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Chlorination of Cellulose with
Thionyl Chloride in a Pyridine Medium

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THE CHLORINATION OF CELLULOSE WITH
THIONYL CHLORIDE IN A PYRIDINE MEDIUM

A thesis submitted by

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INTRODUCTION AND HISTORICAL REVIEW

Except for a few isolated instances, very little interest has been shown in the introduction of halogen atoms into the structure of carbohydrate polymers. The interest which has arisen in this subject has come about by the incidental introduction of halogen atoms into carbohydrate polymers in the course of the preparation of more familiar derivatives.

Perhaps the most familiar halogen-containing, simple carbohydrates are the acetylglycosyl halides. In these compounds, the acetoxy groups on the reducing carbons of acetylated sugars have been substituted with halogen atoms. Colley (1) prepared the first compound of this type (tetraacetylglycosyl chloride) by treating glucose with acetyl chloride. Sugars containing more than one halogen atom per molecule have been prepared by the prolonged reaction of liquid hydrogen bromide upon acetylated sugars (e.g., pentaacetylglucose yielded the 1,6-dibromo derivative) (2). Polyols and their derivatives have also been halogenated using hydrogen halides (3-5).

Sulfuryl halides also act as halogenating agents but frequently sulfuric acid residues are also introduced by the reaction with hydroxy compounds. Helferich (6) treated methyl alpha- and beta-methyl glucosides with sulfuryl chloride in a pyridine and chloroform medium and obtained compounds with the empirical formula: $C_7H_{10}O_6SCl_2$. These compounds were methyl 2,3-sulfuryl-4,6-dichloroglucosides (7). Helferich and co-workers (8) also treated mannitol and trehalose with sulfuryl chloride in a pyridine and chloroform medium and obtained tetrachloromannitol sulfate ($C_6H_8Cl_4O_4S$) and

tetrachlorotrehalose disulfate ($C_{12}H_{14}O_{11}Cl_4S_2$), respectively. The sulfate groups could be hydrolyzed in alkaline media to give the corresponding chlorine compounds (7).

Halogen atoms have also been introduced into carbohydrates during the preparation of p-toluenesulfonyl (tosyl) and methanesulfonyl (mesyl) esters of carbohydrates. Bernoulli and Stauffer (9) esterified glucose with tosyl chloride in a pyridine medium and obtained 1-chloro-2,3,4,6-tetratosylglucose. Upon extension of the reaction, these investigators found that another chlorine atom was introduced into the glucose molecule; dichloro-tritosylglucose was obtained in mixture with the tetratosylchloro derivative.

Hess and Stenzel (7) carried out an intensive investigation concerning the tosylation of both alpha- and beta-methyl glucosides in a pyridine medium. At low temperature (20°C.), yields of practically 100% of methyl 2,3,4,6-tetratosylglucosides were obtained. At higher temperatures, methyl 2,3,6-tritosyl-4-chloroglucosides were formed and, at still higher temperatures (85 to 90°C.), methyl 2,3-ditosyl-4,6-dichloroglucosides were formed. These workers established that chlorination occurred by the action of the pyridinium hydrochloride formed in the tosylation reactions:



Both methyl 2,3,4,6-tetratosylglucoside and methyl 2,3,6-tritosyl-4-chloroglucosides were converted into methyl 2,3-ditosyl-4,6-dichloroglucosides by pyridinium hydrochloride. No reaction was observed when unesterified methyl glucosides were treated with pyridinium hydrochloride. It was also reported that, upon saponification with caustic in aqueous or pure methanol

or with sodium methylate-methanol in chloroform or acetone solution, tosyl groups were lost, but the compounds still exhibited high chlorine contents. Preparations were obtained which had compositions approaching methyl mono- and dichloroglucosides.

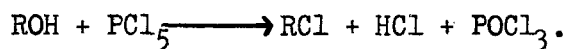
Hess and Ljubitsch (10) prepared a derivative of cellulose containing approximately two tosyl groups per glucose unit using tosyl chloride in a pyridine medium. At room temperature, only small amounts of chlorine were introduced into the cellulose by the tosylation reaction; however, at higher temperatures considerable amounts of chlorine were introduced (approaching one atom per glucose unit). The chlorine content of tosylated cellulose possessing low chlorine contents was substantially increased, with the loss of some tosyl groups, by treatment with pyridinium hydrochloride. Bernoulli and Stauffer (11), in their work on the tosylation of cellulose, reported that the chlorine content of tosylated cellulose increased as the reaction time increased.

Heating tosyl esters of carbohydrates with an acetone or acetonyle-acetone solution of sodium iodide replaces primary tosyl groups with iodine atoms. This treatment usually has no effect upon secondary tosyl groups (12). The difference in the ease of replacement of primary and secondary tosyloxy groups has been utilized to determine quantitatively the number of primary hydroxyl groups in a carbohydrate. Cramer and Purves (13), Mahoney and Purves (14), and Heuser, Heath, and Shockley (15) used this technique to study the esterification of the primary hydroxyl groups of cellulose. Malm, Tanghe, and Laird (16) determined

the presence of unesterified primary hydroxyl groups in a cellulose acetate by tosylation and iodination. These workers found that, in some cases, iodine also replaced chlorine atoms introduced into the tosylated cellulose acetate by the tosylation reaction. They also found that there was an upward drift in iodine content as the iodination reaction was prolonged. This trend was finally interpreted to be due to a slow replacement of secondary tosyl groups with iodine, after corrections had been applied for the presence of absorbed iodine and for the loss of tosyl groups without replacement with iodine atoms during prolonged iodination.

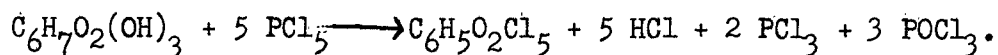
Wolfrom, Sowden, and Metcalf (17) prepared mesyl esters of cellulose, which contained 1.6 to 1.7 mesyl groups per glucose unit, by treating cellulose with mesyl chloride in a pyridine medium. These mesylated celluloses contained considerable amounts of chlorine; greater chlorine contents were obtained by treating mesylated cellulose with pyridinium hydrochloride. Roberts (18), in his investigation of the mesylation of cellulose, found that the chlorine content of mesylated cellulose increased as the reaction temperature rose and as the reaction time increased. It also seemed that greater amounts of chlorine were introduced during mesylation with mesyl chloride than during tosylation with tosyl chloride. In some cases the degree of chlorine substitution rose to almost 0.9.

Phosphorus pentachloride is a common chlorinating agent which reacts with alcohols in accordance with the following equation (19):



The hexachloro derivative of mannitol has been prepared by first breaking the anhydro rings of isomannide (1,4-3,6-dianhydromannitol) with hydrogen chloride and chlorinating the remaining hydroxyl groups with phosphorus pentachloride (20). Phosphorus pentabromide has been used to split the anhydro ring of 2,3,4-triacetyllevoglucosan (2,3,4-triacetyl-1,6-anhydroglucopyranose) to give 1,6-dibromo-2,3,4-triacetylglucose (2). Barham, Stickley, and Caldwell (21) intimately mixed finely ground phosphorus pentachloride with glucose, sucrose, and mannitol and heated the mixtures at temperatures ranging from 100 to 170°C. to obtain products in which the hydroxyl groups were completely replaced by chlorine atoms.

Barham, Stickley, and Caldwell also extended their phosphorus pentachloride study to starch (21). Starch was mixed intimately with an excess of phosphorus pentachloride and was heated at 160 to 170°C. in three stages over long periods of time. The course of the reaction was followed by analysis of the hydrogen chloride evolved and the phosphorus trichloride and phosphorus oxychloride formed; the product was found to contain five chlorine atoms. The following reaction was suggested:



Pentachlorostarches were found to be yellow amorphous solids which became tarry and finally charred when heated. They were insoluble in water and soluble in a number of organic solvents; a solution of pentachlorostarch in an equal weight of acetone was found to be viscous.

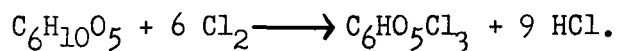
When the product was heated with an acetone solution of sodium iodide and then treated with aqueous sodium thiosulfate, a loss of two chlorine atoms occurred, with the formation of the suggested unsaturated tri-chloride: $C_6H_5O_2Cl_3$.

The authors claimed, on the basis of chlorine content alone, that only slight degradation of the starch occurred. Attempts to hydrolyze pentachlorostarch, even with 50% sulfuric acid, were unsuccessful; the inertness was attributed to steric blocking of the glycosidic linkages with chlorine atoms. Adsorption experiments with chromatographic columns gave no indication of bonding, and it was assumed that degradation took place in an orderly manner to form a product of greater homogeneity than the original starch. The equivalence of the hydroxyl groups in starch and the phosphorus oxychloride formed led these investigators to believe that the normal chlorination reaction had taken place with the introduction of three chlorine atoms on carbon atoms two, three, and six. After consideration of the ease with which two chlorine atoms were removed by treatment with sodium iodide and sodium thiosulfate and because of spatial relations within the starch ring, the remaining chlorine atoms were assumed to have substituted carbon-bound hydrogen atoms on carbon atoms one and four.

The work of Barham, et al. did not indicate that carbon and hydrogen had been determined; these additional data might have given an indication of the oxygen remaining in the chlorostarches. Phosphorus pentachloride treatment of polyhydric alcohols and sugars (21) indicated

that only hydroxyl groups had been replaced with chlorine. This might have also been the case with starch. It is possible that the phosphorus trichloride formed during the reaction was due to the dissociation of phosphorus pentachloride into phosphorus trichloride and chlorine. It is known that, above 300°C., phosphorus pentachloride is 97% dissociated (22).

Barham and Thomson (23) treated starch with anhydrous liquid chlorine under pressure at 70°C. and found that oxidation as well as substitution with chlorine occurred. Trichlorostarch was prepared; the following reaction was proposed:

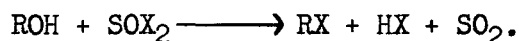


Chlorostarches were yellow solids; as the degree of chlorination increased, the products became progressively less soluble in polar solvents and more soluble in nonpolar solvents. Products, up to the monochloride, dissolved in and reacted with water. One of the chlorine atoms of dichlorostarch was found to be readily removed by cold dilute caustic solution. The presence of carbonyl groups in dichlorostarch was indicated by the formation of a dark brown, relatively stable product when the dichlorostarch was reacted with o-phenylenediamine. Starch trichloride reacted very rapidly with fuchsin aldehyde reagent. The authors assigned a preliminary structure to trichlorostarch, assuming that no changes had occurred in the ring structure. Of the nine hydrogen atoms eliminated as hydrogen chloride, six represented the oxidation of the hydrogen atoms and the hydroxyl groups on carbon atoms two, three, and six to carbonyl groups. The three remaining carbon-bound

hydrogens were substituted by chlorine on carbon atoms, one, four, and five. There were no carbon and hydrogen data listed to corroborate the results. These speculations should be tested by further work.

