excess of iodine solution is added to the xanthate solution made just acid with acetic acid, and after standing for some time the excess iodine is back titrated with thiosulfate using starch KI indicator.

Dixanthogen was prepared by the above procedure. It is apparently insoluble in all solvents, but in water is swelled and appears to be highly hydrated. In the wet form it is jellylike and is colorless. Upon extraction with alcohol to remove the water, the dixanthogen shrinks and becomes brittle. Of particular note also, is the fact that it becomes colored a deep yellow, and that such color cannot be removed by washing with MeOH. On drying to remove the alcohol at a low temperature (below 35°C) the color deepens even more, and obnoxious odors develop. The dry material then will swell somewhat if placed in water, and the yellow color goes into the water and H₂S is evolved. The white solid remaining is not changed on treatment with MeOH.

This above experimental observation was checked by several such experiments. It seems to be in contradiction to the observations of Leiser (42), who says that the compound:



is absolutely stable. It may be that in the experi-

mental work a higher dixanthogen was first prepared which was lower in cellulose than Leiser's molecule, and that on standing it tended to change over to the Leiser compound, with liberation of colored inorganic sulfur compounds. Why such a change should have taken place in MeOH and not in water is not explainable. As the material contained sulfur formed by action of the iodine on thiocarbonates and sulfides, an analysis for sulfur would tell little.

Leiser has reduced the dixanthogen back to xanthate by means of sodium amalgam. The alkyl dixanthogens are reduced to xanthate by heating with copper salts and sulfites, (8). Such a treatment indicated no xanthate with the experimental cellulose dixanthogen. Possibly the method is not applicable. It was not tried (and it should have been) on the dixanthogen before the MeOH and drying treatment. Use of acetone in place of the MeOH for the drying of the dixanthogen seemed to cause the yellow color to deepen, indicating even greater decomposition before the drying with warm air. Ethyl alcohol acted as did the MeOH.

Action of Heat on Cellulose Xanthate

The effect of heat on the xanthate has never been systematically investigated, though some information regarding it is available.

Doreé (60b) states that an increase of 5°C in temperature doubles the rate of ripening of viscose; that is, presumably the speed of decomposition.

According to Dr. P. C. Scherer (71), the xanthate decomposes rapidly (even in the absence of water at temperatures around 45°C). Lillienfeld (64), has patented a process whereby viscose is heated to 60-80°C to precipitate a water insoluble xanthate which can be dissolved in NaOH and used for making threads and films.

One naturally questions what happens when the xanthate is heated. Some work has been done with the alkyl xanthates in this connection (8), and many different compounds have been found to result from heat treatment. Possibly the changes in the cellulose xanthate are similar but take place at much lower temperatures. Cellulose dixanthogen, and even monoxanthogen maybe formed, the latter having the formula:



Lilliennfeld's insoluble xanthate may have such a formula. Other workers have likewise reported insoluble xanthates, and they have had mixtures of cellulose and sulfur, or mono- and dixanthogen forms just as well as xanthates, judging by the data, and by the methods of analysis used.

Again, the insoluble xanthates might be those containing a low ratio of CS₂ to C₆ groups.

Analytical Methods for Cellulose Xanthate

Methods for analyzing viscose have never been satisfactorily worked out, though there are many methods available, particularly in Doree's book (60).

Sodium may be determined accurately by igniting the xanthate and covering the sodium in the residue to the sulfide and either weighing immediately or first purifying it and then drying and weighing.

Total sulfur may be determined by the method of Carius. However, the method of oxidation with bromine is much easier and has been found to give good results by Atsuki and Mitarbeiter (46). Oxidation with NaCl has been used by Muma (72). Vitale and Maresca (65) have used the method of Parr-oxidation with Na_2O_2 . Apparently there is no great difficulty in determining the sulfur comparable to that met with in the case of alkyl xanthates, where the method of Carius or that of Parr must be used because of the tendency of the sulfur compounds to vaporize without being oxidized. However, no comparative results are available for analysis of cellulose xanthate, and as one can never know the true composition of cellulose xanthate, and as one can not know if the analyses are correct. Under the circumstances it would be wise to consider the absolute knowledge of the case of the alkyl xanthates, and to use the Carius or Parr methods for accurate work.

Determination of thiocarbonate groups can be done by titration with iodine, whereby dixanthogen results from titration of xanthate and free sulfur from titration of sodium thiocarbonates. To distinguish between the two, attempts have been made to use our knowledge of the stabilities of the compounds in acids. A solution of impure xanthate is titrated with iodine to get total thiocarbonate groups (66). A second sample is made acid with acetic acid to destroy inorganic thiocarbonates, and CO₂ is bubbled through the solution to remove the H₂S formed. The solution is then titrated with iodine to get the xanthate thiocarbonates. The difficulty here lies in inability to remove all H₂S and in the fact that the acetic acid may decompose the xanthate far more than is generally appreciated (see section on decomposition by acids). One thing must be noted; decomposition of one molecule of xanthate can form two sulfide ions whose iodine titration value is four times that of the original xanthate molecule. Under the circumstances the results of the method might be either high or low, but certainly could not be accurate, unless chance should allow compensating errors. Furthermore, there is no method available for checking the results. This method cannot be used in determining alkyl xanthates accur-

ately (67) (9b), and they are much more stable than cellulose xanthate. In their case the solution must be brought exactly to a PH of 7, and then titrated immediately with iodine. If this is done with the cellulose xanthate all sulfide present is titrated unless the xanthate has been purified, and the accomplishment of the latter is difficult, if possible at all (see under Purification of Xanthate), without change in the molecule.

A method has been used by Wyss (55), whereby the CS₂ from the xanthate is liberated by means of a strong acid after all thiocarbonate CS₂ is first removed by treatment with acetic acid. The CS₂ is absorbed in K-alcoholate and determined as the ethyl xanthate. This method must be criticized on the same basis as the previous determination, as well as from other standpoints, among them the fact that the formation of the ethyl xanthate is by no means quantitative, and that its determination is tricky. Hegel (68) has used a similar method and has absorbed the CS₂ in triethyl phosphine to give an addition product which can be weighed, possibly a better procedure.

Alkali can be determined by addition of a strong standard acid and backtitrating.

Sulfate can be determined by treating the xan-

thate solution with $ZnCl_2$ to precipitate the thiocarbonate, sulfide, and xanthate, and determining sulfate on the filtrate. This does not appear to be important, however.

Total cellulose can be determined by precipitating with acid, washing into a Gooch crucible, washing, drying below $110^\circ C$, and weighing.

No method is available for determining free cellulose in xanthate, as the xanthate disperses cellulose in solution (45). This fact is of importance, because it casts doubt on the theory accepted by many workers that the xanthate polymerizes (23) (15). One method for attacking this problem might be to make use of the fact that copper xanthate is soluble in solutions of $CuCl_2$ in alcohol. It may be that the copper xanthate can be thus quantitatively separated from free cellulose, though no experimental work has been done to justify this other than determination of the fact that the copper xanthate can be dissolved. This might be well worth investigating (see other remarks under Metallic Derivatives).

Purification and Stabilization of Cellulose Xanthate

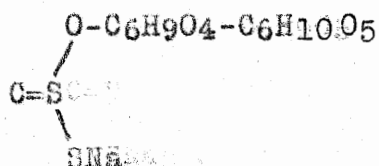
From the information given in the foregoing discussion it should be possible to evolve methods for making pure, stable, cellulose xanthate. This has been attempted by many workers, who have attained varying degrees of success. Removal of impurities and complete dehydration to insure stability have been the objects sought for.

Richter and Scherer (69), after extensive investigations, obtained a patent for the stabilization of cellulose xanthate. Their method depends on dehydration of the xanthate. The xanthate in viscose solution is precipitated with MeOH or EtOH acidified with 2% acetic acid, followed by washing and drying at a low temperature. The drying may be done in vacuum or by vacuum distillation under some organic solvent such as benzene. An alternative method is to dehydrate the xanthated crumbs. The product is said to remain stable for months, even in the air. A similar French patent specifies removal of impurities from the xanthate by means of CH_3OH . The purification is to be carried out at a low temperature and the solvent eliminated by pressing, other drying being avoided. It is to be noted that this difference in specifications is not due to any attempts to get around other patents, but is in accord with the

experimental results of the patentee. The patent might be taken as giving indication that the xanthate decomposes on being subjected to drying treatments.

Kita, Tomihisa, Azanu, and Fujemoto (53) report that xanthate prepared by precipitation with salt and dilute acetic acid is not washed free of alkali by MeOH, and that purified xanthate is gradually decomposed by drying. They say that the Na xanthate is more stable than the NH₄ xanthate, and that addition of ZnSO₄ to xanthate solution precipitates a white solid insoluble in water and soluble in NaOH, and that the CS₂ content of the xanthate is not affected by this treatment, but is decreased by subsequent drying of the Zn precipitate.

The most extensive work reported in the literature concerning the purifications of the xanthate is that of Leiser (42 a). He reports trying differing times and temperatures of xanthation in an attempt to directly prepare a pure xanthate, but with no success. He then went over to the purification process, using MeOH to extract impurities, and obtained a stable compound which he analyzed and to which he assigned the formula:



He obtained a value of Na equal to 7 to 7.5% against a theoretical 5.45%, and attributed the difference to the great difficulty with which the last of excess NaOH can be removed by the MeOH. It seems surprising that the results of such indefinite analyses whose only explanation lies in an unproved theory (polymerization of the xanthate) should have been as widely accepted as they have been. Other workers have similarly obtained xanthates which did not give analyses corresponding to stoichiometric proportions of the groups involved, and while it is very easy to say that xanthates showing such stoichiometric proportions do not exist, consideration of the facts of the case cannot but fail to leave one with the thought-in all probability the xanthates have not yet been prepared pure.

Leiser (42d), says that a solution of his purified xanthate will remain stable for months but that the cellulose content in solution, and even in the solid state unless some other metal is substituted for the sodium, will change over to an alkali soluble form.

However, others (33d) say that such solutions are not stable, but that decomposition takes place continuously. Such disagreements in the field of cellulose chemistry are not unusual, and, for lack of a better

explanation must be attributed to differences in the cellulose which the experimentors used.

III. EXPERIMENTAL PREPARATION OF PURE XANTHATE
AND DIXANTHOGEN

General Procedure

In all the following experiments, Brown Company alpha-cellulose wood pulp was used. The pulp sheets had been stored indoors for several years and had deteriorated slightly so that the alpha-cellulose content ran about 94% on a bone dry basis.

The soda-cellulose was prepared by soaking the pulp sheets in 18% NaOH solution for one hour at room temperature. The caustic solution was made from 99% electrolytic caustic and was titrated to insure a content of NaOH within the limits 17-18%. The soaked sheets were pressed to a weight of three and one-third times the alpha-cellulose content, by means of a hydraulic press, and were then ground in a Werner and Pfleuderer shredder for from two and one-half to three hours, the longer time being necessary when a small charge of cellulose was used. This gave soda cellulose crumbs showing a bulk test of about 190, usually, and these were placed in steel drums in a constant temperature room and allowed to age at 18°C for the times stipulated in the experiments. Large batches of crumbs were xanthated in a laboratory size xanthating drum,

and the drum was evacuated before introducing the CS₂ and again before dissolving the xanthate. Smaller batches were xanthated in a two-quart fruit jar fastened to the side of the xanthating drum, and in such cases no eva^uction was possible, unless the xanthated crumbs were transferred to a different container to allow evacuation to remove excess CS₂. For viscose syrup the crumbs were xanthated one and three-quarters hours with 47% CS₂ and then dissolved in dilute NaOH to make a solution containing 7% cellulose and 6.5% NaOH. Varying procedures are specifically cited.