Barham (24) has taken out three patents on the chlorination of starch, cellulose, and the esters and ethers of cellulose, starch, and sugars, using liquid chlorine under pressure and at elevated temperatures. When cellulose was treated with liquid chlorine at 70°C. for eight days, chlorine was found to be chemically combined to the extent of 22.8%.

Thionyl halides are used quite commonly in the preparation of halogen compounds from alcohols. The halogenating reaction proceeds as follows (19):



The halogenation reaction occurs most frequently between hydroxy compounds and thionyl halides; the presence of a tertiary base (e.g., dimethylaniline) and an excess of thionyl halide facilitates the formation of halides (25). However, sometimes thionyl halides form intermediate unstable chlorothionyl compounds with hydroxyl substances (e.g., EtOSOX). In this eventuality, the halides may usually be obtained by heating; sulfur dioxide is removed by this action (25). In some instances, thionyl halides produce simple sulfite esters in reactions with hydroxy compounds (e.g., EtO·SO·OEt).

Majima and Simanuki (26) studied the reaction of thionyl chloride with various polyhydroxy alcohols without the use of a pyridine medium. Ethylene glycol gave principally the sulfite ester ($\text{H}_2\text{C} \overset{\text{O}\cdot\text{SO}\cdot\text{O}}{\text{---}} \text{CH}_2$);

1,3-propanediol gave principally 1,3-dichloropropane; glycerol gave good yields of the chlorosulfite derivative ($\text{ClCH}_2\text{---}\overset{\text{O}\cdot\text{SO}\cdot\text{O}}{\text{CH}}\text{---CH}_2$); mannitol produced mannitol trisulfite ($\overset{\text{O}\cdot\text{SO}\cdot\text{O}}{\text{CH}_2}\text{---}\overset{\text{O}\cdot\text{SO}\cdot\text{O}}{\text{CH}}\text{---}\overset{\text{O}\cdot\text{SO}\cdot\text{O}}{\text{CH}}\text{---}\overset{\text{O}\cdot\text{SO}\cdot\text{O}}{\text{CH}}\text{---}\overset{\text{O}\cdot\text{SO}\cdot\text{O}}{\text{CH}}\text{---}\overset{\text{O}\cdot\text{SO}\cdot\text{O}}{\text{CH}_2}$). When mannitol was treated with thionyl chloride in the presence of pyridine, a tetrachlorohexyleneglycol sulfite was formed; when this product was hydrolyzed, a tetrachlorohexyleneglycol was produced. These investigators also found that meso-inositol, treated with thionyl chloride in a pyridine medium, formed a monochlorocyclopentitol, a tetrachlorocyclohexanediol, and some polychlorobenzenes and polychlorophenols (5).

Carre and Maucière (27) found that glycerol reacted with thionyl chloride and pyridine in equimolar quantities to give the mono-, di-, and trichloro derivatives according to the amounts used. Trichloropropane was obtained in yields of 80%. Mannitol, subjected to this reaction, was dehydrated to the 1,4-3,6 mannide in poor yield; the remaining two hydroxyl groups were replaced by chlorine atoms upon continuation of the reaction. Stilbene dichloride ($\text{C}_6\text{H}_5\text{CHClCHClC}_6\text{H}_5$) was prepared from hydrobenzoin ($\text{C}_6\text{H}_5\text{CH}(\text{OH})\text{CH}(\text{OH})\text{C}_6\text{H}_5$) by treatment with two moles each of thionyl chloride and pyridine. Cotton was also treated in this manner and gave a substance with the formula ($\text{C}_6\text{H}_9\text{O}_4\text{Cl}$) after regeneration from cuprammonium solution; the cotton turned dark and suffered a loss of tenacity. This was the only reference found in which cellulose had been subjected to a thionyl chloride treatment.

Kitasato and Sone (28), in their studies concerning the action of thionyl chloride upon glycolic hydroxy compounds, found that the products

consisted principally of thionyl compounds. The diethyl ester of tartaric acid ($C_2H_5OOCCH(OH)CH(OH)COOC_2H_5$), boiled with thionyl chloride, formed the sulfite ester: $C_2H_5OOCCH \overset{O.SO.O}{\text{---}} CHCOOC_2H_5$. Mannitol yielded mannitol trisulfite when boiled with thionyl chloride: $(H_2C \overset{O.SO.O}{\text{---}} CH \overset{O.SO.O}{\text{---}} CH \overset{O.SO.O}{\text{---}} CH_2)$. In some instances, two molecules of compounds containing only one hydroxyl group per molecule were bridged together with a thionyl linkage. Cholesterol ($C_{27}H_{45}OH$) reacted with thionyl chloride in a pyridine-benzene medium to form dicholesteryl sulfite: $(C_{27}H_{45}O)_2SO$. Cyclohexanol, treated with thionyl chloride in pyridine and carbon disulfide, formed dicyclohexanol sulfite: $(C_6H_{11}O)_2SO$. These compounds readily split off the thionyl groups in the form of sulfurous acid upon treatment with alkali, to form the original alcohols.

Govaert and Hansens (29) found that thionyl chloride or thionyl bromide, with or without a pyridine or diethylaniline medium, reacted with pentaerythritol $[C(CH_2OH)_4]$ to form the disulfite ester in quantitative yield. Thionyl bromide and pyridine reacted with isoamyl alcohol, capryl alcohol, and tert-butyl alcohol to form the corresponding bromides.

Wiggins (30), in his work on the constitution of isomannide, had occasion to treat some of his hydroxy compounds with thionyl chloride. Isomannide (1,4-3,6-dianhydromannitol), heated with thionyl chloride and pyridine, produced 2,5-dichloro-1,4-3,6-dianhydromannitol in 70% yield. Treatment of 1,6-dichloro-3,4-monoacetone-mannitol with thionyl chloride and pyridine at 100°C. led to the formation of 1,2,5,6-tetrachloro-3,4-monoacetone-mannitol.

Libermann (31) treated cyclohexanol with an excess of thionyl chloride until hydrogen chloride evolution ceased. A small amount of pyridine was added to the mixture and the mixture was heated to drive off the sulfur dioxide. Apparently the decomposition point of the cyclohexanol chlorosulfite which had been formed was lowered by the presence of pyridine. After the evolution of sulfur dioxide, the product consisted of cyclohexyl chloride. The same procedure gave 95% yields of ethyl methylchloroacetate, ethyl phenylchloroacetate, and ethyl diphenylchloroacetate from the corresponding alcohols.

Bissinger and Kung (32) studied the effects of varying experimental conditions upon the reactions of propyl alcohols and thionyl chloride. In order to prepare unstable propyl sulfite esters it was desirable to remove hydrogen chloride from the alcohol-thionyl chloride reaction. The reaction, therefore, was carried out in refluxing solvents in which all the components except hydrogen chloride and sulfur dioxide were soluble. Propyl alcohol, when the hydrogen chloride concentration was constant and at a minimum, formed either the sulfite or the chlorosulfite, depending upon the molar ratios of the alcohol and thionyl chloride used. At higher temperatures the chlorosulfite yield decreased, and the yields of olefin and propyl chloride increased. Isopropyl alcohol gave good yields of sulfite ester at low temperatures. At higher temperatures, the yields of olefin and isopropyl chloride predominated.

PRESENTATION OF THE PROBLEM

The primary over-all objective of the problem was to examine the reaction product of thionyl chloride and cellulose. Since it was found that sulfur was also introduced into cellulose by thionyl chloride, secondary objectives were to determine the stability of the sulfur groupings present and to eliminate as many of these groupings as possible without damaging the chlorinated cellulose (chlorocellulose).

Another secondary objective of the problem was to isolate constituents from the hydrolyzates of chlorocelluloses in order to determine both the manner in which chlorine had entered cellulose and the position occupied by the chlorine. Other secondary objects were the development of a method of purification of chlorocelluloses and the investigation of some of their chemical properties.

EXPERIMENTAL PROCEDURES

PREPARATION OF COTTON LINTERS

A commercial grade of cotton linters, obtained from the Buckeye Cotton Oil Company, Memphis, Tennessee, was used as the cellulosic material in reactions with thionyl chloride and pyridine. The commercial treatment of these linters consisted of a cook with dilute caustic, chlorine bleaches under both acid and alkaline conditions, and a thorough water wash; the linters contained 98.5% alpha-cellulose, 0.067% ash, and showed a solubility of 4.1% in hot 5% caustic soda (33). The degree of polymerization was about 1200 (34). These linters were the same as those used by Roberts (18) in his study of the mesylation of cellulose.

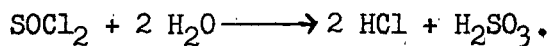
The linters were treated in a laboratory Wiley mill; the milled linters were screened through a shaker sieve for seven minutes. Milling was interrupted when the temperature of the mill rose to a point where the hand could not be comfortably placed on the face plate for about a minute; this temperature was in the range of about 45 to 50°C. The shaker sieve was equipped with standard 30-, 100-, and 325-mesh screens. The fiber fraction which passed through the 100-mesh screen and was retained by the 325-mesh screen was collected for experimental purposes. Fractions which passed through the 30-mesh screen and were retained by the 100-mesh screen were remilled and rescreened twice. All the 100- to 325-mesh fractions were combined and were sealed in a metal can, which was rotated overnight to insure thorough mixing.

PURIFICATION OF THIONYL CHLORIDE

Mathieson thionyl chloride and Eastman Kodak practical-grade thionyl chloride were purified in several stages. The impure thionyl chloride was boiled under reflux with sulfur and acetone to remove the sulfuryl chloride and sulfur chlorides which may have been present (35, 36). The thionyl chloride was then distilled using a spiral condenser as a distilling column; only the fraction which boiled between 75.5 and 76.7°C. (742 mm. of mercury pressure) was collected. The second stage of purification consisted of a distillation of thionyl chloride with quinoline to remove any acids which may have been present (37); only the fraction which boiled between 75.5 and 76.3°C. (735 mm. of mercury pressure) was collected. The final stage of purification was a distillation with linseed oil to remove the remaining color (37). The fraction which boiled between 75.0 and 75.5°C. (732 mm. of mercury pressure) was collected. Purified thionyl chloride was a clear, water-white liquid, whereas unpurified thionyl chloride was yellow.