Experiments

A) 200 cc of well aged viscose syrup, obtained from Dr. P. C. Scherer, was treated with 95% EtOH containing 2% acetic acid. The mass gelled after an equal volume of the alcohol was added, but addition of more alcohol caused the gel to disintegrate somewhat so that it could be filtered. The xanthate now had a yellow color. Washing with much acidified-alcohol made the color become bluish and the gel take on a fibrous character. It was washed twice with pure 95% EtOH and once with absolute MeOH, being filtered as dry as possible and dried in a vacuum at 40°C for four hours. The product had an obnoxious odor and

a slight yellow color. It would not dissolve sufficiently to give precipitates with heavy metal salts. Apparently the xanthate had entirely decomposed.

B.) Fresh viscose syrup was treated with saturated salt solution, but no precipitation took place.

C.) 500 cc of viscose syrup aged until the NH_4Cl number was 19 (about 48 hours) was treated in a glass jar with 95% EtOH containing 2% acetic acid, a high speed electric stirrer being used for agitation. Addition of 750 cc of the alcohol caused separation of a yellowish material which was filtered, yielding a greenish rubbery mass. This was broken up as much as possible, washed with alcohol, and disintegration attempted with the stirrer, but with no success. The material was washed successively with fresh alcohol until it finally became hard, with the green color remaining. Attempts to grind it in a mortar met with failure. It swelled in water, became lighter in color, and slowly dissolved. Testing the solution with heavy metal salts gave precipitates whose colors indicated considerable impurities in the xanthate. After standing over night the decomposition had progressed extensively, so that very little xanthate was left.

D.) A second portion of the same viscose syrup used in (C), but aged 52 hours, was treated with saturated NaCl solution containing 2% acetic

solution containing 2% acetic acid. A precipitate formed which was much more easily filtered than that precipitated by the alcohol. It was washed with more salt solution and became perfectly white, then it was washed with alcohol several times and dried in a vacuum. Removal of final traces of solvent was difficult. The material dissolved readily in water to form a colorless solution which gave, with heavy metals, precipitates whose colors indicated high purity. After standing overnight in a dessicator the material turned yellow, and would dissolve only slightly, while treatment with Cu and Pb salts indicated a negligible xanthate content.

E.) A viscose syrup aged until the NH_4Cl number was 10, was treated with saturated NaCl solution, containing 1% acetic acid, in a glass vessel equipped with a high speed stirrer. A gelatinous precipitate was formed and was filtered. A second treatment with the acidified brine caused H_2S and CS_2 to be given off in appreciable quantities. The material was then wholly insoluble and gave no precipitates with heavy metal salts. It would appear that the xanthate had aged to such an extent that decomposition with the acetic acid was too rapid to allow use of the method.

F.) Other attempts were made, with precipitation being tried at different times with 95% alcohol or brine, with and without acetic acid. No success was attained. With the alcohol, whether the viscose was added to the alcohol or the alcohol to the viscose, a rubbery material was obtained which could not be broken up to allow thorough purification, and from which last traces of the 95% alcohol could not be removed by drying in vacuum, even with addition of heat. With the brine, a better purification was possible, but removal of the salt by the alcohol was difficult and slow, and the same difficulties in drying were encountered as in the above case. It appeared that the heat conductivity of the xanthate is so low that the only way of getting heat to the substance to allow evaporation. When a vacuum is used, is by radiation, and this is too slow. Further, the fresh viscose would not precipitate unless much acetic acid was used, causing decomposition. The aged material decomposed when even small amounts of acetic acid were used, and the thiocarbonates could not be removed unless the acid was used. At some intermediate time of aging, conditions might be optimum for precipitation, but this time appeared too indefinite. At some times more success was encountered than others, but there seemed to be no rule which would predict this.

No detailed record has kept of the work, which followed a course similar to that in the foregoing experiments, and it was finally concluded that the methods being used were not suitable, contrary to the statements of other experimentors. Differences may have been in the facts that a soluble xanthate was insisted upon, and that one which would not give light colored precipitates with Zn, Pb, and Cu salts was not considered pure. Also, development of such dark colored precipitates was taken to indicate decomposition, whether or not the xanthate remained somewhat soluble. A xanthate which had partially decomposed would be just as unsuitable for flotation testing as one which was used directly without purification.

G.) It was felt that changing the conditions of the xanthation might make possible the production of a pure xanthate. This had been investigated by Leiser. However, he reported no success along this line (42).

It was known that to produce alkyl xanthate almost 98% pure all that is necessary is to keep the temperature very low and avoid an excess of CS₂ at any time.

G-1) 75 g of crumbs were placed in a filter flask which was then evacuated, and 9 cc of CS₂ admitted, without admission of air, through a short glass stopcock burette placed in the stopper. The flask was

shaken and allowed to stand at a temperature of 28°C. In fifteen minutes a yellow color had developed and the mass had begun to shrink. This procedure continued. At the end of two hours the color was mustard and the mass was gummy. At the end of three hours the color was orange-brown and the material had agglomerated into gummy lumps.

G-2) The above procedure was repeated at a lower temperature (as low as could be secured using tap water to cool the reaction vessel), which was down to 15°C, and the dark color did not develop, nor did the material become gummy in nearly so short a time.

In G-1, presumable reactions between CS₂ and NaOH had progressed to an extreme stage.

H.) It was felt that if xanthation were carried out at a fairly low temperature, and the product directly extracted with some solvent, without being ^{put} into solution, a good pure xanthate might be made. A continuous extractor for use of cold solvent was designed so that the solvent had no contact with anything but glass and cork, and so that change of solvents might be made easily. A syphoning extractor was used so that the solvent would remain on the xanthate until a certain level was reached and then drain back into a recovery apparatus where it was distilled; the

cold distillate flowing back into the extraction thimble. NaOH was placed in the distilling bulb into which the used solvent was run, and this tended to hold back volatile sulfur compounds. In some instances lead nitrate was used for the same purpose.

H-1) Crumbs were xanthated at 18°C and placed in the extractor and treated with EtOH. Extraction for two hours with change of solvent yielded a light yellow product. It was left in a flask overnight and had decomposed greatly by the next morning. Some of the unextracted crumbs had not changed greatly by the next morning.

H-2) Crumbs xanthated in the foregoing procedure were extracted with 50% alcohol, with no great change in color.

H-3) Cellulose xanthate crumbs prepared as above were treated three times with 60% EtOH, filtered, and placed in the extractor and treated with 95% alcohol, then with acetone. The xanthate was a light blue-grey color. It was placed in a flask and evacuated. Presumably no water was present, as the acetone should have removed this, being continually distilled off CaCl₂ and through a two foot column in the extractor. The material turned yellow, developed a sharp odor, and would only partially dissolve in water to yield a solution which gave,

with heavy metals, precipitates indicating quite high purity. The material was placed in a dessicator, and after a very few days had completely decomposed.

I.) It was now decided to attempt to synthesize the xanthate under more closely controlled conditions. A 250 cc Erlenmeyer flask was equipped with a four hole stopper in which were placed a thermometer, and a connection to vacuum. The whole arrangement was placed in a water bath so that temperature could be controlled or kept constant.

I-1) 25 g of crumbs (14% NaOH and 29.5% Cellulose) placed in the flask and the vessel evacuated. 3.1 cc of CS₂ was added slowly through the burette. This CS₂ should have occupied a volume of over 400 cc at the temperature used (16°C) and the last of it should have remained liquid in the apparatus, but it seemed to evaporate as it entered the flask. After two hours, the pressure in the flask had decreased considerably, indicating that much of the CS₂ had reacted. The flask was evacuated to remove the excess CS₂. The product was light yellow, soluble in water to a solution which gave tan precipitates with Pb and light brown with Cu salts. Part of the solid material was put in the continuous extractor and extracted with cold EtOH, giving a dark yellow extract at first, but changing to color-

less or very light yellow. It was then extracted with fresh alcohol and finally with absolute acetone. The extracted product was the same color as the starting material. On standing, the acetone extracted material decomposed, turned brown, and developed a bad odor.

These phenomena seemed to take place more rapidly than with the unextracted material. On the second day some of the xanthate would still dissolve, but on the third, decomposition was complete.

I-2) The above procedure was carried out more carefully, using the same conditions. On a basis of pressure measurement, less than half of the CS_2 added reacted in five hours at 16°C , though leakage of air into the apparatus would have caused an error indicating reaction of less CS_2 than had actually reacted and it was known that such leakage did take place. The crumbs at the end of the time had shrunk and taken on a pronounced yellow color. The material was dissolved in water and made just acid with acetic acid and oxidized with iodine solution. The dixanthogen was filtered off as a white mass and was placed in the extractor and treated with cold acetone. The acetone turned the material dark yellow. It was thought that this was due to decomposition, though it was recognized that the dixanthogen might show a different color in organic solvents.

or when dry, than it does when wet with water.

J.) A reaction vessel was made up from two 100 cc wide-mouth bottles connected together by a piece of glass tubing with a right angle bend. One of the bottles was thus horizontal, and the crumbs were placed in this. The other bottle was vertical and was equipped with a second glass tube closed off through a piece of pressure tubing through which the vessel was evacuated and CS₂ was introduced. The setup was thus permitted having an excess of liquid CS₂ present, an absence of air, and only CS₂ vapor in contact with the crumbs. Crumbs xanthated in this system, at a low temperature, did not become as intensely colored as when liquid CS₂ was in contact with the crumbs.

J-1) Crumbs aged 72 hours were xanthated at a temperature of 16°C for three hours. Half of the xanthated crumbs were oxidized to dixanthogen and washed 15 times with water to remove all inorganic materials. The material was then white, but on being extracted with EtOH it darkened, and on drying in vacuum became tan in color. It was treated with sodium sulfite, HCl, and CuSO₄, but no test for dixanthogen could be obtained. The second half of the xanthated crumbs was placed in water and the solution saturated with salt. The xanthate would not precipitate but

did come out on standing overnight (15 hours). It was then filtered, extracted with EtOH, and drying the material attempted in vacuum. This was very slow, and after 8 hours the material was insoluble in water and gave no test for xanthate, indicating complete decomposition.

K.) At this point it appeared that acetone would decompose the xanthate, so that it could not be used for drying. Drying with the 95% EtOH was not satisfactory because the water associated with this could not be removed satisfactorily by drying and would be present all during the drying treatment at best. Use of absolute EtOH was considered impractical, but since MeOH can be freed from water by straight distillation this was considered the best possibility. The supply of MeOH on hand was very low so attempts were made to get considerable quantities of it and in the meantime a different procedure was inaugurated. To free the xanthate from impurities it seemed that a large surface would be necessary, as the organic solvents take water from the xanthate surface and leave it in a hardened condition which prevents access of the solvent to the interior. The drying would also be facilitated by a large amount of surface. It had previously been tried to approach such a condition by pouring the

viscose solution into the alcohol, but the high viscosity prevented pouring in a fine enough stream. Use of a spinnerette seemed to be the most logical method. The use of absolute ether to remove the alcohol previous to drying also seemed to offer good possibilities.

K-1) Crumbs aged 14 days were xanthated in the standard manner and made into viscose solution which ^{was} aged 20 hours. The NH_4Cl number was above 50 and was indeterminate, but the xanthate precipitated readily when forced from a pipette into a bath of 95% EtOH containing 2% of acetic acid. The precipitated xanthate was immediately removed from the precipitation bath and washed four times with pure EtOH and twice with ether. It was then a white fluffy mass and was dried in vacuo at 35°C for about eight hours. The final product was brittle, light-colored, and odorless. It would only partially dissolve in water, but the solution gave precipitates with heavy metal salts which indicated high purity. Analyses showed 6.76% sulfur and 4.94% sodium, or a ratio of one sulfur to one sodium, and a possible composition approaching:



However, as previously noted, the material was not entirely soluble and therefore was not homogenous,

and must have consisted of cellulose mixed with a xanthate higher than that given in the above formula.

A solution of this xanthate remained perfectly stable for three days, but on the fourth day a precipitate appeared though the solution still gave tests for xanthate. On the fifth day the solution had gelled, but when the gel was broken up and shaken with water a solution of xanthate was obtained. This indicated that even after coagulation, soluble xanthate, as well as cellulose or insoluble xanthate, was present. The solid xanthate was kept in a desiccator. It slowly turned yellow in spots, but the decomposition was slow and the xanthate content was still high after two months. At the end of four months the xanthate had entirely decomposed.

K-2) Crumbs aged 45 hours were xanthated for two and one-half hours and made up to viscose solution. The syrup was aged 18 hours and precipitation attempted by running in a fine stream into EtOH acidified with 2% acetic, but the xanthate would not precipitate. The NH_4Cl number was indeterminate and after 24 hours additional aging it remained so and precipitation was impossible. After 90 hours aging the NH_4Cl number reached 16, but the viscosity was now very high. Due to the high viscosity high air pressure was necessary

to force the syrup through the glass spinnerette, and even then the precipitation was very poor due to the high viscosity and tendency of the viscose to form droplets. It appeared that the only way such a solution could be spun would be by use of a rayon machine. That is, unless the crumbs were aged so long as to give a syrup of very low viscosity as in the previous test, a rayon spinning machine equipped with a pump would have to be used. Some of the material was precipitated by using a high speed stirrer and pouring the syrup into alcohol. The xanthate so made was put into solution, giving a yellow solution which became colorless after standing 24 hours. It decomposed after 48 hours.

K-3) Crumbs were xanthated two more times and put into solution. Precipitation was attempted with a glass spinnerette equipped so that compressed air could be used to force the syrup through the orifice. Unless the thread size was made quite large it was impossible to force the syrup through the glass capillary, and then precipitation was very poor as the acidified alcohol could not penetrate through the outside skin to the inner material.

L.) It was concluded that possibly the only effective way to make pure xanthate from normally aged

crumbs would be through spinning into alcohol by means of a rayon machine.

Five gallons of pure synthetic methanol (absolute) was donated by the Du Pont Company and was used for an investigation of this. Washing with ether was largely dispensed with because this is not an efficient drying agent, having the power to take up only small amounts of water even when absolute. The MeOH on the other hand should readily remove water, and would possess only one disadvantage--that of much greater chemical reactivity than the ether.

L-1) Crumbs aged 60 hours were used for a viscose syrup which was aged 96 hours, at which time the NH_4Cl number was 10. The syrup was spun into methyl alcohol containing 2% acetic acid, by means of a laboratory rayon spinning machine. The thread had low tensile strength and spinning was difficult. The xanthate thread was washed directly on the aluminum spool on which it was reeled with successive portions of pure alcohol until it was free of color. The procedure took about one-half hour. The product was silvery white in color and entirely soluble in water. It was stripped from the spool and dried in vacuum below 35°C . During the drying it took on a slight yellow color, and after drying (about 8 hours) it

was only partially soluble in water. The dry material was placed in a dessicator, and after standing overnight it was bright yellow and entirely insoluble in water, (except for the soluble inorganic decomposition products).

L-2) The above procedure was repeated except that the product was washed twice with absolute ethyl ether (distilled from sodium) before drying. The behavior of the product was the same as in L-1.

M-1) Viscose syrup having an NH_4Cl number of 12.2 was precipitated by pouring into methanol with no acetic acid and was kneaded with successive portions of the solvents until it was a very light color. It did not become so hard and rubbery as when this process is tried with 95% ethanol, and purification was accomplished much more easily. The material was put into water solution and remained stable for two days.

N-1) Viscose syrup aged 90 hours and made from crumbs aged 70 hours was spun into methanol without the use of acetic acid. It was washed free of color and dried in vacuum at temperature of 35°C . It was placed in a dessicator filled with fresh soda lime and CaCl_2 . It was perfectly white after drying and was soluble in water, but after standing in the dessicator four days, it had developed a bad odor, a yellow color, and was partially insoluble in water. After standing a week

it was wholly insoluble.

O-1) Crumbs aged 90 hours were xanthated and the xanthated crumbs split and made into two solutions; one containing 9% cellulose and 5.5% NaOH and the other 7% cellulose and 6.5% NaOH. These solutions were aged 24 hours, filtered and spinning into MeOH attempted. Coagulation was very poor and the spinnerette could not be kept free of masses of syrup. The syrups were aged a total of 42 hours and spinning again attempted. Low tensile strength prevented spinning in the regulation manner, but it was found that if the spinnerette was inverted and the threads allowed to fall away from it through the methanol that they would coagulate separately and that the mass of xanthate thread thus formed in the spinning path could be periodically removed. This was the most effective way found to spin the xanthate. The product was silver colored and was washed several times with MeOH to remove all water and traces of impurities. It was then dried in vacuum, but, due to its fluffiness and low heat conductivity, drying was extremely slow and after 18 hours the material was still wet with traces of the solvent. Further, though presumably no water was present, the xanthate had decomposed and taken on a yellow color. Very obnoxious odors as of organic as well as inorganic sulfur compounds were in evidence.

The dry material would only partially dissolve.

P.) It was concluded that drying in vacuum was unsuitable, and a hot air drying system was set up. An iron pipe was placed on an electric hot plate and one end of it connected through a CaCl_2 and soda lime absorption system to a tube inserted to the bottom of a filter flask. The side arm of the flask was connected to an aspirator. Thus by controlling the flow of air and the temperature of the hot plate it was possible to control the temperature of dry, CO_2 -free air flowing through the flask in which the material to be dried was placed. This flask was equipped with a thermometer. With the system, drying could be accomplished in a very short time. Also through the vacuum drying the water flowing through the aspirator would exist throughout the apparatus unless solvent were being evaporated fast enough to prevent it, but in the air-drying system the constant flow of air would prevent this water vapor pressure manifested in the drying chamber.

P-1) Crumbs aged 66 hours were xanthated and put into a solution containing 9% cellulose and 6% NaOH and aged six hours. Spinning into MeOH was attempted but the syrup was too fresh to spin well. The xanthate thread obtained was washed several times with MeOH

and then pressed as free of solvent as possible by means of a hydraulic press. The pressing caused the material to become decidedly greenish in color. Part of it was then immediately placed in a dessicator over CaCl_2 and soda lime and the other was dried in the air-drying apparatus and placed in a separate dessicator. Both materials decomposed, though that wet with alcohol decomposed more rapidly. Odors as of organic sulfur compounds (mercaptans) were evident in the latter case.

P-2) The syrup from the previous experiment was spun from a 20 hole spinnerette after aging 20 hours. It spun well and was washed twice with MeOH and then pressed to a pressure of 1000# with a hydraulic press, washed twice with MeOH and again pressed. It was then disintergrated by hand and dried with dry CO_2 -free air at a temperature below 30°C , and was placed in a dessicator. It continually decomposed though it contained some xanthate for over a week.

P-3) Standard viscose syrup was made up and spun into MeOH after aging 24 hours. The xanthate was washed with eight portions of twice redistilled methyl alcohol, the solvent being carefully drained away on a Buchner filter after each washing. This procedure was carried out very rapidly and the product was dried thoroughly (8 hours) at a temperature below 30°C with

dry CO₂-free air. Part of the product was placed in a desiccator over fresh CaCl₂ and the remainder was put into a small tightly stoppered brown glass bottle so that the bottle was filled. At the end of four days both products were examined and were found to have practically entirely decomposed. The results indicate that cellulose xanthate will decompose, even when great precautions are taken to dry it, and that light is not a critical factor in this decomposition.

It was recognized that the xanthate had already decomposed in the viscose solution, possibly to such an extent that it would more readily decompose than fresh xanthate.

Q-1) It was thought that the water solution of the xanthate might be used for spinning, but not enough of the xanthate would dissolve in such a solution to permit spinning into alcohol without excessive dilution of the alcohol.

R-1) Finally it was decided to directly purify the xanthated crumbs. Crumbs aged 48 hours to 70 hours were xanthated at about 25°C and the excess of CS₂ removed by vacuum. The xanthate was then ground in a mortar with MeOH until colorless, the solvent being filtered off between extractions. In this way a very light colored powdery xanthate was prepared.

It was dried carefully below 35°C with dry air and stored partly in a dessicator and partly in a tightly stoppered brown glass bottle. In every case the xanthate decomposed in less than a week. The procedure was repeated several times with different crumbs, but results were always similar.

S-1) Some crumbs were placed in an Erlenmeyer flask with CS₂ and the flask was placed in a snow bank and removed and shaken every few hours. After standing for 24 hours the crumbs had taken on a light yellow color and were entirely soluble in water. Part of the material was purified as in R-1, but was found to decompose as usual. A second portion was left in the flask at room temperature. This latter material lost water and became brittle. It decomposed slowly, but after three days some xanthate was still left. Indications were that by such a method a fairly good xanthate might be prepared without purification. However, warm weather and lack of time prevented further work along this line.

T-1) Xanthation of anhydrous soda-cellulose would certainly give a pure product, if it were at all possible. Though others had reported inability to xanthate such material it was decided to try it. Soda-cellulose aged 70 hours was thoroughly dried with dry CO₂-free

air and was then placed in an Erlenmeyer flask with an excess of CS₂. After 48 hours no reaction had taken place. The soda-cellulose was white and insoluble in water, indicating no xanthate or thiocarbonate formation.

General Conclusions

Though no explanation can be given as to how or why dry cellulose xanthate should decompose, the highest refinement of experimental technique used did not give a stable product. Xanthate formed by precipitation from viscose solution through spinning from a rayon machine into pure MeOH, or by treating xanthated soda-cellulose crumbs with pure MeOH, and washed with as many as fifteen portions of absolute MeOH (the solvent being eliminated as well as possible each time by pressing and filtering and followed by drying with dry CO₂-free air at a low temperature or by washing with absolute diethyl ether and then drying, gave a product which decomposed even when stored in a desiccator or out of the light (in brown bottles).

It seems certain from observations made in the experimental work that MeOH will decompose the xanthate, as xanthate left in this solvent decomposed and odors of organic sulfur compounds such as mercaptans became evident. No doubt ethanol would serve in a similar role though if absolute it might be expected to be less reactive than the methanol because of its lesser polarity. However, the methanol could not have been the only cause of decomposition of the xanthates prepared, because decomposition took place even when it was wash-

ed out with absolute ether.