ANALYSIS OF THIONYL CHLORIDE

Thionyl chloride purity was ascertained by hydrolyzing the thionyl chloride in an excess of standardized sodium hydroxide solution and titrating the excess caustic to the phenolphthalein end point with standardized hydrochloric acid. Thionyl chloride has been found to hydrolyze quantitatively to hydrochloric and sulfurous acids according to the following reaction (38):



The purity of thionyl chloride was calculated from the following equation:

$$\text{Purity of SOCl}_2, \% = \frac{(\text{equivalents of NaOH})(118.97)(100)}{4 (\text{grams of sample})}$$

Each thionyl chloride sample was weighed into a small tared weighing vial. The weighing vial was uncovered and quickly inserted into a 125-ml. glass-stoppered flask which contained a known volume of standardized sodium hydroxide solution. A short stirring rod prevented the vial, which contained the thionyl chloride, from overturning and spilling its contents into the caustic solution. Since mixtures of thionyl chloride and caustic solution reacted violently, the reaction was allowed to proceed slowly; the thionyl chloride was found to completely distill into the caustic solution when allowed to stand overnight at room temperature.

This method gave the following results:

Mathieson thionylchloride	99.78%
Eastman thionylchloride (practical-grade)	99.95%
Purified thionylchloride	100.0 %

CHLORINATION OF CELLULOSE

In his study of the mesylation of cellulose, Roberts (18) found that treatment of cotton linters with 18% sodium hydroxide solution prior to reaction with mesyl chloride produced a greater degree of activation than any other technique studied. Since the linters prepared for the present study were the same as those used by Roberts, it was decided to employ the same activation technique.

A caustic solution of approximately 18% concentration was made up and standardized by titration to both the phenolphthalein and methyl orange end points with standardized hydrochloric acid. The solution was found to have a concentration of 18.28% sodium hydroxide and 0.37% sodium carbonate.

Two to three grams of linters were activated with the equivalent of 50.00 ml. of 18.00% sodium hydroxide for every 2.000 grams of cellulose (ovendry basis). The calculated volume of water necessary to dilute the 18.28% sodium hydroxide solution to 18.00% was pipetted into the linters before the addition of the caustic solution. Caustic treatment was allowed to proceed for four hours at a temperature of 24 to 26°C. After the mercerization time had elapsed, the linters were collected on a tared, coarse fritted-glass crucible and were washed with absolute methanol until the washings were no longer alkaline to phenolphthalein. The alcohol was displaced by washing five successive times with anhydrous pyridine, which had been prepared by distilling and storing high-purity pyridine over barium oxide. In all the washing steps the liquid was removed by suction filtration, but care was taken to prevent drying of the cellulose. The pyridine-soaked linters were transferred to a reaction flask; the residual cotton left in the filtering crucible was determined by drying the tared crucible for 30 minutes in an oven maintained at 103 to 105°C. Since the yield of mercerized linters had been determined previously, the quantity of mercerized linters available for the thionyl chloride reaction could then be calculated.

A sufficient quantity of anhydrous pyridine was added to the pyridine-soaked, mercerized linters so that the total quantity of pyridine present equaled 50.0 moles per mole of anhydroglucose unit. Thionyl chloride was then added slowly until 10.0 moles were present per mole of anhydroglucose unit. Upon addition of the thionyl chloride, the temperature of the reaction flask rose considerably; when the reaction was carried out at room temperature, it was necessary to cool the reaction flask in an ice bath to prevent excessive heating. Every reaction was protected from moisture by means of a calcium chloride drying tube. Reaction mixtures at room temperature were agitated by placing the reaction flasks on a mechanical shaker. Reactions at elevated temperatures were carried out in a heated water bath; agitation was provided by a motor-driven, mercury-sealed stirrer.

At the end of the reaction period, the reaction mixture was washed slowly into a beaker containing about 500 ml. of cold distilled water. If the reaction mixture was introduced into water too rapidly, a violent reaction occurred between the water and the excess thionyl chloride. After standing in water for 30 to 60 minutes, the reaction product was filtered on a coarse fritted-glass crucible and washed thoroughly with water. The product was soaked overnight in 500 ml. of one-half saturated sodium bicarbonate solution, which was prepared by mixing equal volumes of water and saturated sodium bicarbonate solution. Water washing was accomplished by soaking the product in water and filtering and repeating until the filtrate was colorless. After washing, the product was air dried and finally dried to constant weight in vacuo at 44 to 46°C.

Two reactions were terminated by pouring the contents of the reaction flask into 300 ml. of absolute methanol. After standing for an hour, the products were filtered on coarse fritted-glass crucibles, washed several times with absolute methanol, and allowed to soak in absolute methanol overnight. Each product was extracted with absolute methanol in a Soxhlet extractor, which was operated under somewhat reduced pressure to effect extraction between 30 and 40°C. The products were dried in vacuo at 44 to 46°C.

Larger-scale reactions were carried out employing 25 grams of cotton linters. The same mercerization and reaction techniques used in the smaller reactions were employed. However, after the thionyl chloride reaction product was washed with water; it was suspended in dilute sodium hydroxide to eliminate as much sulfur as possible. A suspension of each product in about four liters of distilled water was allowed to stand overnight with an excess of about 10 ml. of 18% sodium hydroxide beyond the phenolphthalein end point; this excess caustic resulted in an approximately 0.015 N solution. The suspension was neutralized by the addition of sulfuric acid to slightly beyond the phenolphthalein end point. Water washing was accomplished by soaking the product in water and filtering and repeating until the filtrate was colorless. The product was air dried and placed in a sealed sample bottle. A sample of each product was dried to constant weight in vacuo at 44 to 46°C.

Every chlorocellulose prepared by the treatment of cotton linters with thionyl chloride in a pyridine medium was dried in vacuo at 44 to 46°C. Filter paper dried under these conditions produced essentially the same oven-dry factor as when dried in an ordinary oven maintained at 103 to 105°C.

CHLORINE ANALYSIS

The extent of chlorination of chlorocelluloses was followed by analyzing the samples for chlorine by the Parr peroxide bomb method (39). About 0.2 gram (accurately weighed) of sample was mixed well with 0.2 gram of benzoic acid, 0.1 gram of sucrose, 1.0 gram of potassium nitrate, and 15 grams of sodium peroxide. After ignition of the mixture, the bomb was cooled and the melt dissolved in about 100 ml. of hot, chloride-free water. The solution was acidified with nitric acid, filtered to remove carbon particles, and treated with an excess of silver nitrate solution. The precipitated silver chloride was determined gravimetrically.

A similar technique was employed for micro chlorine analyses. The water used for these analyses was specially prepared by distillation over silver nitrate. Chlorine contents were calculated as follows:

$$\text{Chlorine, \%} = \frac{(24.74) (\text{grams of AgCl})}{(\text{grams of oven-dry sample})}.$$

SULFUR ANALYSIS

The amount of sulfur introduced into chlorocelluloses was also

determined by the Parr peroxide bomb method (39). About 0.2 gram of sample (accurately weighed) was mixed well with 0.2 gram of benzoic acid, 0.1 gram of sucrose, 0.2 gram of potassium perchlorate, and 15 grams of sodium peroxide. After ignition of the mixture, the bomb was cooled and the melt dissolved in about 100 ml. of hot, sulfate-free distilled water. Concentrated hydrochloric acid was added to an excess of about one milliliter beyond the methyl orange end point. After filtering to remove carbon particles, the solution was neutralized to the methyl orange end point with sodium hydroxide and reacidified with 1.00 ml. of 1.00 N hydrochloric acid. The solution was heated to boiling, treated with an excess of barium chloride solution, and kept warm for at least four hours. The barium sulfate was then filtered into a tared Gooch crucible and treated in the conventional manner. Sulfur contents were calculated as follows:

$$\text{Sulfur, \%} = \frac{(13.73) (\text{grams of BaSO}_4)}{(\text{grams of oven-dry sample})}$$

CARBON AND HYDROGEN ANALYSIS

Carbon and hydrogen analyses were made by the analytical group of the Institute using Institute Method 706.

ASH DETERMINATION

An accurately weighed sample of chlorocellulose was placed in a tarred porcelain crucible and heated gently in the flame of a Meker burner until the sample had completely carbonized. The crucible was then brought

up to a red heat and maintained at this temperature for 30 minutes. The cooled crucible was then weighed on an analytical balance.

ACIDIC SODIUM CHLORITE TREATMENT OF CHLOROCELLULOSES

Upon the suggestion of Dr. L. E. Wise, chlorocelluloses were purified by treatment with acidic sodium chlorite solution. The chloriting procedure used was that described by Cundy and Beck (40). An accurately weighed sample of chlorocellulose (1.0 to 1.5 grams) was suspended in 50 ml. of distilled water and acidified with 0.125 ml. of glacial acetic acid. After the addition of 0.50 gram of sodium chlorite, the mixture was heated at 70 to 80°C. on a steam bath for 0.5 hour. The bleached product was then washed with water. In some cases it was necessary to repeat the chloriting procedure a second time for one hour and a third time for 1.5 hours. In every case in which three chlorittings were involved, the color of the product after the third chloriting was not appreciably lighter than the product after the second chloriting. The product was washed with water until free of chloride ion and was then dried in vacuo at 44 to 46°C.

Several larger-scale chlorite treatments, each employing six grams of chlorocellulose, were also carried out. Each sample was suspended in 200 ml. of water and treated with 0.50 ml. of glacial acetic acid. After the addition of 2.00 grams of sodium chlorite, the mixture was heated at 70 to 80°C. on a steam bath for 0.5 hour. The chloriting procedure was repeated for one hour and again for 1.5 hours if necessary.

Water washing of the product was continued until no trace of chloride ion remained.

PAPER PARTITION CHROMATOGRAMS

The concentrated chlorocellulose hydrolyzates, which were prepared in the course of the hydrolysis study, were chromatographed on paper strips. A small portion of each hydrolyzate (40 to 70% concentration) was spotted carefully on a line which was drawn three inches from the end of a 24-inch strip of Whatman No. 1 filter paper. Spotting was accomplished most successfully when a very fine capillary tube was employed. Each spotting tube was discarded after use to avoid any contamination which might occur if the tube was reused. The spotted strip was then suspended in a solvent tray located at the top of a large, sealed, stainless steel tank. A developer solution consisting of pyridine, n-butanol, and water in the volume ratios of 3:10:3 was placed in the solvent tray and allowed to flow down over the paper strip for various periods of time ranging from 12 to 72 hours. The atmosphere within the sealed tank was saturated with the vapors of the developer solution.