It is possible that the xanthate treated as above was not thoroughly dry. Though Leiser (42) has reported the preparation of a stable xanthate by such methods (though not as highly refined as were used here), P. C. Sherer has reported that the stability depends on complete removal of water and that this is difficult. The difficulty of washing NaOH out of the xanthate is well known. Possibly it is held by secondary valences, and if this is so, it is also entirely possible that water will be similarly held. Anhydrous cellulose is a good desiccant, and it is conceivable that the cellulose xanthate retains some water of hydration whose vapor pressure is so low that it is only difficultly removable at the low temperatures which must be used for drying. Such water of hydration, held by secondary or coordinate valences, might tend to shift on the cellulose and to assume positions so that rearrangement to form cellulose and sodium hydrogen trithiocarbonate from the xanthate could take place. If excess of NaOH were also held to the xanthate by such secondary valences we might consider that the water would assume a catalytic role, causing the xanthate and the NaOH to rearrange to form sodium trithiocarbonate and cellulose. In such a hypothetical system only a very small amount of water

would be necessary to cause extensive decomposition. Though this is all in the realm of speculation, it is justified somewhat by the fact that the xanthate was never obtained in a stable condition and that the instability cannot be explained except by an assumption of the presence of water or alcohol.

The one case in which a relatively stable cellulose xanthate was obtained (see K-1) is an outstanding exception to the general results of the experimental work. The procedure used in preparing this xanthate was notably different in only one respect; crumbs aged an exceptionally long time were used for making the xanthate. If this aging tends to break down the cellulose micelles and to rupture the oxygen bridges holding the C6 units together, it might well affect the stability of the xanthate. Such changes would reduce the tendency of the cellulose molecules to group together, as they would be made into independent units. Also, the capacity of the cellulose for hydration would be affected, though this should be in a direction opposite to that necessary to explain the relative stability of the xanthate; that is, increased. However, though the capacity for hydration should be increased, the water so taken up might not be held as tenaciously as by the only moderately aged soda-

cellulose. In short, the age of the crumbs may be intimately connected with the stability of the xanthate produced from them.

P. C. Scherer has reported (71) that a highly effective method for drying the xanthate is to place it in benzene or some other organic solvent and to distill the solvent off in vacuo at a low temperature until it comes over free of water. This would be good method but it is difficult to see why it should be more effective than drying with dry CO₂ free air at a low temperature. Both methods would depend on the vapor pressure of the water associated with the cellulose at the temperature used. The only difference would be if the organic solvent tended to replace the water held by the xanthate, and this does not seem likely, in view of the differences in polarities of benzene and water. However, the method should be used before other conclusions are definitely drawn.

Finally, it must be remarked that different batches of cellulose, though presumably the same, do not always behave the same from the standpoint of cellulose chemistry. This makes duplication of results difficult, and has not infrequently made it impossible for different experimentors to check each others results. Only one source of cellulose was used throughout the work of this thesis. Possibly this was a mistake and different batches of cellulose should have been tried in

the preparation of the xanthate.

IV. THE BEHAVIOUR OF CELLULOSE XANTHATE IN ORE-FLOTATION

General Aspects of Flotation Testing

The action of flotation agents (other than frothers) may be studied according to at least three different schemes. The first of these is the study of the action in flotation tests with naturally occurring ores. This is difficult because of the large number of variables which may necessarily be introduced, among them the degree of liberation of the respective minerals. Analyses of products of such tests are usually complicated also, unless an exceptionally simple ore is used. The second method is to treat a sample of mineral having a clean surface with the reagent or reagents and to measure the gas-liquid-solid contact angle formed when a bubble of air is brought into contact with a mineral under water or the solution of the reagent being tested. The flotability of the mineral and the efficacy of the reagent being used are functions of the contact angle. This method is the "bubble Machine" method (3a) which has been criticized on several grounds, (73). Though it does give data of fundamental importance, the contact angle formed under the conditions of the test may not be the angle formed in a flotation circuit where a much smaller amount of reagent is used (7d). By far the most satisfactory method of testing reagents which has been proposed so far

is that which was originated at the University of Utah, and which was made use of in determining important data published in the bulletins (74) of the Engineering Experiment Station of that institution. This method makes use of actual flotation test using synthetic mixtures of pure minerals. With such a method the ore can be made just as simple or as complicated as desired; the liberation of minerals if perfect (as they are separated to begin with); and the data obtained have a much more universal applicability than those obtained by any other method. Using this method it is possible to vary any or all of the reagents used, to control the pH, to vary the mineral size, and to thus obtain the effect of any one reagent on any one mineral under all possible conditions. Then, using the data for the separate minerals it is possible to predict proper treatment of mineral mixtures.

Such predictions may in general be nullified by two factors: a time factor, enabling a reagent to react with one mineral before another, so that the normal effect of the reagent cannot take place and the maximum effect with a mineral will not be the same as when the mineral is present alone; and a second very important factor which is the tendency of atoms from one mineral to go into solution and replace surface

atoms of another. This last tendency causes the two minerals to act alike, since the flotation depends only on the character of the surface and mono-molecular surface replacement coatings can thus probably entirely alter the characteristics of a mineral so far as flotation is concerned.

The last of the testing methods outlined was chosen for the work with cellulose xanthate. However, besides the complications outlined above, it was found that this reagent presented many others, which will be discussed later.

One outstanding thing about flotation, and the cause of much trouble in research work in this interesting field, is the remarkable effect which even traces of substances will have on the flotation processes. Perhaps the most notable of these, given here by way of illustration, is the case of the flotation of sphalerite. Early workers with this mineral found that it was impossible to get consistent results with it. To avoid contamination of the mineral, flotation cells of glass or celluloid were tried and distilled water was used. At the University of Utah difficulties were experienced even after these precautions, and it was only after it was found that the distilled water was dissolving sufficient copper from a copper condenser used to activate

the sphalerite, and after the correction of this fault, that it was possible to get reliable data. Small amounts of salts may have a great toxic effect, pH has been found to be highly important, and contamination from grinding or flotation equipment must be constantly guarded against.

In view of the above considerations, it is advisable to use distilled or quite pure water for flotation work. A water high in lime is objectionable unless the effect of the lime is taken into account, because it is especially capable of affecting flotation results. Grinding equipment should be kept scrupulously clean, and particular care be taken to clean the mill between grinds with different minerals which might activate each other (copper minerals followed by sphalerite). The flotation cell itself should be cleaned after each test, and use of large quantities of reagents which might remain in the mill should be avoided. For ordinary work, and unless special problems prohibit their use, commercial laboratory size flotation machines are very satisfactory and are now available in many designs and sizes. The sub-aeration machines are the most easily controlled and are the most modern type; of these, the Denver-Lab machines marketed by the Denver Equipment Company are very satisfactory. Where use of metal in

the machine is prohibited, and where special precautions must be taken, a machine made of some inert material should be used. A. M. Gaudin (75) has reviewed such machines in the literature.

Since surface oxidation is an important factor in flotation of sulfides, it must be guarded against in making flotation tests. The mineral is usually ground wet and floated immediately after grinding. High oxidation of some minerals not only makes the surfaces polar, requiring more collecting agent to increase the flotability, but throws metallic ions into solution and these react with the soluble reagents used and remove them from the system as insoluble precipitates. Very probably many sulfides would float without reagents if they were free from surface oxidation, and this has recently been positively shown to be true in the case of galena (76), which when ground and floated in an atmosphere of oxygen-free nitrogen was found to be amazingly floatable without reagents. At the same time it is worthy of note in this connection that other workers (77) have recently found that the surface oxidation of galena takes place so slowly that the charge upon fine galena exposed to atmosphere oxidation for several hours is not changed appreciably. However, it is well known that exposure to the air for

even a few minutes will entirely alter the floatability of galena, while galena treated with sodium sulfide is enormously increased in floatability.

Time of contact of reagents with the mineral is also an important variable. In industry conditioning tanks are sometimes used, in which the mineral is allowed to react with the reagent for a given time before addition of another reagent or before flotation. On the other hand, some reagents seem to react instantly.

Place of addition and order of addition of reagents will sometimes entirely alter their effects and this must be considered.

The action of some salts in affecting flotation has been explained on a chemical basis. Such phenomena have only partially been worked out, however, though there are numerous empirical data upon them (10).

The effect of pH is sometimes almost unbelievable. A flotation process which will work perfectly at one pH may be entirely useless in another pH range. The theory of this is also incomplete, though much has been done upon it, and besides the theoretical information there is a great amount of empirical data.

The above discussion is necessarily very general. The subject is so complicated that to particularize

here would be impossible, and for further information reference to the literature is suggested. Formerly such information was carried largely in the journals and publications of the mining and metallurgical world, but more recently the chemical literature has been concerned with it. There are also several good texts which discuss the problems (78).

Expression of Results of Flotation Tests

In determining the efficacy of a flotation separation, samples of tailing and concentrate are taken and analyzed for the ore mineral and gangue, or, in the case of a separation of two minerals, for the proportions of each mineral in each product. It is also customary to dry and weigh the products. If a simple two component system is used it is sometimes sufficient to analyze the concentrate only, and if the weights of the feed and concentrate are known it is then possible to calculate the percentage.

It is a simple matter to calculate the percentage recovery of each valuable constituent and the grade of each concentrate; that is, percent of the desired constituent in the concentrate.

To express the overall efficiency of a flotation process different methods have been proposed: ratio of concentration; metallurgical efficiency; and selectivity index (79). All of these have been discussed by Gaudin (1e). The selectivity index, the most valuable of all, is an index of separation of two minerals or groups of minerals and is expressed as:

$$S.I. = \frac{R_a \cdot J_b}{R_b \cdot J_a} \quad \text{or} = \frac{M \cdot n}{m \cdot N}$$

where R_a is the recovery of a in the concentrate, R_b the recovery of b in the tailing, J_a the rejection of

a in the tailing, and J_b the rejection of b in the concentrate; M and N are the assays for a and b in the concentrate and m and n the assays for a and b in the tailing.

Particular Problems Concerned with the Testing of
Cellulose Xanthate as a Flotation Reagent

In using cellulose xanthate in flotation, besides all the usual considerations which must be taken care of, there are many particular problems which are peculiar to this reagent.

It is usual procedure to test a pure reagent of known composition and, of course, to keep exact control of the amounts of the reagent used. Unfortunately cellulose xanthate does not lend itself well to such a procedure. It has already been shown (parts II and III of this thesis) that cellulose xanthate is an extremely unstable substance, and that to purify it and keep it in a stable condition is well nigh impossible. It has also been pointed out that the exact composition, of the xanthate is not known, and may be variable. Thus, time of aging of the crumbs, though not apparently affecting the degree of xanthation, if resulting in breaking down of the cellulose micelle, might be expected to affect the flotation properties of the resulting xanthate. Degree of xanthation, as well as amounts of impurities present, would also be important variables to be taken into account. The great difficulty with all of these is that they cannot be quantified by any analytical methods we now have. This results in difficulty of control of

flotation tests, and to get around it, advantage must be taken of empirical methods. Besides finding out the behaviour of any one cellulose xanthate in flotation according to usual criteria it would also be desirable to know the effect of time of aging of the soda cellulose, of time and temperature of xanthation, of presence of the various impurities, and of time of aging of the xanthate in solution.

Before any such extensive investigation were undertaken, it would be logical to find out if the xanthate has any particular effect in the flotation processes. In this connection two effects might be expected: the effect of a xanthogenate depressor which has already been discussed in part I, and the effect of a negatively charged colloid. This latter effect is problematical. It is known that some protective colloids such as gelatin and glue, have an effect on flotation (1d)., though generally it is to disperse the gangue particles and improve flotation of sulfides. They are not used except in a few unimportant cases and have not been greatly studied in this connection. If the cellulose xanthate were adsorbed at a sulfide surface as a colloid the effect would be the same as if it reacted with the surface to form a coating of polar cellulose xanthate metallic

derivative, and the sulfide would be depressed. If it were adsorbed at the gangue surfaces, the effect would be reversed and flotation would improve. It is not the purpose of this thesis to discuss whether the adsorption or reaction would be the more important. Reasoning by analogy from the known action of alkyl xanthates one might conclude that the action of cellulose xanthate, if depressing sulfides, would be a chemical one.