After the constituents of the hydrolyzate had separated sufficiently, the paper partition chromatogram was removed from the solvent tank and dried. The length of time necessary to effect a suitable separation of hydrolyzate components was determined empirically. The dried chromatogram was then sprayed with a solution of aniline hydrogen phthalate,

which was prepared by dissolving 1.66 grams of phthalic anhydride and 0.92 gram of aniline in 100 ml. of water-saturated n-butanol. Each chromatogram was then oven dried at 105°C. for a few minutes.

CELLULOSE CHROMATOGRAPHIC COLUMN

The hydrolyzate of a chlorocellulose was chromatographed quantitatively on a large cellulose chromatographic column. The column employed in this investigation consisted of a glass cylinder which was 22 inches long and 2.25 inches in diameter. The column was packed with Whatman standard-grade cellulose powder. One-half water-saturated n-butanol, which was prepared by mixing equal volumes of n-butanol and water-saturated n-butanol, flowed through the column at a rate of 140 ml. per hour. During the course of the chromatographic separation, however, the rate of flow of the column effluent was reduced to 20 or 25 ml. per hour by placing a fine capillary tube at the bottom of the column. Collection of the column effluent was accomplished by a mechanical fraction collector, which automatically replaced the test tube beneath the capillary tip of the column at 30 minute intervals. The collector was similar to the one described by Hough, Jones, and Wadman (40A).

The sample of the hydrolyzate was distributed evenly over the one-half water-saturated n-butanol-soaked cellulose powder at the top of the column. The chromatogram was developed by allowing one-half water-saturated n-butanol to flow through the column. The course of the chromatographic separation was followed by selecting test tubes at regular

intervals and spotting the contents on paper partition chromatograms after the solutions had been concentrated to sirups on a steam bath. The contents of all test tubes which possessed the same hydrolyzate component were combined to form a large fraction.

CALCULATION OF THE DEGREE OF SUBSTITUTION

After analysis of the cellulose derivatives for various substituents, the degrees of substitution were calculated by means of simultaneous equations in which the following nomenclature was used:

\underline{x} = Degree of substitution of sulfurous acid ester

\underline{y} = Degree of substitution of chlorine atoms

FOR CHLOROCELLULOSES

Sulfur, % = $3206\underline{x} / (162.1 + 46.04\underline{x} + 18.45\underline{y})$.

Chlorine, % = $3546\underline{y} / (162.1 + 46.04\underline{x} + 18.45\underline{y})$.

Although the exact type of sulfur linkages in chlorocelluloses have not been definitely established, the sulfur groups are very probably present in the form of sulfurous acid esters. Since it has been found in a number of cases (26, 28, 29, 33) that thionyl chloride reacted with hydroxy compounds to form sulfurous acid esters linked to two hydroxyl groups ($\overset{\text{O}}{\underset{\text{O}}{\text{C}}}\text{SO}\overset{\text{O}}{\underset{\text{O}}{\text{C}}}$), this type of linkage will be assumed in order to facilitate the calculations.

The numerators of these equations represent the amount of sulfur and chlorine (multiplied by 100) present in a substituted anhydroglucose unit of chlorocellulose, respectively. The denominators represent the molecular weight of the substituted anhydroglucose unit. The molecular weight

of an anhydroglucose unit of cellulose is 162.1. Since the atomic weight of chlorine is 35.46 and the molecular weight of a hydroxyl group is 17.01, the molecular weight of the anhydroglucose unit would be increased by $35.46y - 17.01y = 18.45y$ if y chlorine atoms replaced y hydroxyl groups. Also, since the molecular weight of the sulfite radical (O-SO-O) is 80.06, the molecular weight of the anhydroglucose unit would be increased by $80.06x - 34.02x = 46.04x$ if $2x$ hydroxyl groups were replaced by x sulfite radicals.

FOR CUPRAMMONIUM-REGENERATED AND SODIUM HYDROXIDE-TREATED CHLOROCELLULOSES

$$\text{Chlorine, \%} = 3546y / (162.1 + 18.45y).$$

FOR HYDROLYZED CHLOROCELLULOSES

$$\text{Chlorine, \%} = 3546y / (180.2 + 18.45y).$$

PRESENTATION AND DISCUSSION OF RESULTS

CHLORINATION STUDY

All thionyl chloride treatments of cellulose were carried out with cotton linters which had been activated by a four-hour treatment with 18% sodium hydroxide solution at 24 to 26°C. After the mercerized linters had been washed with absolute methanol and anhydrous pyridine, the linters were suspended in a total of 50.0 moles of pyridine per mole of anhydroglucose unit and were treated with 10.0 moles of thionyl chloride per mole of anhydroglucose unit.

Upon the addition of thionyl chloride to the activated cellulose and pyridine mixture, the temperature of the reaction rose considerably. When the reaction was carried out at room temperature, it was necessary to cool the reaction flask in an ice bath to prevent overheating of the reaction. After the addition of thionyl chloride, the contents of the reaction flask gradually darkened; the color slowly changed from a water-clear color, to pale yellow, to bright yellow, to tan, to light brown, to dark brown and, if the reaction continued for a long enough time, to a very dark brown. The rate of darkening increased as the temperature of the reaction was increased. The carbohydrate end product of the reaction also darkened; the extent of darkening depended upon both the reaction time and the temperature at which the reaction occurred.

When thionyl chloride was added to pyridine alone, an exothermic reaction took place, and the same series of color changes were observed.

Upon standing at room temperature for several days, the material in the flask solidified. The solid material could be dissolved in water; a sample of linters, which was treated overnight with a water solution of this solid showed no evidence of changing color. No attempt was made to identify the reaction product of thionyl chloride and pyridine.

Runs 1 and 2 were carried out with unpurified thionyl chloride at room temperature (24 to 26°C.) for 4 and 12 hours, respectively. At the end of the reaction period, the contents of each flask were slowly poured into about 500 ml. of distilled water. After standing for an hour, the fibers were collected on a coarse fritted-glass crucible, washed thoroughly with water, and allowed to soak in water overnight. The next day a very noticeable sulfur dioxide odor was discernable above the water suspensions of the chlorocelluloses; the supernatant liquids were acidic to methyl orange indicator. The wash waters were still acidic to methyl orange after the chlorocelluloses had been soaked in frequent changes of wash water for a week. If at the end of a week of water soaking, the filtered chlorocelluloses were placed in sealed weighing bottles for an hour, the odor of sulfur dioxide could still be discerned. When the chlorocelluloses were finally treated with 500 ml. of one-half saturated sodium bicarbonate solution, bubbles of carbon dioxide were rapidly evolved. After soaking in sodium bicarbonate solution overnight, the fibers were washed with water and were again allowed to cook in water overnight. The supernatant liquids were finally found to be neutral to methyl orange. Samples of indicator papers which were placed in an oven along with the chlorocelluloses showed no evidence of acidic conditions during oven

drying in vacuo at 44 to 46°C. Product 1 was light tan in color; product 2 was light brown in appearance.

Runs 3 and 4 were carried out in the same manner as Runs 1 and 2 except that pure thionyl chloride was employed. The reactions were terminated in water and the chlorocelluloses were washed with water as in the case of Reactions 1 and 2, but the chlorocelluloses were treated with sodium bicarbonate solution directly. Carbon dioxide was rapidly liberated from the fibers immediately after the addition of sodium bicarbonate solution. After soaking overnight in sodium bicarbonate solution, the fibers were filtered, washed with water, and dried. The appearance of products 3 and 4 was very similar to that of products 1 and 2.

Treatment of hydroxy compounds with thionyl chloride has been found to result in products which contained both chlorine and sulfur. However, some investigators have found that increased reaction temperatures caused the reaction to produce the chlorinated derivatives rather than the thionyl derivative (25, 31, 32). In addition, workers who have studied the reactions of tosyl and mesyl chlorides with carbohydrates reported that an increase of the reaction temperature tended to increase the chlorine contents of the resulting tosyl and mesyl esters (7, 10, 18). In this study the reaction of cellulose with thionyl chloride in a pyridine medium was carried out at elevated temperatures in order to ascertain whether higher degrees of chlorine substitution could be attained in this manner.

Runs 5 and 6 were carried out at 100°C. on a steam bath for 4 and 0.75 hour, respectively. The contents of each reaction flask became very dark and lumpy. When the contents of the flasks were poured into water, the end products were black, gritty, and had lost all their fibrous characteristics. Apparently the linters had been charred or dehydrated during the reaction. The products could not be handled satisfactorily and were discarded.

Runs 7 and 8 were subjected to much less drastic temperature conditions. These reactions were carried out in a water bath maintained at 48 to 50°C. for 4 and 1.5 hours, respectively. The reactions were terminated by pouring the contents of the reaction flasks into water and allowing the mixtures to stand for 0.5 hour. The fibers were filtered, washed, treated overnight with sodium bicarbonate solution, washed, soaked overnight in water, washed, and dried. Product 7 was brown in color; product 8 was tan.

Runs 9 and 10 were carried out in a water bath maintained at 69 to 70°C. for 3 and 1.5 hours, respectively. Product 10 was carried through the same procedure as products 7 and 8; product 10 was dark brown in color. Run 9 was scheduled for four hours but, at the end of three hours, the reaction mixture became very viscous and dark. This resembled the action which occurred during Reactions 5 and 6. Reaction 10, therefore, was stopped immediately by pouring the contents of the reaction flask into water. After standing in water for 0.5 hour, the product seemed to be contaminated by a small amount of granular material; the mixture was then

mechanically stirred for 0.25 hour. The product could not be filtered through a coarse fritted-glass crucible; filtration was accomplished on a filter paper in a Buchner funnel. The mass still retained its fibrous appearance but was very dark brown in color. The fibers were washed into fresh water, stirred 0.25 hour, and again filtered on a Buchner funnel. The washing procedure was repeated, and the fibers were allowed to soak in sodium bicarbonate solution overnight; carbon dioxide was evolved immediately after the addition of sodium bicarbonate solution. Product 9 was filtered on a coarse fritted-glass crucible, washed free of sodium bicarbonate, and allowed to soak in water overnight. It was necessary to soak the product in several changes of water for three additional nights before the supernatant water was free from color. Product 9 was then filtered and dried.

Treatment of the chlorocelluloses mentioned above with water and sodium bicarbonate solution resulted in the loss of sulfur dioxide from the products. The chlorocelluloses obtained after these treatments were obviously not the same as those prepared in the reaction flasks. In order to obtain chlorocelluloses from the thionyl chloride reaction as nearly unchanged in form as possible, two thionyl chloride reactions were terminated in absolute methanol.

Runs 11 and 12 were carried out at room temperature (24 to 26°C.) for 4 and 12 hours, respectively. At the end of the reaction periods, the mixtures were poured into about 300 ml. of absolute methanol and allowed to stand for one hour. The chlorocelluloses were then filtered on coarse

fritted-glass crucibles, washed several times with absolute methanol, and allowed to soak in absolute methanol overnight. Each product was extracted with absolute methanol in a Soxhlet extractor, which was operated under reduced pressure to effect extraction between 30 and 40°C. Product 11 was extracted for six hours; product 12 was extracted for eight hours. The chlorocelluloses were dried in vacuo at 44 to 46°C. but never attained constant weight. This loss was probably due to the loss of sulfur dioxide caused by the unavoidable contact of the products with atmospheric moisture during the transfer of the products to and from the oven. Products 11 and 12 were somewhat lighter in color than the corresponding water- and sodium bicarbonate solution-washed products (products 1 and 3, and 2 and 4, respectively).

All the reaction products except products 5 and 6 retained their fibrous characteristics. Chlorocelluloses were analyzed for the presence of chlorine and sulfur; they gave no test for nitrogen. The results of the chlorine and sulfur analyses of chlorocelluloses, together with the calculated degrees of substitution of chlorine atoms and sulfurous acid esters (OSO₂) are summarized in Table I.

Examination of the data in Table I revealed that the chlorine content of chlorocelluloses increased with both increased reaction time and increased temperature of reaction. Chlorocelluloses washed with absolute methanol exhibited somewhat higher degrees of chlorine substitution than those treated under the same reaction conditions, but which were washed with water and aqueous sodium bicarbonate.

TABLE I

ANALYSIS OF CHLOROCELLULOSES

10.0 Moles of Thionyl Chloride and 50.0 Moles of Pyridine Per Mole of Cellulose

Product	Reaction Temp., °C.	Reaction Time, hrs.	Reaction Ended With	Color of Product	Cl, %	S, %	D.S. of Cl	D.S. of OSO ₂
1	24 - 26	4	H ₂ O + NaHCO ₃	light tan	4.42	4.86	0.22	0.27
2	24 - 26	12	H ₂ O + NaHCO ₃	light brown	6.40	5.02	0.33	0.28
3	24 - 26	4	H ₂ O + NaHCO ₃	light tan	4.36	3.68	0.22	0.20
4	24 - 26	12	H ₂ O + NaHCO ₃	light brown	6.54	4.75	0.33	0.27
5 ^a	100	4	H ₂ O + NaHCO ₃	black	--	--	--	--
6 ^a	100	0.75	H ₂ O + NaHCO ₃	black	--	--	--	--
7	49 - 50	4	H ₂ O + NaHCO ₃	brown	12.58	2.69	0.64	0.15
8	48 - 49	1.5	H ₂ O + NaHCO ₃	tan	8.84	3.62	0.45	0.20
9 ^b	69 - 70	3	H ₂ O + NaHCO ₃	very dark brown	23.43	4.00	1.30	0.25
10	69 - 70	1.5	H ₂ O + NaHCO ₃	dark brown	20.45	1.56	1.07	0.09
11	24 - 26	4	CH ₃ OH	light tan	5.23	11.65	0.30	0.73
12	24 - 26	12	CH ₃ OH	light brown	5.84	14.21	0.35	0.94

^aThese products were charred or dehydrated. They were gritty and nonfibrous.^bThis product may be charred.

No definite trends were observed between either the reaction times or the reaction temperatures and the sulfur contents of chlorocelluloses washed with water and sodium bicarbonate solution. Chlorocelluloses washed with absolute methanol; however, exhibited much greater sulfur contents than those treated with water and aqueous sodium bicarbonate.

The quantity of chlorocelluloses prepared from two grams of cotton linters was too small to lend itself readily to extensive experimentation. In order to obtain larger quantities of chlorocelluloses three large-scale reactions (each employing 25 grams of cotton linters) were carried out. Run 13 was carried out under the same reaction conditions as Runs 1 and 3--that is, for four hours at room temperature (25.5 to 26.5°C.); Run 14 corresponded to Run 7 and was allowed to proceed for four hours at 49 to 51°C.; Run 15 corresponded to Run 10 and was carried out for 1.5 hours at 68.5 to 69.5°C. Because of the larger quantity of reactants used, Run 13 became overheated during the addition of thionyl chloride; the reaction cooled down to the desired temperature (26°C.) approximately 15 to 20 minutes after the reaction was initiated.

The large-scale thionyl chloride reactions were terminated in water. After filtering and washing, each product was suspended in about four liters of distilled water and slowly treated with 18% sodium hydroxide solution. In each case, the sodium hydroxide was rapidly consumed as evidenced by the color changes of phenolphthalein indicator which had been added to the suspension. The suspension of each product was allowed to stand overnight with an excess of about 10 ml. of 18% sodium hydroxide

solution beyond the observable phenolphthalein end point. The excess caustic resulted in an approximately 0.015 N sodium hydroxide solution. A total of approximately 60 ml. of 18% sodium hydroxide solution was added to the suspension of product 13, 50 ml. to product 14, and 40 ml. to product 15. Dilute caustic washes were employed instead of sodium bicarbonate washes in an attempt to remove as much sulfur as possible from the products.

The suspension of each product was still alkaline to phenolphthalein upon standing overnight. Each suspension was neutralized by the addition of sulfuric acid to slightly beyond the phenolphthalein end point; the odor of sulfur dioxide was observed in each case. Each product was immediately filtered, washed with water, and allowed to soak in water, which was replaced frequently, until the washings were colorless. Samples of each product were dried in vacuo at 44 to 46°C. and analyzed for chlorine and sulfur.

The results of the chlorine and sulfur analyses of chlorocelluloses, which were prepared from 25 grams of cellulose, are presented in Table II, together with the corresponding values for the smaller-scale preparations.

Examination of the data in Table II revealed that the agreement between the calculated degrees of substitution of chlorine for comparable products was fairly good. The small differences in the degrees of chlorine substitution of comparable products can be satisfactorily explained by slight differences in reaction temperatures. The larger differences between the degrees of chlorine substitution of products 13

and products 1 and 3 can be attributed to the initial overheating of Reaction 13 upon the addition of thionyl chloride.

TABLE II
LARGE-SCALE PREPARATION OF CHLOROCELLULOSES

Product	Reaction Temp., °C.	Reaction Time, hrs.	Cl, %	S, %	D.S. of Cl	D.S. of OSO
13 ^a	25.5-26.5	4	6.12	0.70	0.29	0.04
1	24-26	4	4.42	4.86	0.22	0.27
3	24-26	4	4.36	3.68	0.22	0.20
14	49-51	4	12.9	2.30	0.66	0.13
7	49-50	4	12.58	2.69	0.64	0.15
15	68.5-69.5	1.5	19.66	2.04	1.04	0.12
10	69-70	1.5	20.45	1.56	1.07	0.09

^aThis reaction became overheated during the first 15 to 20 minutes of the reaction.

Washing of the large-scale products with dilute sodium hydroxide solution did not appear to be much more effective in removing sulfur groups from chlorocelluloses than did washing with sodium bicarbonate solution. Only product 13 appeared to have an appreciably reduced sulfur content. Product 15, on the other hand, exhibited a greater sulfur content than product 10, which had been washed with sodium bicarbonate solution.

Products 13 to 15 were analyzed for ash content. The brown ash was apparently insoluble in water; the supernatant liquid was free from sulfate ion, was basic to methyl orange indicator, and was not basic to

phenolphthalein indicator. The ash was partially soluble in concentrated hydrochloric acid, but no trace of sulfate ion was observed. The ash contents of the chlorocelluloses are listed in Table III.

TABLE III
ASH CONTENT OF CHLOROCELLULOSES

Product	Ash, %
13	0.09
14	0.08
15	0.10

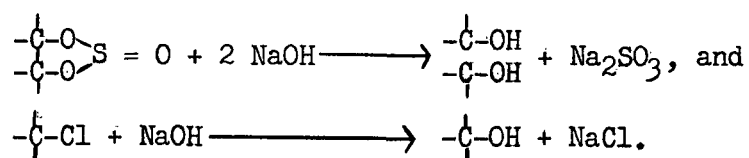
The ash of chlorocelluloses was apparently not composed of soluble sodium compounds (e.g., sodium carbonate or sodium sulfate). It probably consisted of the ash (0.067%) originally present in the cotton linters.

TREATMENT OF METHANOL-WASHED CHLOROCELLULOSES WITH
DILUTE SODIUM HYDROXIDE SOLUTION

Products 11 and 12, which were washed with absolute methanol, exhibited much higher sulfur contents than any of the other chlorocelluloses prepared. Samples of products 11 and 12 were treated overnight at room temperature with an excess of 0.15 N sodium hydroxide solution to determine the stability of the sulfur groups present. The excess sodium hydroxide was then titrated with standardized sulfuric acid to the phenolphthalein end point; the fibrous products were filtered on coarse fritted-glass crucibles, washed with water, and dried in vacuo at 44 to 46°C. in preparation for chlorine and sulfur analyses. The filtrates and the water washings were collected quantitatively and analyzed for chlorine. Upon

further acidification of the filtrates, a very strong odor of sulfur dioxide was detected.

It was assumed that sodium hydroxide was consumed by the hydrolysis and neutralization of the sulfurous acid esters present in the chlorocelluloses to form sodium sulfite and the removal of chlorine atoms from the chlorocelluloses to form sodium chloride:



The results of the dilute sodium hydroxide treatment of products 11 and 12 are given in Table IV.

TABLE IV
TREATMENT OF CHLOROCELLULOSES 11 AND 12
WITH 0.15 N SODIUM HYDROXIDE SOLUTION

	Cl, %	S, %	Sample, g.	Cl, g.	S, g.	D.S. of Cl	D.S. of OSOO
Product 11	5.23	11.65	100.0	5.23	11.65	0.30	0.73
Caustic-treated product 11	6.44	0.62	76.0	4.89	0.47	0.31	0.03
Caustic treatment solution ¹	0.51	11.15	--	0.51	11.15	--	--
Total	--	--	--	5.40	11.62	--	--
Product 12	5.84	14.21	100.0	5.84	14.21	0.35	0.94
Caustic-treated product 12	7.62	0.87	70.1	5.34	0.61	0.37	0.05
Caustic treatment solution ¹	0.46	13.25	--	0.46	13.25	--	--
Total	--	--	--	5.80	13.86	--	--

¹The chlorine and sulfur contents of the solutions were based on the weight of the original products.