Methods and Materials used in the Experimental Flotation

Work With Cellulose Xanthate

The behaviour of cellulose xanthate in flotation was partially determined through a series of flotation tests with a silica gangue and four sulfide minerals; chalcocite, pyrite, galena, and sphalerite.

Grinding

Charges of 50 grams of the sized sulfide and 450 grams of sized silica gangue were ground with 200 cc water for exactly one hour in a 500 gram porcelain pebble mill charged with 1500 grams of flint pebbles. The mills were thoroughly washed between grinds and where danger of contamination from a previous grind was likely, the mill was cleaned by grinding silica in it.

Water

Since the Blacksburg water supply is very high in lime it was considered unsuitable for the flotation work. However, since the use of distilled water would have been very inconvenient, (it being available only in bottles and large quantities being necessary) use was made of a Permutite water softener to render the city water supply better suited to the work. Since this softener did not remove any salts from the water but only replaced calcium and magnesium with sodium, all the water used, except where acid was used, contained appreciable amounts

of sodium carbonate and had a high pH. Rain and snow seemed to have a marked effect on the hardness of the city water so that the softened water varied in content of dissolved salts depending on the weather conditions. For this reason the pH and salt content of the water used could not be controlled as rigidly as might have been desired.

Flotation

After being ground the ore was washed out of the mill and introduced into the flotation machine. To facilitate this transfer of ore the entire contents of the mill was emptied onto a colander and the ore washed with a stream of water into an enameled pan and then poured into the machine. The flotation machine used was a 1000 gram Denver-Lab machine. Since a reduced charge was used, it is to be noted that excessive pulp dilution prevailed in all the tests.

Flotation tests were made on the ore immediately after opening the mills. The order of addition of reagents was not always the same, but five minutes was allowed between additions of the respective reagents. The reagents used in the tests are given in tables with the results of the tests. The order of addition is as given in the tables.

Determination of Results

The concentrate was removed from the flotation cell by scraping into a tared enameled pan with a wooden paddle. All of the apparatus was kept scrupulously clean to avoid contamination from any source. The concentrate was dried on an electric hot plate, care being exercised not to roast the sulfides, and the pans were weighed with the concentrates. Then by subtracting the tared weight the weight of the concentrate was found. The concentrates were placed in small paper bags and later mixed thoroughly, sampled, and analyzed.

All results are expressed in terms of the minerals rather than in terms of metallic content, so all analytical reagents used were standardized in terms of the ores. Chalcocite was determined by means of the thiosulfate-iodide method for copper; pyrite by the permanganate method for iron using Zimmerman Reinhardt reagent; galena by the volumetric molybdate method for lead with tannin acid as an outside indicator; and sphalerite by the potassium ferrocyanide method for zinc, using uranium acetate as an outside indicator. In chalcocite-pyrite flotation tests the concentrate was analyzed by after separating the copper electrolytically, and in galena-pyrite tests after separating the lead as the sulfate. Precautions were taken in the analytical work to insure accuracy.

Minerals

Since the flotation tests were to be made on pure minerals, care had to be exercised in their selection. The sulfides used were obtained through the courtesy of Professor A. M. Gaudin from the stocks of the Montana School of Mines and were specially obtained for flotation work with pure minerals. The origin and purification treatment of the minerals were as follows: SILICA GANGUE used to mix with pure sulfides was a glass sand obtained from the Virginia Agricultural Experiment Station through the courtesy of Dr. N. A. Pettinger. It was thoroughly washed with softened water until free of soil and soluble material, then it was sized to 30/65 mesh and stored in glass bottles. It had a negligible iron content.

CHALCOCITE was obtained as a table middling from Kennecott, Alaska. It contained considerable copper carbonate and gangue, but retabling resulted in a concentrate which was quite pure. This concentrate was then treated with 1:1 HCl until free of carbonates, washed free of acids, treated with NH_4OH to remove oxides, washed free of ammonia with distilled water, and dried at a low temperature. It was sized to 35/65 mesh and bottled. Analysis showed 68.5% copper, whereas pure chalcocite contains 79.8% copper.

Microscopic examination showed some silica and a great deal of covellite as impurities. The presence of the latter mineral would have reduced the copper content, as it contains only 66.5% copper, being the cupric sulfide. Covellite was not considered objectionable in the chalcocite.

GALENA was obtained as a gravity concentrate from the Missouri lead area, and contained considerable iron. It was washed repeatedly with water until most of the iron had been removed, then was treated with a solution of NH_4Cl - HCl to remove the remaining iron and any lead sulfate. It was then heated with dilute HCl , and finally with fresh portions of distilled water until free of chlorides. It was dried carefully, sized to 35/65 mesh, and bottled. It contained 82.2% lead, whereas pure PbS contains 86.5%.

SPHALERITE was obtained as a jig concentrate from Missouri. Under the microscope it showed only small amounts of impurities, mostly silica, so that no purification treatment seemed necessary. It was sized to 35/65 mesh and bottled. It analyzed 66.7% zinc as compared to 67.1% for the pure ZnS .

PYRITE used was from Butte, Montana and was presumably free from pyrrhotite. Microscopic examination showed it to be high grade, and it was sized to 35/65 mesh

and bottled. It showed 43% iron, which is almost exactly the iron content of pure FeS_2 .

REAGENTS used were all standard except for cellulose xanthate. Ethyl and Amyl xanthates were products marketed by the Denver Fire Clay Company. The amyl xanthate contained appreciable dixanthogen and was washed several times with ether to remove this. Marmor pine oil was used as a frother in all tests. Where the mineral was extremely floatable the froth tended to break so that it was difficult to collect the concentrate, and though another frother would have given more satisfactory results in such cases, it was not used because of the desirability of keeping all the tests uniform.

CELLULOSE XANTHATE was never successfully made in a pure and stable condition, so that it was necessary to use several different batches of the xanthate for different tests. For this reason all the tests are not comparable; the xanthate used in some way may have been much more effective than that used in others. It was impossible to express the amount of reagent used in ordinary terms. In some cases, and especially where a purified cellulose xanthate was used, the cellulose xanthate is expressed in terms of reducing value equivalent to amyl xanthate. For example,

cellulose xanthate equivalent to .1# amyl xanthate means that the titration of the cellulose xanthate with iodine would have required the same amount of solution as titration of .1# of amyl xanthate. This reducing value was not due to xanthate alone, but included the titration of sulfides and thiocarbonates present in the xanthate. In some cases the cellulose xanthate was further analyzed. In the later tests the xanthate was expressed in terms of pounds of cellulose per ton of ore, though the solutions were also titrated with iodine.

Flotation Tests with Cellulose Xanthate:

Series A,B,C,D, and E

CHARACTERISTICS

The experiments of Series A,B,C,D are given in Table I and show the effect of additions of cellulose xanthate upon the normal flotation (with 0.1# amyl xanthate and 0.1# pine oil per ton) of synthetic ores made up of 450g of silica and 50g of sulfide mineral. The cellulose xanthate was added before other reagents except where noted in the tests with sphalerite, and is expressed as pounds per ton of amyl xanthate equivalent in reducing value to the cellulose xanthate used.

The cellulose xanthate for these tests was made up fresh twice and was prepared from soda cellulose crumbs aged 62 hours. Xanthation was carried on for two and one-half hours at room temperature and the product freed of excess CS₂, washed free of color with MeOH, dried, and stored in a dessicator. For the flotation tests it was extracted with water and the solution titrated with iodine to get the reducing value. The tests were made over a period of several days, during which the xanthate was constantly decomposing in the solid state, so that the results of the tests are not perfectly comparable. On the second day after preparation the soluble xanthate of one xanthate pro-

duct used gave analyses of .883 moles sulfur and .935 equivalents of reducing ions per mole of $C_6H_{10}O_5$. If all the sulfur is assumed to have been present as sodium sulfide and cellulose xanthate the composition can be calculated as $3C_6H_{10}O_5 \cdot CS_2 \cdot Na_2S$. This may not be even approximately right, but it is certain that the xanthate was far from pure.

DISCUSSION: The results show that the material used as cellulose xanthate had a decided depressing effect on all the minerals. It was not possible to judge from these tests alone as to which minerals it affected most, because the composition of the xanthate and the pH of the pulp varied from test to test.

The fact that the pyrite seemed to be depressed least seemed unusual, as the high pH should have aided the depressing action, as shown by tests A-3 and D-1, where the pyrite floated much better in an acid circuit. It was thought that the pyrite might have had some unusual effect on the hydroxyl groups of the xanthate, this view arising from knowledge of the tendency of iron to form complexes with hydroxy-organic compounds, and to investigate this a test was run with citric acid, as shown in E-1. It is seen here that the citric acid caused a higher recovery of pyrite but decreased the grade of the concentrate (compare

E-1 and A-3). It might have been expected that the citric acid would have cleaned the mineral surface and made the pyrite more floatable, but why it gave a lower grade of concentrate is not explainable unless it caused flocculation of the gangue with the sulfide. At any rate, no light was cast on the action of the cellulose xanthate with pyrite.

In the results it appears that the grade of the concentrate was consistently decreased when cellulose xanthate was used. This effect may have been accentuated by the use of a higher rotor speed in the flotation machine when the mineral was less floatable. The speed of the machine used was variable and was increased to aid floatation whenever necessary.

The depression was not as great as expected and it was decided that this could have been due to the size of the collector molecule which might have made possible that the amyl groups would stick out beyond the surface coating of cellulose xanthate. In such a case a much greater depressing effect would be expected with methyl or ethyl xanthate being used as a collector.

It was also deemed possible that the impurities of the xanthate might be either accentuating or decreasing the effect of the cellulose xanthate. Thus sodium sulfide is said to be an activator for pyrite and galena

but a depressor for sphalerite or chalcopyrite while with chalcocite it would be expected to form covellite and thus give the mineral characteristics of that mineral, which is known to be quite floatable. The effect of trithiocarbonate might be expected to be the same as of sodium sulfide, while other thiocarbonates might tend to depress all minerals, having the power to form oxygen containing compounds with them. However, where such inorganic compounds (sodium sulfides) are used in flotation work they are used in much greater amounts than could possibly have been present in the tests with cellulose xanthate, and no data were available for the actions of small amounts of such compounds in flotation.

TABLE I

Tests with 450 grams of silica and 50 grams of the sulfide mineral. 0.1# Na amyl xanthate and 0.1# pine oil added per ton of ore after addition of the cellulose xanthate, which is expressed in terms of #/ ton of amyl xanthate equivalent in reducing value to the cellulose xanthate used. S. I. represents selectivity index.