As shown in Table IV, dilute sodium hydroxide treatment of methanol-washed chlorocelluloses eliminated almost all the sulfur in the form of sulfur dioxide. The ease with which sulfur was removed from chlorocelluloses by aqueous and alkaline media, and the results of the quantitative sodium hydroxide treatment study substantiated the assumption that sulfur existed in the form of a sulfurous acid ester. The chlorine atoms in the products seemed to be quite stable under conditions of dilute alkalinity at room temperature. The amounts of chlorine and sulfur present in the original chlorocelluloses and in the end products of the dilute sodium hydroxide reaction appeared to agree fairly well in the material balances.

PURIFICATION OF CHLOROCELLULOSES

Chlorocelluloses, prepared from the reaction of cotton linters with thionyl chloride in a pyridine medium, ranged in color from very light tan to very dark brown, even after the products had been thoroughly washed with water and sodium bicarbonate or dilute sodium hydroxide solutions. The color of the chlorocelluloses was probably due, at least in part, to the presence of contaminants produced in the side reactions which occurred between thionyl chloride and pyridine. Coloration of products has been reported in some tosylation studies (41) but to a much lesser degree. In those studies it was suggested that the color was associated with the introduction of chlorine into tosylcellulose but colorless, high-chlorine content tosylcellulose has been prepared (10). Roberts (18) encountered highly colored products in his study of the mesylation of cellulose. He found that mesylcellulose could be reprecipitated from a

solution of acetonylacetone to form only slight colored products. He also found that extraction of mesylcellulose with formamide resulted in the removal of considerable amounts of color.

Chlorocelluloses were treated with a number of organic liquids but no good solvent was found. Solubility tests were made by placing about 0.05 gram of an airdry chlorocellulose in about 10 ml. of solvent and allowing the mixture to stand for several days with frequent shaking. The mixture was then heated for several hours to determine whether elevated temperatures facilitated solution. Solvents tested included methanol, formamide, diethyl ether, acetonylacetone, petroleum ether, benzene, carbon tetrachloride, chloroform, pyridine, acetone, dioxane, ethyl bromide, diacetone alcohol, ethyl acetate, carbon disulfide, and 60% ethylenediamine.

With the exception of 60% ethylenediamine, heating of the solvent and chlorocellulose mixture did not appear to aid solution. At elevated temperatures (80 to 140°C.) chlorocelluloses dissolved in 60% ethylenediamine to form colored solutions. Treatment of the basic amine solutions with sulfuric acid to the methyl orange end point did not regenerate the chlorocelluloses. The neutralized solution did not appear to contain reactive chlorine when tested with silver nitrate solution. The reaction of chlorocelluloses with amines, especially ethylenediamine, might be worth further investigation.

Treatment of chlorocelluloses with acetonylacetone at 130 to 140°C. resulted in the extraction of some color from the chlorocelluloses. Hot formamide seemed to extract more color, but the chlorocelluloses were still very dark; product 15 seemed to coagulate when heated with formamide at 130 to 140°C.

All the attempts to purify chlorocelluloses by solution in or by extraction with various organic solvents were unsatisfactory.

In the last stages of the study of the chlorination of cellulose, small portions of chlorocelluloses were treated with acidic sodium chlorite solution upon the suggestion of Dr. L. E. Wise. The procedure employed was that described by Cundy and Beck (40) in their work on the chloriting of wood pulps. In the preliminary purification study, about 0.3 gram each of products 13 and 15 was suspended in 10 ml. of water, acidified with 0.5 ml. of 10% acetic acid, treated with 0.1 gram of sodium chlorite, and heated about 45 minutes at 70 to 80°C. on a steam bath. Product 13 was white after this treatment; the bleached product was washed thoroughly and a portion was dried in vacuo at 44 to 46°C. in preparation for chlorine and sulfur analyses. Product 15 was bright yellow in color.

The residual bleached product 13 and the bleached product 15 were chlorited again for an hour. Product 13 experienced no change in color; the product was washed with water and dried for analysis. Product 15, which was lemon yellow in color, was washed with water and a portion was dried for analysis. The remainder of product 15 was chlorited a third time for 1.5 hours, washed, and dried for analysis; the third purification resulted in only a slight decrease of color.

The results of the preliminary purification of chlorocelluloses with acidic sodium chlorite solution are presented in Table V.

The preliminary study of sodium chlorite purification chlorocelluloses revealed that much of the colored material present in chlorocelluloses

TABLE V

PRELIMINARY PURIFICATION OF CHLOROCELLULOSES
WITH ACIDIC SODIUM CHLORITE SOLUTION

	No. of Purifications	Cl, %	S, %
Original product 13	0	6.12	0.70
Chlorited product 13	1	6.85	0.36
Chlorited product 13	2	6.83	--
Original product 15	0	19.66	2.04
Chlorited product 15	2	21.0	0.43
Chlorited product 15	3	21.0	--

could be removed. The resulting products were fibrous and ranged in color from white to yellow. Examination of the preliminary data disclosed that the chlorine contents of chlorited chlorocelluloses attained a constant value when the color of the purified chlorocelluloses was not appreciably altered by subsequent chloriting treatments. Preliminary acidic sodium chlorite treatments of chlorocelluloses resulted in a loss of sulfur; the chlorine contents of the products, however, seemed to increase.

The acidic sodium chlorite purification of chlorocelluloses was continued. Accurately weighed samples (1.0 to 1.5 grams) of products 3, 4, 7, 8, 9, and 10 were each suspended in 50 ml. of distilled water, which was adjusted to pH 4 to 5 by the addition of 0.125 ml. of glacial acetic acid. After the addition of 0.5 g. of sodium chlorite, the mixture was heated at 70 to 80°C. on a steam bath. Chlorocelluloses were chlorited until the color of the products could not be appreciably altered by

additional chlorite treatments. Successive sodium chlorite treatments were carried out for 1.5, 1.0, and 1.5 hours with water washes between each stage. After the final chloriting treatment, the number of which depended upon the color of the product, chlorocelluloses were washed with water until all traces of chloride ion had been removed.

Products 13, 14, and 15 were purified in larger quantities. Six grams (accurately weighed) of each product were suspended in 200 ml. of water, acidified with 0.5 ml. of glacial acetic acid, treated with 2 grams of sodium chlorite, and heated at 70 to 80°C. on a steam bath. The number of purifications again depended upon the color of the product, but the same reaction times used for the smaller-scale purifications were employed. Each product was then washed with water until there was no trace of chloride ion present.

The purified chlorocelluloses were dried in vacuo at 44 to 46°C. prior to chlorine and sulfur analyses. Qualitative treatment of purified chlorocelluloses with 72% sulfuric acid or 85% phosphoric acid resulted in the evolution of sulfur dioxide.

The results obtained from the acidic sodium chlorite purification study of chlorocelluloses are presented in Table VI. Since the purification treatment of all chlorocelluloses was carried out quantitatively, it was possible to compare the amounts of chlorine in chlorocelluloses both before and after purification. These data are presented in Table VII.

A more intensive study of the purification of chlorocelluloses revealed that the degrees of chlorine substitution in chlorocelluloses did

TABLE VI

PURIFICATION OF CHLOROCELLULOSES WITH
ACIDIC SODIUM CHLORITE SOLUTION

Product	No. of Purifications	Color of Product	Cl, %	S, %	D.S.		D.S.	
					Cl	OSOO Purified	Cl	OSOO Original
3	1	white	4.18	3.26	0.20	0.18	0.22	0.20
4	2	sl. yellow tinge	6.47	3.57	0.32	0.20	0.33	0.27
7	3	pale yellow	12.5	1.66	0.63	0.09	0.64	0.15
8	1	sl. yellow tinge	8.60	2.92	0.43	0.16	0.45	0.20
9	3	yellow	23.45	1.61	1.26	0.10	1.30	0.25
10	3	lemon yellow	20.08	0.54	1.03	0.03	1.07	0.09
13	1	white	6.96	0.13	0.33	0.01	0.29	0.04
14	3	lemon yellow	13.50	0.30	0.67	0.02	0.66	0.13
15	3	lemon yellow	20.16	0.93	1.04	0.05	1.04	0.12

not change appreciably upon purification. Since it was generally noted in Table VII that chlorine was lost during sodium chlorite treatment, it was evident that chlorinated impurities or highly degraded chlorocelluloses were removed. Chlorine losses, based on the original chlorocelluloses, generally tended to increase as the yield of purified chlorocelluloses decreased. Since the degrees of chlorine substitution of chlorocelluloses were not appreciably altered by purification, and appreciable chlorine losses were encountered during purification, it was probable that the material

removed during purification had approximately the same chlorine content as the chlorocelluloses.

TABLE VII
PURIFICATION OF CHLOROCELLULOSES WITH
ACIDIC SODIUM CHLORITE SOLUTION

Product	Original Product		Yield ¹ , %	Purified Product		Cl on Basis of 100 g. Original Product, g.		S on Basis of 100 g. Original Product, g.	
	Cl, %	S, %		Cl, %	S, %	unbl.	bl.	unbl.	bl.
3	4.36	3.68	98.34	4.18	3.26	4.36	4.11	3.68	3.20
4	6.54	4.75	--	6.47	3.57	6.54	--	4.75	--
7	12.58	2.69	87.79	12.5	1.66	12.58	11.0	2.69	1.46
8	8.84	3.62	98.06	8.60	2.92	8.84	8.43	3.62	2.86
9	23.43	4.00	86.28	23.45	1.61	23.43	20.23	4.00	1.38
10	20.45	1.56	82.96	20.08	0.54	20.45	16.66	1.56	0.45
13	6.12	0.70	96.81	6.96	0.13	6.12	6.74	0.70	0.13
14	12.9	2.30	82.95	13.50	0.30	12.9	11.20	2.30	0.25
15	19.66	2.04	84.38	20.16	0.93	19.66	17.01	2.04	0.78

¹The yield was calculated on the basis of the unpurified product.

Sulfur losses were clearly indicated in the study of the acidic sodium chlorite purification of chlorocelluloses. The sulfur which remained in purified chlorocelluloses, however, still seemed to be present in the form of a sulfurous acid ester; sulfur dioxide was evolved upon treatment with 72% sulfuric acid or 85% phosphoric acid.

In general, the yield of purified chlorocelluloses exhibited a tendency to decrease as the color of the original chlorocelluloses darkened and as the chlorine content increased.