Test No.:	Sulfide Mineral:	pH:	Cell-X as # amyl-X per ton:	Recovery %:	Grade of Conc. % sulfide:	S. I.:
A-1	Cu ₂ S	10.2	0.	99.2	98.6	282.0
A-2	PbS	9.2	0.	98.8	98.8	565.0
A-3	FeS ₂	9.2	0.	94.3	97.8	86.0
A-4	ZnS	9.2	0.	25.0	----	-----
A-5***	ZnS	9.2	0.	98.4	95.8	112.0
B-1	Cu ₂ S	9.1	0.10	99.8	99.1	660.0
B-2	PbS	9.1	0.15	81.2	91.6	22.85
B-3	FeS ₂	8.8	0.15	92.0	93.0	38.25
B-4***	ZnS	8.5	0.15	87.5	83.5	19.00
B-5***	ZnS	8.5	0.15	86.0	89.0	22.65
C-1	Cu ₂ S	8.7	0.7	9.93	58.6	3.75
C-2	PbS	9.6	0.7	51.6	84.9	10.15
C-3	FeS ₂	9.6	0.7	92.6	84.5	25.65
C-4	FeS ₂	8.4	0.7	84.0	90.0	22.30
C-5***	ZnS	8.4	0.7	68.4	88.5	14.80

Test with 12#/ ton of H₂SO₄ added before other reagents
66

D-1	FeS ₂	7.0	0.	99.8	97.1	386.0
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Test with .5#/ton citric acid added before other reagents

E-1	FeS ₂	8.2	0.	97.8	90.8	60.7
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***Note: In A-5, B-5, C-5, mineral activated with 0.5# CuSO₄ before addition of other reagents. B-4 activated with 0.5# CuSO₄ after treatment with cellulose xanthate.

Flotation Tests with Cellulose Xanthate:

Series F, G, H, and I

CHARACTERISTICS

The experiments of series F and G are shown in Table II and are the same as those of series A and B except that ethyl xanthate was used as a collector in place of amyl xanthate. The cellulose xanthate was the same as in the previous series, and is again expressed in terms of reducing equivalent of amyl xanthate.

The experiments of series H were run to determine the effect of sodium sulfide upon the flotation and are given in Table III. The tests are the same as those of series F except that sodium sulfide was added before other reagents, in amounts equivalent in reducing value to 0.15# of amyl xanthate per ton of ore. Thus, if all the reducing value of the cellulose xanthate used were due to sodium sulfide, the tests of this series would be identical with those of series G.

The tests of series I, given in Table IV, were made in view of the fact that the cellulose xanthate was known to have contained impurities other than sodium sulfide and it was desired to get a more comprehensive knowledge of the effects of all impurities which might have been present. To do this, use was made of the liquor separating from a gelled viscose syrup. Such a liquor would

be expected to contain all the decomposition products of the cellulose xanthate. The liquor separating from a viscose syrup which had gelled several weeks previously and had been kept in a closed bottle was diluted and titrated with iodine and used in amounts equivalent in reducing value to 0.15% of amyl xanthate per ton. The undiluted syrup was dark brown in color and had a noxious odor of many unidentifiable compounds.

DISCUSSION: The data of series P, G, H, and I, in conjunction with those of previous series, made possible the drawing of certain conclusions. Comparisons of A and F tests show that the ethyl xanthate is not as strong a collector as amyl xanthate, which is in agreement with known facts. However, the test F-4 is not as it should be and an error must be acknowledged in the comparison of this test with A-5 and other tests.

Comparison of experiments of series G and F indicates a strong depression of all sulfides by the cellulose xanthate used, and reference to B-1 now indicates that this test should not be considered typical. Further comparison of tests of A, B, F, and G indicates that the cellulose xanthate has a greater depressing effect when used with ethyl xanthate than with amyl xanthate. It is to be noted that the recoveries in the G tests are comparatively low.

Comparison of the G, H, and I tests shows conclusively that, though the sodium sulfide or other inorganic decompositions products of viscose may have some depressing effect with all the minerals used except galena, such depressing action is not of the same order of magnitude as that caused by the cellulose xanthate used, so that the depressing action of the cellulose xanthate cannot be due to the impurities it contains. The logical conclusion to this is that cellulose xanthate is a depressing agent for the sulfide minerals tested. Examination of all the data now seems to justify a further conclusion that chalcocite is the most highly depressed with activated sphalerite coming second.

TABLE II

450 g silica and 50 g sulfide. 0.1# ethyl xanthate and 0.1# pine oil added after cellulose xanthate which is expressed in terms of #'s amyl xanthate having an equivalent reducing value.

Test No.	Sulfide Mineral	pH	Cell-X as: #'s amyl-X per ton	Recovery %	Grade of: conc. % sulfide	S. I.
F-1	Cu ₂ S	8.7	0.	99.8	92.5	230.0
F-2	PbS	8.4	0.	96.4	92.0	169.5
F-3	FeS ₂	8.2	0.	98.0	92.4	73.8
F-4***	ZnS	8.2	0.	99.4	94.4	157.0
G-1	Cu ₂ S	8.6	0.15	46.5	88.0	11.15
G-2	PbS	8.6	0.15	76.8	86.5	15.78
G-3	FeS ₂	8.4	0.15	48.5	81.9	8.84
G-4***	ZnS	8.4	0.15	67.3	91.1	16.65
G-5***	ZnS	8.4	0.15	37.2	79.2	7.33

***Note: F-4 and G-5 activated with 0.5# CuSO₄ per ton before addition of other reagents. G-4 treated with 0.5# CuSO₄ after addition of the cellulose xanthate.

TABLE III

Tests with no cellulose xanthate but with sodium sulfide equivalent in reducing value to 0.15# amyl xanthate per ton. 450 g SiO₂ and 50 g sulfide with 0.1# ethyl xanthate and 0.1# pine oil added after the sodium sulfide.

Test No.	Sulfide Mineral	pH	Na ₂ S as: #'s amyl-x per ton	Recovery %	Grade of: conc. % sulfide	S. I.
H-1	Cu ₂ S	8.8	0.15	99.5	91.2	133.5
H-2	PbS	8.6	0.15	92.5	90.1	166.0
H-3	FeS ₂	8.6	0.15	94.4	94.8	54.9
H-4***	ZnS	8.6	0.15	98.0	92.5	105.0

*** Note: H-4 activated with 0.5# CuSO₄ after addition of the sodium sulfide.

TABLE IV

Tests with no cellulose xanthate but with the soluble residue* left after gelation of viscose solution in amounts equivalent in reducing value to 0.15# amyl xanthate per ton of ore, followed by 0.1# ethyl xanthate and 0.1# pine oil. Ore: 450 g SiO₂ and 50 g sulfide.

Test No.	Mineral	pH	Sol. Residue from viscose gel as #'s amyl X per ton	Recovery %	Grade of sulfide conc. %	S. I.
I-1	Cu ₂ S	8.8	0.15	96.6	88.7	45.6
I-2	PbS	8.8	0.15	99.8	96.4	248.5
I-3	FeS ₂	8.8	0.15	96.4	95.3	70.6
I-4***	ZnS	8.8	0.15	98.0	92.1	71.5

***Note: I-4 activated with 0.5# CuSO₄ after treatment with the soluble residue from the viscose gel.

*Note: This soluble residue was from a normal viscose syrup which had gelled in a sealed glass container and had been allowed to stand in the container for several days. See text.

Flotation Tests with Cellulose Xanthate:

Series J and K

CHARACTERISTICS

The tests of series J and K are given in Table VI and were made in an attempt to determine if time of aging of the soda cellulose would affect the depressing properties of the xanthate produced from the crumbs. Series J was obtained with galena and series K with pyrite, and the same xanthate was used for the corresponding numbered tests of each series. Cellulose xanthate was added first and followed by 0.1# ethyl xanthate and 0.1# pine oil per ton of ore. The tests were comparable to others in all respects except in the cellulose xanthate used.

The cellulose xanthate was made under controlled conditions. Soda cellulose was aged at 18°C and xanthated at various times and the product used for flotation tests. For the xanthation, soda cellulose was weighed into a 100cc glass stoppered bottle equipped with a mechanism to tightly hold the stopper in place. Exactly 2.1 cc of CS₂ was introduced (110% of that necessary for production of C₆H₁₀O₅·CS₂) and the bottle quickly sealed. It was then attached to the side of a laboratory xanthation drum and allowed to rotate for exactly two hours at a temperature kept as close to 22°C as possible under the conditions. At the end of

the xanthation the product was colored light yellow. The bottle was opened and a rubber stopper inserted so that the excess CS₂ could be removed by evacuation for exactly five minutes. The xanthate was then transferred to a volumetric flask and made up to two liters of solution as rapidly as possible. 50cc of this solution were used with each 500 grams of ore, or an amt. of xanthate equivalent to 0.5% cellulose per ton of ore. The solutions were also titrated with iodine. Data obtained for relating reducing value to equivalents of cellulose are shown in Table V.

These data indicate that the xanthate may have contained approximately one CS₂ per C₆ residue. The xanthate solution gave quite light colored precipitates with heavy metal salts, indicating a good degree of purity and an absence of appreciable amounts of inorganic sulfides and thiocarbonates. The data given in Table V also bear out the observation of other workers that the aging of the soda-cellulose does not affect the degree of xanthation. The variations observed in the data might have been caused by changes in temperature of xanthation, which was known to have been highest in the tests in which the xanthate had the highest reducing value. This increase in temperature might have increased the content of impurities, and

thus increased the titration value.

DISCUSSION: The tests of series J and K cannot be considered as conclusive, as they would have to be repeated before any definite conclusions could be deemed justifiable. It would appear, however, that the aging of the soda-cellulose does affect the depressing qualities of the resultant xanthate. It is to be noted that the tests with pyrite and galena follow the same general trend, with test J-2 standing out as a marked exception for which no explanation can be given except that an error may have been made in the amounts of reagents used in it. The variations in the results of the other tests might have been due to the effects of aging of the soda-cellulose, but they might also have been due to differences in the xanthate caused by variations in the conditions of xanthation.

The mineral was not particularly floatable in any of the tests, and this made necessary high rotor speeds and a long collecting period. It would have been very easy to have altered the conditions enough to have caused the variations shown by the different tests, but the fact that the two series of tests, follow the same course of change indicates that any variation must have been due to differences in the xanthate used at the different times rather than in any differences in manipulation.

It is not at all illogical to suppose that the aging of the soda-cellulose might affect the properties of the xanthate for flotation purposes. If the cellulose were oxidized in the aging it might be expected to become a better depressor. If it were hydrolyzed or otherwise changed so that the cellulose micelles were broken up into smaller units one might expect that a given weight of the xanthate would contain more individual cellulose xanthate molecules if made from an aged pulp than if made from fresh soda-cellulose. In this connection there might be two factors working: the increase in number of xanthate molecules should increase the depressing ability, but the smaller molecules might not have as great a depressing effect per molecule as the larger molecules. The net effect could be that the depressing action might be either increased or decreased by the aging. Thus, as an example of this, one pound of ethyl xanthate contains more molecules than one pound of amyl xanthate, but the molecules of the latter are so much more efficient that a given weight of the amyl xanthate is also more efficient. In view of this it is not impossible that, as the cellulose molecules are changed during the aging, the depressing effect of the cellulose xanthate might follow some peculiar curve such as is indicated by the data of the tests of series J and K. This would be of theoretical as well as pract-

ical interest, and further investigations would be valuable.

TABLE V

Time of aging of the soda-cellulose in hours at 18°C	No. of C ₆ H ₁₀ O ₅ residues in 2L of the solution	Equivalents of reducing ions per 2L .
19	0.0309	0.0325
41	0.0309	0.0325
63	0.0309	0.0335
88	0.0309	0.0355
113	0.0309	0.0340
137	0.0309	0.0330

666

TABLE VI

Tests with 450 g silica and 50 g sulfide. Cellulose xanthate equivalent to 0.5% cellulose per ton, or approximately 0.625% amyl xanthate in reducing value, followed by 0.1% ethyl xanthate and 0.1% pine oil. Properties of cellulose xanthate as given in TABLE V.