Several purified chlorocelluloses were analyzed for ash content. Larger amounts of ash were found in purified chlorocelluloses than in the original chlorocelluloses. The higher ash content of purified chlorocelluloses may be due to impurities introduced with the sodium chlorite. Ash contents of purified chlorocelluloses are listed in Table VIII.

TABLE VIII

ASH CONTENT OF PURIFIED CHLOROCELLULOSES

Purified Product	Ash, %
13	0.08
14	0.2
15	0.27

YIELD OF CHLOROCELLULOSES

Reactions of mercerized cotton linters with thionyl chloride in a pyridine medium to form chlorocelluloses were carried out quantitatively in the case of the small-scale preparations. Purifications of chlorocelluloses with acidic sodium chlorite solution were also performed quantitatively. It was possible, therefore, to obtain the experimental yield of purified chlorocelluloses from mercerized cotton linters. The experimental yield of chlorocelluloses was compared with the calculated theoretical yield of chlorocelluloses to determine the percentage of the

theoretical yield actually obtained. Theoretical yields of various purified chlorocelluloses prepared from one gram of mercerized cotton linters were obtained from the following equation:

$$\text{Chlorocellulose (theoretical), g.} = \frac{162.1 + 46.06x + 18.45y}{162.1}$$

where x = degree of sulfurous acid ester substitution and y = degree of chlorine substitution of purified chlorocelluloses. The results of this study are presented in Table IX.

TABLE IX
YIELD OF CHLOROCELLULOSES

Product	3	4	7	8	9	10
Product from 1 g. mercerized linters, g.	1.122	1.173	1.183	1.176	1.348	1.252
Purified product from 1 g. product, g.	0.9834	--	0.8779	0.9806	0.8628	0.8296
Purified product from 1 g. mercerized linters, g.	1.103	--	1.039	1.153	1.163	1.039
Purified product from 1 g. mercerized linters (theoretical), g.	1.073	--	1.098	1.094	1.170	1.126
Percentage of theoretical yield of purified product.	102.8	--	94.6	105.4	99.4	92.3

In general very good yields of purified chlorocelluloses were obtained. Yields of chlorocelluloses over 100% of theory may have been due to impurities still present in the products; the chlorocelluloses which exhibited these high yields were given only one acidic sodium chlorite purification.

CARBON AND HYDROGEN ANALYSES OF CHLOROCELLULOSES

Samples of chlorocelluloses were analyzed for carbon and hydrogen content before any acidic sodium chlorite purifications had been performed. The experimental carbon and hydrogen contents of unpurified chlorocelluloses are presented in Table X, together with theoretical carbon and hydrogen contents, which were calculated from the degrees of substitution of both chlorine atoms and sulfurous acid esters. Theoretical calculations of carbon and hydrogen contents were performed employing the assumption that chlorine had replaced cellulosic hydroxyl groups and sulfurous acid had esterified with the hydroxyl groups of cellulose.

In general, the agreement between experimental and theoretical carbon and hydrogen values was poor. Experimental and theoretical carbon and hydrogen values checked most closely in the case of product 3; in this instance, the agreement was very good. It was noted that the discrepancy between the experimental and theoretical carbon values generally increased as the severity of the reaction conditions increased; the discrepancy tended to increase as the color of the chlorocelluloses deepened, or as the chlorine content of the products increased. A trend of this nature seemed probable, since the color of chlorocelluloses was probably an indication of the amount of impurity present.

Several carbon and hydrogen determinations were also carried out on purified chlorocelluloses. These data are presented in Table XI.

The agreement between experimental and theoretical carbon and hydrogen values of purified chlorocelluloses was also poor. When the empirical

TABLE X

CARBON AND HYDROGEN ANALYSIS OF
UNPURIFIED CHLOROCELLULOSES

Product	Cl, %	S, %	D.S. of		C, %	H, %	Calculated	
			Cl	OSOO			C, %	H, %
3	4.36	3.68	0.22	0.20	41.35	5.33	41.09	5.39
4	6.54	4.75	0.33	0.27	40.68	5.13	39.89	5.09
7	12.58	2.69	0.64	0.15	40.98	4.90	39.81	5.04
8	8.84	3.62	0.45	0.20	40.97	5.06	40.09	5.12
9	23.43	4.00	1.30	0.25	39.98	4.28	36.48	4.19
10	20.45	1.56	1.07	0.09	40.65	4.64	38.71	4.73
11	5.23	11.65	0.30	0.73	36.38	4.70	35.80	4.13
12	5.84	14.21	0.35	0.94	34.77	4.31	34.02	3.70
11 ¹	6.44	0.62	0.31	0.03	43.77	5.45	42.56	5.74
12 ¹	7.62	0.87	0.37	0.05	43.64	5.39	42.12	5.62

¹These products had been treated with an excess of 0.15 N sodium hydroxide solution.

TABLE XI

CARBON AND HYDROGEN ANALYSIS OF
PURIFIED CHLOROCELLULOSES

Product	Cl, %	S, %	D.S. of		C, %	H, %	Calculated	
			Cl	OSOO			C, %	H, %
13	6.96	0.13	0.33	0.01	43.67	5.42	42.75	5.78
14	13.50	0.30	0.67	0.02	42.43	4.86	41.13	5.35
15	20.16	0.93	1.04	0.05	41.23	4.43	39.19	4.85

formulas (II) of purified products 13, 14, and 15 were calculated from the various elemental analyses [carbon, hydrogen, chlorine, sulfur, ash, and oxygen (by difference)] and expressed on the basis of six carbon atoms, smaller numbers of oxygen and hydrogen atoms were found than in similar empirical formulas (I) calculated from merely the degrees of substitution of chlorine atoms and sulfurous acid esters. The results of these calculations are illustrated in Table XII.

TABLE XII
EMPIRICAL FORMULAS OF CHLOROCELLULOSES

Product	Empirical Formula (I) From D.S. of Cl and OSOO	Empirical Formula (II) From C, H, Cl, S, and Ash Analyses
13	$C_{6.00}H_{9.65}Cl_{0.33}S_{0.01}O_{4.68}$	$C_{6.00}H_{8.87}Cl_{0.32}S_{0.01}O_{4.51}$
14	$C_{6.00}H_{9.29}Cl_{0.67}S_{0.02}O_{4.35}$	$C_{6.00}H_{8.19}Cl_{0.65}S_{0.02}O_{4.11}$
15	$C_{6.00}H_{8.86}Cl_{1.04}S_{0.05}O_{4.01}$	$C_{6.00}H_{7.68}Cl_{1.00}S_{0.05}O_{3.60}$

Examples of these calculations are given in the next two paragraphs.

Empirical formula (I) of product 13 was calculated as follows:

$$\text{D.S. of Cl} = 0.33 \quad \text{D.S. of OSOO} = 0.01$$

$$\text{Residual hydroxyl groups} = 3.00 - 0.33 - 2(0.01) = 2.65.$$

$$\text{The number of oxygen atoms} = 2.00 + 2.65 + 3(0.01) = 4.68.$$

$$\text{The number of hydrogen atoms} = 7.00 + 2.65 = 9.65.$$

Hence, the empirical formula (I) is $C_{6.00}H_{9.65}Cl_{0.33}S_{0.01}O_{4.68}$.

Empirical formula (II) of product 13 was calculated as follows:

Carbon	= 43.67%	$43.67 / 12.01 = 3.636$	$3.636 (1.650) = 6.00$
Hydrogen	= 5.42%	$5.42 / 1.008 = 5.38$	$5.38 (1.650) = 8.87$
Chlorine	= 6.96%	$6.96 / 35.46 = 0.196$	$0.196 (1.650) = 0.32$
Sulfur	= 0.13%	$0.13 / 32.06 = 0.004$	$0.004 (1.650) = 0.01$
Oxygen	= 43.74%	$43.74 / 16.00 = 2.734$	$2.734 (1.650) = 4.51$
Ash	= <u>0.08%</u>		
Total	=100.00%		

Hence, the empirical formula (II) is $C_{6.00}H_{8.87}Cl_{0.32}S_{0.01}O_{4.51}$.

Assuming that the skeletal structure of cellulose less its hydroxyl groups was $C_6H_7O_2$ and that each sulfur atom in chlorocellulose was linked to three oxygen atoms to form a sulfurous acid ester, it was calculated that the empirical formulas (II) of chlorocellulose contained excesses of oxygen atoms above and beyond the number necessary to combine with hydrogen atoms to form hydroxyl groups. The empirical formula (II) of product 13 exhibited an excess of 0.61 oxygen atom, of product 14 an excess of 0.86 oxygen atom, and of product 15 an excess of 0.77 oxygen atom.

An example of this calculation is given for the case of product 13

$(C_{6.00}H_{8.87}Cl_{0.32}S_{0.01}O_{4.51})$.

Oxygen atoms not tied up by the skeletal structure or sulfurous acid ester linkages = $4.51 - 2.00 - 3 (0.01) = 2.48$.

Non-skeletal hydrogen atoms = $8.87 - 7.00 = 1.87$.

Excess of oxygen atoms = $2.48 - 1.87 = 0.61$.

These excesses of oxygen atoms in empirical formulas (II) of chlorited chlorocelluloses may be indicative of the presence of anhydro or inner ether groupings ($-\overset{\text{O}}{\text{C}}-\overset{\text{O}}{\text{C}}-$) or carbonyl groups in chlorocellulose. No experimental work, however, has been carried out to definitely establish the existence of carbonyl or anhydro groupings.

CUPRAMMONIUM SOLUBILITY STUDY

Accurately weighed samples of unpurified chlorocelluloses were treated with cuprammonium solution to determine the dissolving effect of the solvent upon chlorocelluloses and to ascertain whether chlorocelluloses could be regenerated from cuprammonium solution. Approximately 0.1 to 0.15 gram of a chlorocellulose (about 1% on the basis of the cuprammonium solution) was treated with cuprammonium solution (15.0 grams of copper and 200 grams of ammonia per liter) in a sealed test tube. The test tube was wrapped in opaque paper and rotated mechanically overnight at room temperature; agitation within the test tube was provided by the presence of a short length of freely sliding glass rod.

After mixing overnight, a small portion of the cuprammonium solution of each product was examined under a microscope (20X). It was observed that the samples ranged from being almost completely dissolved in the case of products 1 and 2 to being almost completely undissolved in the case of product 9. Cuprammonium solutions of chlorocelluloses exhibited only small qualitative viscosities. Each solution was filtered through a coarse fritted-glass microfiltration tube to remove the insoluble material present. Only the cuprammonium solutions of products 9 and 10 contained

sufficient quantities of insoluble material to render possible their collection for chlorine analyses.