Test No.	Sulfide Mineral	Age of crumbs: hours	pH	Conc.: wt. g	Recovery: %	Grade of: conc. % sulfide	S. I.
J-1	PbS	19	8.6	32.4	50.5	77.9	7.95
J-2	PbS	41	8.8	21.5	27.3	63.5	4.59
J-3	PbS	63	8.6	34.1	53.5	78.4	8.25
J-4	PbS	88	8.6	43.2	68.8	79.5	10.50
J-5	PbS	113	8.6	33.3	51.0	76.6	7.68
J-6	PbS	137	8.6	32.0	47.6	74.25	7.00
K-1	FeS ₂	19	8.4	33.9			
K-2	FeS ₂	41	8.6	37.9	57.4	75.7	8.04
K-3	FeS ₂	63	8.5	35.7			
K-4	FeS ₂	88	8.5	45.1	71.2	78.9	10.71
K-5	FeS ₂	113	8.5	34.1			
K-6	FeS ₂	137	8.5	33.0	52.3	79.3	8.40

Flotation Tests with Cellulose Xanthate:

Series L, M, N, and O

CHARACTERISTICS

The tests of series L, M, N, and O are given in Table VII and were run to determine the depressing effect of the cellulose xanthate on the sulfides in an acid pulp.

DISCUSSION: It is known that pyrite is more floatable at a low pH than in an alkaline pulp, and this is shown by L-1. However, the other tests of series L show that the depressing effect of cellulose xanthate on pyrite is much greater in acid than in alkaline. This may be contradictory evidence to the idea that the reason pyrite ordinarily floats better in acid pulp is due to the cleaning action of the acid with removal of inhibiting coatings. Such cleaning action would be expected to make the mineral more floatable when the cellulose xanthate is used in acid than in alkaline pulp. Also, the acid might be expected to tend to decompose the cellulose xanthate and render it ineffective. There is the possibility that the regenerated cellulose would have some effect, though not as great as was observed. The mineral of L-5 could not be floated even by large additions of amyl xanthate.

Test M-1 was run to find out the floatability of sphalerite in an acid pulp, and it was found to be more floatable than in alkaline medium. However, the depressing effect of cellulose xanthate was found to be greater

in combination with acid than without it. Compare tests number five of previous series.

Chalcocite and Galena are known to be floatable over a wide pH range, so no comparative tests were made without cellulose xanthate. Tests N-1 and O-1 show that these minerals are not depressed as greatly as pyrite or sphalerite, by cellulose xanthate in an acid pulp. The mineral in each of these tests behaved similarly. After addition of the collector and frother there seemed to be no tendency to float for several minutes, then the froth began to darken and the mineral floated slowly but continuously. It was thought that this might have been due to slow decomposition of the cellulose xanthate by the acid, so a test was made with galena in which the acid and cellulose xanthate were placed in the pebble mill with the mineral after grinding, and the mill sealed and agitated slowly for one hour. At the end of that time there was a strong odor of H₂S and when the mineral was placed in the flotation machine it was found to be much less floatable than in test O-1. This made it appear that the decomposition of the cellulose xanthate had nothing to do with the slow flotation of O-1. No further explanation seems justified without more work on the problem. In O-2, the formation of PbSO₄ may have aided the depression.

It is to be noted in the tests with pyrite that the order of addition of the reagents seemed to have a marked effect on the depressing action. Thus, addition of acid before the cellulose xanthate gave more depression than the reverse process. This would indicate that a clean sulfide surface would be desirable for a minimum depressing action by cellulose xanthate, and does not seem logical. This is of theoretical interest so far as flotation is concerned.

TABLE VII

Tests with 450 g silica and 50 g sulfide. 0.1# ethyl xanthate and 0.1# pine oil added after the other reagents which are given in order of addition and as #'s per ton. Cell-X given as #'s cellulose per ton.

Test No.	Sulfide Mineral	Age of Soda-Cell. -hours	pH	Conc. Wt. g	Special reagents and notes on the flotation.
L-1	FeS ₂		3.6	52.3	16# H ₂ SO ₄ ; Very good flotation.
L-2	FeS ₂	39	3.4	2.5	16# H ₂ SO ₄ , .5# Cell-X; No flotation.
L-3	FeS ₂	39	3.6	14.1	.5# Cell-X, 16# H ₂ SO ₄ ; Better flotation than in L-2.
L-4	FeS ₂	66	3.5	2.0	16# H ₂ SO ₄ , .5# Cell-X; No flotation even with much Amyl-X.
L-5	FeS ₂	39	8.4	28.3	No acid, .5# Cell-X; Much better flotation than in L-3.
M-1	ZnS		5.0	52.3	16# H ₂ SO ₄ , .5# CuSO ₄ ; Very good flotation.
M-2	ZnS	39	4.9	3.4	.5# CuSO ₄ , .5# Cell-X, 16# H ₂ SO ₄ ; No flotation - see text.
M-3	ZnS	66	4.8	4.8	16# H ₂ SO ₄ , .5# CuSO ₄ , .5# Cell-X; Slightly more floatable than M-2. Conc. contained more ZnS.
N-1	Cu ₂ S	66	4.	26.4	16# H ₂ SO ₄ , 15# Cell-X; White froth at first, but floatability increased consistently with time.
O-1	PbS	66	4.	28.4	Exactly the same reagents and results as in N-1.
O-2	PbS	66	4.	10.3	16# H ₂ SO ₄ , .5# Cell-X added to mill after grinding and mill sealed and allowed to stand with occasional agitation for one hour. The mineral was much less floatable than in O-1. This test renders the time effect in N-1 and O-1 inexplicable.

Selective Flotation with Cellulose Xanthate: Series S

GENERAL ASPECTS

The foregoing work on flotation using cellulose xanthate gives data which may be used to predict an order of depressing effect with the various minerals. This appears to be different in acid and alkaline pulps and may be stated to approximately be as given in Table VIII.

TABLE VIII

Order of Depressing Action of Cellulose Xanthate

With alkaline pulp

With acid pulp

Chalcocite	Max. depression	Pyrite
Sphalerite		Sphalerite
Galena		Galena
Pyrite	Min. depression	Chalcocite

EXPERIMENTAL

Using the data of Table VIII it would be theoretically possible to predict methods for selective flotation. This was tried out on four flotation tests, which are shown in Table IX.

From Table VIII one would predict that pyrite could be floated away from chalcocite in an alkaline pulp. Test S-1 shows that a tendency toward this was obtained, but that the copper became increasingly floatable as more

collector was added. With amyl xanthate added after .1# ethyl xanthate the normal behaviour was obtained with the pyrite tending to be depressed as it ordinarily is in an alkaline pulp.

With pyrite and chalcocite in an acid pulp it would be expected from previous data that the chalcocite would float away from the pyrite. However, in test S-2 this did not take place, the iron floating slightly better with ethyl xanthate and also with amyl xanthate added subsequently. Both minerals seemed to behave the same, and this may have been due to surface replacement in the acid pulp. Again, possibly insufficient Cellulose xanthate was used.

Table VIII shows that pyrite should be depressed in an acid pulp so that lead might float away from it. This was tried in S-4, and though only .3# of cellulose xanthate was used both minerals became so unfloatable that they would not float even with large amounts of amyl xanthate. This may have been due to surface atom replacement.

In an alkaline pulp one would expect, from the data given, that pyrite would float away from galena. This was tried in S-3. It will be seen that the reverse of the expected action took place though total recovery of each mineral was very low. No explanation can be given for this anomalous behaviour in the mixture.

DISCUSSION

Thus far the selective flotation has indicated little possibility of being practicable. The actions of the minerals in mixtures do not follow the same course as when the minerals are present alone.

Possibility of selective flotation must not be regarded as entirely impossible, however, as only a few tests were made and a slight change in conditions might have altered the results remarkably. There is also a possibility of selective floatation using cellulose xanthate in conjunction with collectors other than alkyl xanthates. Thus, some collectors exhibit a selective action for certain minerals, and if cellulose xanthate were used in conjunction with these to decrease the native floatability of sulfides which it was desired not to collect, a new field in flotation might be opened. Thus, aromatic and aliphatic mercaptans, sulfides, and amines might be made use of. It would seem to be theoretically possible that sulfide lead-zinc ore be treated with cellulose xanthate to reduce the floatabilities of all the minerals and then with a high amine to make the sphalerite float away from the galena. Other similar actions might be predicted, and to work with them a knowledge of the action of the different collecting agents would be necessary.

TABLE IX

Selective flotation tests using the reagents indicated in the table in the order in which they are given. Ores consisted of 25 grams of each sulfide and 450 grams of gangue.

Test No.	Ore	pH	#'s Reagent per Ton				Am-X	Conc. No.	Conc. Wt. g	Recoveries		Conc. % FeS ₂	Grade % FeS ₂	Selectivity Indices
			H ₂ SO ₄	Cell-X	P-oil	Et-X				Cu ₂ S %	FeS ₂ :Cu ₂ S %			
S-1	Cu ₂ S	8.4	0.4	0.1	.06		1	14.1	17	33	30	58	1.55FeS ₂ /Cu ₂ S	
	FeS ₂								12	19	33	53	1.53FeS ₂ /Cu ₂ S	
	SiO ₂								25	4	69	11	2.44Cu ₂ S/FeS ₂	
S-2	Cu ₂ S	4.	16	0.3	0.1	0.1	1	9.6	7	24	20	63	2.04FeS ₂ /Cu ₂ S	
	FeS ₂								71	72	43	44	2.36FeS ₂ /Cu ₂ S	
S-3	PbS	8.4	0.4	0.1	0.1		1	15.5	32	16	51	25	1.57PbS/FeS ₂	
	FeS ₂								32	22	45	32	1.58PbS/FeS ₂	
S-4	PbS	4.	16	0.4	0.1	0.1		No Flotation.	PbS and FeS ₂ both seemed to be depressed 100%. There was no tendency to float even upon addition of 0.5# of amyl xanthate.					
	FeS ₂													
	SiO ₂						0.5							

Cellulose Dixanthogen in Flotation

To test the action of cellulose dixanthogen in flotation, fresh cellulose xanthate was oxidized with iodine and the product filtered, washed with water, then with several portions of pure MeOH and dried at a low temperature. The product was yellow in color. Two grams of the dixanthogen were ground with 50 g Cu₂S and 450 c SiO₂ for one hour and the mixture was floated with .1# ethyl xanthate and .1# pine oil per ton. There was not the slightest trace of a depressing action or any other observable action by the cellulose dixanthogen. The mineral floated perfectly.

It must be concluded that under the alkaline conditions prevailing in the above test the cellulose dixanthogen has no effect on flotation of sulfides. Other dixanthogens will act as collectors under like conditions, but they are liquids and must be somewhat soluble in water, however slight. The cellulose dixanthogen, being a solid and presumably very insoluble in water, would have to react with the mineral surface in the solid phase, and as this is certainly unlikely to occur it may be used to explain the failure of the cellulose dixanthogen to have any effect on flotation. It might be that in an acid pulp the dixanthogen would react differently, though this is unlikely.

Since the dixanthogen is presumably a stable compound it would be more suitable than the xanthate for flotation purposes if it had a similar action.

V. ECONOMIC CONSIDERATIONS PERTAINING TO THE USE OF
CELLULOSE XANTHATE IN FLOTATION

General Aspects

Most flotation mills do not manufacture their own xanthates for collecting purposes but buy them from manufacturers of these reagents. This is because of the technique and expense of making the xanthates and because of certain economic advantages gained by shipping the xanthate rather than the raw products for its manufacture.

In the case of very small mills it would be impossible for the mill to manufacture its own xanthate under any circumstances, because the cost of labor and equipment involved in the manufacture would prohibit it.

Cellulose xanthate seems to present a unique problem. If it were to be used for flotation purposes it would undoubtedly be desirable to purchase it rather than to make it on the mill site. However, such a process would appear to be impossible from the results expressed in part III of this thesis. Also, even though a stable xanthate were to be made it would presumably contain less CS₂ than a xanthate made up fresh, and would be less efficient for flotation. Apparently the material would have to be made at the mill.

This economic problem is the most serious concerned with the use of the cellulose xanthate in flotation.

Although no separation has been worked out which would justify the commercial use of this xanthate, such a process is conceivable, and were it to be found, the economic problem would be the determining factor of whether or not it could be used.

Costs of Manufacture of Cellulose Xanthate for
Ore Flotation Purposes

The cost of manufacturing cellulose xanthate at a mill is scarcely predictable except within a wide range, and would be extremely variable. In general, the costs might be divided into fixed costs independent of the xanthate used and operating costs dependent on the xanthate consumption.

EQUIPMENT: The equipment to make the xanthate would be an important matter. It seems likely that the constant temperature room could be dispensed with, but a steeping press, a shredding machine, and a xanthating drum, besides miscellaneous mixing apparatus and storage containers for raw materials and products would be necessary. Avram (22) describes such equipment and says that the capacity of apparatus of usual size is about 250 pounds of cellulose per charge. Since approximately two and one-half hours would be necessary per charge, the daily capacity might be taken as approximately one ton of cellulose per day per unit. The number of units necessary would depend on the capacity of the plant and on the xanthate required per ton of ore, but one unit might be well able to take care of any plant now operating, since the use of 0.2# of the cellulose per ton seems a reasonable figure in the light of the experi-

mental work and would allow treatment of 10,000 tons of ore per day with one xanthate unit. Presumably the plant could be located in the mill building, so that construction costs would be low. However, in view of the possibility of obsolescence and the low resale value of the machinery it would be well to charge the entire cost of the plant to the first year of operation. If this were done, costs of replacements could be neglected for the first year. The first cost of a unit might be estimated as 10,000 dollars.

LABOR: The cost of labor would be a variable quantity. If the full capacity of the xanthate unit were to be utilized, the full time of one man per shift would be necessary to operate the unit. If the full capacity of the unit were not necessary and it proved possible to manufacture the xanthate at intermittent periods without undue decomposition taking place between periods so as to change the composition of the xanthate and make it unfit for use, only part of one man's time would be necessary to operate the xanthate unit. For instance, if it were possible to stabilize the xanthate in dilute ^{NaOH} ~~value~~ throughout a shift of eight hours, a man would be able to make one charge of xanthate per shift and do many other things besides, in which case the labor charge would be reduced. Presumably the xanthate would be made up to a fairly con-

concentrated solution and its depressing value determined by the regular laboratory staff, after which it could be diluted sufficiently to give it a certain depressing value per unit volume, making unnecessary changes in rate of feed to the flotation circuit. This control work could be maintained at very low cost by the regular laboratories, and might consist of chemical analysis or control flotation tests, depending on which would prove to be satisfactory. The cost of labor would be then varied from about \$12 per day down to around \$3 per day.

POWER: The power to run the xanthate unit would be appreciable and would depend on the amount of xanthate needed. An estimate might be made of 100 KW hours per ton of cellulose used, or .05KW hours per pound, with a cost of .1¢ per pound with power at 2¢ per KW.

MATERIALS: One ton of cellulose requires approximately one-half ton of CS₂ and one-half ton of NaOH for xanthation. The costs of these substances are variable, but a fair estimate, allowing some excess to take care of shipping costs and storage losses would be:

One ton of wood pulp	\$ 50.00	
1000# of CS ₂	\$ 70.00	
1000# of 96% NaOH	\$ 40.00	
	<u>\$160.00</u>	per ton of cellulose or
		.08 per ton # of cellulose

TOTAL COSTS ESTIMATES: The above data may be combined to show costs of manufacture of varying amounts of xanthate:

TABLE X

Daily cost for: (see text)	2000# cellulose	1000# cellulose	500# cellulose	100# cellulose
equipment	\$ 30.00	\$ 30.00	\$ 30.00	\$ 30.00
labor	12.00	6.00	3.00	3.00
power	2.00	1.00	1.00	0.50
materials	160.00	80.00	40.00	8.00
Total	\$204.00	\$117.00	\$74.00	\$ 41.50
cost per #	0.102	0.1170	0.158	0.415
Cost per ton of ore treated:				
0.2#/Ton	\$0.02	\$0.025	\$0.03	\$0.08
1.0#/Ton	0.10	0.12	0.15	0.400

It will be seen that the estimated cost of cellulose xanthate for flotation might be from 2¢ to 40¢. This is in the range of that usually experienced for flotation reagents, the cost per ton running from as low as two cents for a simple ore to 30 cents for a complex ore. The costs of frothers, collectors and other reagents would have to be added to that of the cellulose xanthate so that the total cost of treating a ton of ore using this reagent would be increased considerably. It would be practical only where a large tonnage would be treated, according to the cost data given. It is possible that certain of the costs could be reduced if a smaller amount of xanthate were to be used, for instance, it might be possible to cut down on the equipment cost considerably, though not if standard rayon machinery were to be used.

VI. SUMMARY AND CONCLUSIONS

1. The chemistry of cellulose xanthates has been reviewed. It is concluded that a pure cellulose xanthate has probably never been prepared, and that this is the reason for the statements of other investigations that cellulose xanthate compounds having a constant stoichiometric proportion of elements do not exist. Theoretical knowledge concerning the material known as cellulose xanthate is meager and the methods which are available for research into its composition are inadequate. The material is unstable and undergoes rapid change in water solution and in the solid state (not dry), but the stability is increased in dilute caustic solution. The composition of the material known as cellulose xanthate is variable and depends on many factors in its preparation, but the qualitative composition is probably a mixture of inorganic sulfur-bearing compounds, cellulose, and cellulose xanthates conceivably ranging in composition from a cellulose trixanthate to some polycellulose xanthate.
2. The impure cellulose xanthate may be freed from most inorganic impurities by several methods. The solid xanthated soda-cellulose (cellulose treated with NaOH of mercerizing strength) may be washed with MeOH, EtOH, or saturated salt solution to leach out the impurities, or the xanthate may be dissolved in dilute caustic and spun

into a bath of alcohol so as to coagulate the xanthate and leave the impurities in solution. In the latter process coagulation is helped by dilute organic acids, but these also tend to decompose the xanthate.

3. The purified cellulose xanthate, consisting of a mixture of cellulose and true cellulose xanthates should remain stable if dried, according to present theories for its decomposition. In the experimental work a stable xanthate was prepared only once, and this was made from soda-cellulose which had been aged an exceptionally long time. It is concluded that either the cellulose xanthate will decompose in the solid state or the experimental products were not sufficiently dried. Since great care was taken to dry the material and since the products gave every evidence of being dry, except for stability, it is concluded that the cellulose xanthate may retain water in some form with a very low vapor pressure, as by combination with coordinate valences, and that such water may become available for decomposition of the xanthate. It is further hypothesized that water may act as a catalyst in the decomposition of the xanthate, since only small amounts could have been retained by the xanthate made in the experimental work. Evidence was also obtained that alcohols may decompose the xanthate.

4. The impure product resulting from xanthation of soda-

cellulose has a marked depressing effect on sulfide minerals when used in flotation processes. The depressing action is due to the actual cellulose xanthate and not to impurities. The effect appears to vary with different minerals and the order is not the same in acid as in alkaline pulps. The depressing effect may be affected by the time of aging of the soda-cellulose, but sufficient data are not available for the drawing of definite conclusions on this score. The cellulose xanthate has a greater depressing effect when used in conjunction with ethyl xanthate as a collector than when used with amyl xanthate, and also a greater effect in acid than in alkaline pulps. Cellulose dixanthogen appears to have no effect on flotation, though this was not extensively investigated.

5. The depressing action of the cellulose xanthate may be due to the formation of a water-avid film of heavy metal cellulose xanthate at the mineral surface. However, in view of the fact that the xanthate decomposes rapidly in acid solution and that the depressing action is greater in acid pulps, it appears that this theory may not entirely account for the action of the cellulose xanthate. The fact that it seems to be a negatively charged colloid may be important in this connection. The complete depression of pyrite by cellulose xanthate

in acid pulp does not appear to fit in with the usual theories as to flotation of pyrite, particularly if the idea of formation of a film of water-avid iron cellulose xanthate is adopted.

6. The action of the cellulose xanthate on minerals in mixtures of sulfides is not the same as on the pure minerals. This complicates the matter of use of the reagent in selective flotation. It is concluded that the cellulose xanthate might be used in conjunction with specific collectors for certain minerals so as to reduce the native floatabilities of all minerals present so that these not affected by the collector would not tend to float. All the experimental flotation work was done with a silica gangue. The matter might be more complicated and the cellulose xanthate made less effective in the case of a limestone gangue because of the possibility of consumption of xanthate to form insoluble calcium cellulose xanthate.

7. The cellulose xanthate might conceivably^{be} used to cause froths to break so as to aid filtering and drying of concentrates.

8. The amount of cellulose xanthate needed to treat a ton of ore, if a satisfactory process using the xanthate were to be developed, would probably be in the range of 0.2 to 1.0 pound. The cost of the xanthate used per ton

of ore might then vary from around two cents up to forty cents, depending on the tonnage of ore treated and the xanthate consumption per ton. The figures are based on costs of manufacturing the xanthate at the flotation concentrator. The lower figure is well within the usual range of flotation reagents costs.

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APPENDIX I: SUGGESTIONS FOR FURTHER WORK

At the time of the writing of the thesis, the possibility that cellulose xanthate will ever be used in flotation is rather remote. However, it is conceivable that some selective flotation process might be worked out which would utilize this reagent.

In view of such a possibility it would be desirable to do more work on the stabilization of the xanthate. If a stable xanthate could be manufactured and shipped to the flotation concentrators for consumption, the use of the reagent would be much more justified. Also, production of such a xanthate would greatly aid in the experimental flotation work. As a first step in the production of such a xanthate it is suggested that the method of drying by distillation with an organic solvent be used. Also, different lots of cellulose might be used for the preparation of the xanthate to see if the pulp characteristics might have some connection with the stability of the product. Xanthation at a low temperature should be investigated, both with the idea of getting a product better suited to stabilization and to getting one free from impurities.

In further flotation work, it might be possible to make considerable progress using only qualitative flotation tests, possibly weighing the concentrates, but not

analyzing them unless such seemed desirable. This would make possible the accumulation of a great deal more information.

Production of a collective concentrate of several sulfides and treating this with the cellulose xanthate to produce a selective concentrate of one of the sulfide would be worth investigating. In this connection, and in other tests, it would be well to investigate the use of collectors other than the alkyl xanthates in conjunction with the cellulose xanthate. Amines might be used with zinc and copper minerals, mercaptans and disulfides with copper minerals, and other reagents known to be somewhat selective for certain minerals used for collecting them. A study of the action of such reagents as reported in the literature would be necessary before beginning such work.

Further work should be done to correlate the history of the cellulose xanthate with its flotation behaviour. Particularly should be investigated the behaviour of a cellulose xanthate solution in flotation during the period of its decomposition; this would be valuable as information relating to the suitability of periodic manufacture of xanthate in mills.