Each filtered cuprammonium solution was diluted with water and treated slowly with sulfuric acid to the methyl orange end point. Chlorocelluloses were regenerated as voluminous, gelatinous precipitates which were lighter in color than the original chlorocelluloses; the color ranged from white in the case of product 1 to brown in the case of product 9. Except for products 2 and 9, chlorocelluloses were regenerated in appreciable quantity. After the sulfuric acid acidification of each cuprammonium solution, the odor of sulfur dioxide was detected.

Regenerated chlorocelluloses could not be filtered; washing was therefore accomplished by alternate centrifugations and decantations with water. The neutralized supernatant reaction liquor of each product, except products 9 and 10, was found to contain only faint traces of chlorine. The reaction liquors of products 9 and 10 contained larger amounts of chlorine and were therefore quantitatively collected, together with the first three water washes of the respective regenerated products, for chlorine analyses. Water-washed, regenerated chlorocelluloses were then washed with methanol and finally with ether to facilitate drying. Regenerated chlorocelluloses were dried in vacuo at 44 to 46°C. and analyzed for chlorine; all the dried products were horny, glasslike solids.

Table XIII contains the chlorine data obtained from the analyses of the regenerated chlorocelluloses, the cuprammonium solution insolubles,

TABLE XIII

TREATMENT OF CHLOROCELLULOSES
WITH CUPRAMMONIUM SOLUTION

Regenerated Products	Yield, %	Cl, %	D.S. of Cl	D.S. of Cl in Original Product
1	52.4	4.38	0.20	0.22
2	regenerated in insufficient amount for analysis			
7	37.4	13.2	0.65	0.64
8	--	9.28	0.45	0.45
9 ¹	1.9	34	1.9	1.30
9In ²	89.8	20.7	1.06	--
9S	--	2.36	0.11	--
10	44.7	17.9	0.90	1.07
10In	2.0	20	1.0	--
10S	--	3.19	0.15	--

In - Designates the cuprammonium solution insolubles.

S - Designates the neutralized cuprammonium solutions. The chlorine content is based on the original product.

¹The amount of regenerated product 9 was very small (2.3 mg.).

²These insolubles may have a low chlorine content because of the presence of entrained copper.

and the neutralized cuprammonium solutions. Since sulfur dioxide was detected upon the neutralization of cuprammonium solutions of chlorocelluloses with sulfuric acid, sulfur was assumed to be absent in calculations of the degrees of chlorine substitution of regenerated chlorocelluloses and cuprammonium solution insolubles but no sulfur determinations were carried out. Experimental yields of regenerated chlorocelluloses

based on the original chlorocelluloses, are also given; these values may be low because small amounts of regenerated chlorocelluloses were lost during washing by decantation.

The cuprammonium solubility study revealed that each chlorocellulose, except product 9, was largely dissolved by cuprammonium solution. Degradation of the cellulose chain occurred in the reaction of cellulose with thionyl chloride in a pyridine medium, as evidenced by the low qualitative viscosities of the cuprammonium solutions of chlorocelluloses and the rather small yields of regenerated material. This was particularly true in the case of product 2, which was regenerated in insufficient quantity for analysis. It is also possible that the small yield upon regeneration was due to a reaction of chlorocelluloses with the cuprammonium solution.

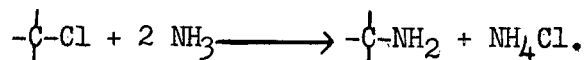
The fact that regenerated chlorocelluloses were obtained with approximately the same degree of chlorine substitution as the original chlorocelluloses signified that chlorine atoms were firmly bound within the cellulose molecule; chlorine was not present as a mere impurity.

Sulfur dioxide was evolved upon the acidification of each cuprammonium solution of chlorocellulose. This indicated that the residual sulfur in chlorocelluloses was probably present in the same form as the sulfur which was eliminated from chlorocelluloses by washes with water, sodium bicarbonate solution, and dilute sodium hydroxide solution. The residual sulfur was probably present in the less accessible regions of chlorocelluloses and, therefore, was inaccessible to attack by the washing reagents; dispersion of chlorocelluloses in cuprammonium solution

probably rendered the sulfur in these regions accessible to chemical reaction.

From the data at hand it was not possible to ascertain whether any difference existed between the degrees of chlorine substitution in the original chlorocelluloses and the fractions of the chlorocelluloses which were found to be insoluble in cuprammonium solution. In the case of product 9, the cuprammonium-insoluble material seem to have been contaminated with copper. The cuprammonium solution of product 10 contained too small a quantity of cuprammonium-insoluble material to insure a reliable chlorine analysis.

The neutralized cuprammonium solutions of products 9 and 10 were the only solutions which contained sufficient quantities of chlorine to warrant chlorine analyses. It is possible that ammonia reacted with the chlorine atoms in chlorocelluloses to form an ionizable chlorine compound:



However, nitrogen analyses of regenerated products 9 and 10 were not performed. The chlorine content of the solutions may also have been due to the presence of organic materials (e.g., chlorinated impurities or sugars) whose chlorine atoms were readily removed by reaction with silver nitrate.

TREATMENT OF CHLOROCELLULOSES WITH 18% SODIUM HYDROXIDE SOLUTION

The reactivity of the chlorine atoms in chlorocelluloses was tested by treatment of chlorocelluloses with concentrated sodium hydroxide solution.

About 0.2 to 0.3 gram (accurately weighed) of products 1, 7, and 10 was treated with 10.0 ml. of 18.28% sodium hydroxide solution. Product 1 was almost completely dissolved by this treatment and formed a viscous amber liquid. Product 7 produced a reddish-brown colored suspension; product 10 formed a brown-colored suspension. The treatment was allowed to continue overnight at room temperature (24 to 26°C.). Each sample was then diluted with water and neutralized to the methyl orange end point with sulfuric acid; in each case the odor of sulfur dioxide was detected above the neutralized solution. It was observed that material was precipitated from each suspension upon acidification. The sodium hydroxide-treated chlorocelluloses could not be filtered and, hence, water washing was accomplished by alternate centrifugations and decantations. Small quantities of sodium hydroxide-treated chlorocelluloses were lost during decantation because of improper settling of the product. The neutralized sodium hydroxide solutions and the first three water washes of the respective sodium hydroxide-treated chlorocelluloses were collected quantitatively, acidified with nitric acid, boiled to expel sulfur dioxide, and analyzed gravimetrically for chlorine by the addition of an excess of silver nitrate.

The washed sodium hydroxide-treated chlorocelluloses were dried in vacuo at 44 to 46°C. and analyzed for chlorine. Sodium hydroxide-treated product 1 was a white, glasslike, flakey solid; sodium hydroxide-treated product 7 was a soft, brown, fibrous solid; sodium hydroxide-treated product 10 was a dark, glasslike, brittle solid.

Products 13, 14, and 15 were treated in the same manner, except that the reaction temperature was elevated to 82 to 83°C. Each product was completely dispersed after an overnight treatment with 18% sodium hydroxide solution. Upon dilution with water and acidification with sulfuric acid to the methyl orange end point, small amounts of material were precipitated from each solution; the odor of sulfur dioxide was noted after acidification. When each suspension was neutralized to the phenolphthalein end point with sodium hydroxide solution, the precipitate dissolved completely; however, upon reacidification to the methyl orange end point the material was reprecipitated. Each acidic suspension was placed in a boiling water bath for five minutes to aid coagulation, cooled immediately, and washed with water by centrifugation and decantation. The neutralized reaction liquor and the first three water washes of each sodium hydroxide-treated product were collected for chlorine analysis. The caustic-treated chlorocelluloses were dried in vacuo at 44 to 46°C. and analyzed for chlorine; all the products were dark-colored brittle solids.

The results of the chlorine analyses of the sodium hydroxide-treated chlorocelluloses are presented in Table XIV. Since sulfur dioxide had been evolved upon the acidification of the alkaline suspensions of chlorocelluloses, degrees of chlorine substitutions of chlorocelluloses were calculated on the assumption that sulfur had been removed completely but no sulfur determinations were carried out. Experimental yields of sodium hydroxide-treated chlorocelluloses may be slightly in error because of the losses incurred during washing.

The results of the chlorine analyses of sodium hydroxide-treated chlorocelluloses and the reaction liquor obtained from each treatment are also presented in Table XIV in the form of a material balance. The chlorine content of the reaction liquor was calculated on the basis of the original product.

Chlorocelluloses suffered considerable losses of chlorine when treated with 18% sodium hydroxide solution. An increase in the treatment temperature caused even greater chlorine losses from the recovered chlorocelluloses; in these cases, practically all the chlorine originally present in chlorocelluloses was found in solution in a reactive form.

It was observed in Table XIV that the end products of the sodium hydroxide treatment reactions which were carried out at room temperature contained considerably less chlorine than the original chlorocelluloses. This indicated that chlorine which was unavailable for reaction with silver nitrate was present in the caustic treatment solutions. Since the yields of sodium hydroxide-treated chlorocelluloses were low, considerable quantities of organic material existed in the sodium hydroxide treatment solutions; the presence of stable, soluble organic chlorides would account for the unreactive chlorine contained in the solutions. It was also observed that at elevated temperatures practically all the chlorine in solution was available for reaction with silver nitrate. These observations signified that chlorine was probably present in solution in the form of chloride ion rather than in the form of soluble, reactive organic chlorides. Elevated reaction temperatures probably facilitated the hydrolysis of unreactive organic chlorides.

TABLE XIV

TREATMENT OF CHLOROCELLULOSES WITH
18% SODIUM HYDROXIDE SOLUTIONChlorine Balance (based on 100 g. original
product)

Caustic-Treated Product	Reaction Temp., °C.	Yield, %	Cl, %	D.S. of Cl	D.S. of Cl in		Original Product, g. Cl	Caustic-Treated Product, g. Cl	Caustic Solution g. Cl	Total Recovery, g. Cl
					Original Product					
1	24 - 26	11.8	3.5	0.16	0.22		4.42	0.41	3.54	3.95
7	24 - 26	42.0	10.7	0.52	0.64		12.58	4.50	5.02	9.52
10	24 - 26	52.0	17.54	0.88	1.07		20.45	9.13	5.02	14.15
13	82 - 83	2.5	6.2	0.30	0.29		6.12	0.15	5.90	6.05
14	82 - 83	2.2	6.2	0.30	0.66					
15	82 - 83	4.7	3.1	0.14	1.04		19.66	0.15	19.29	19.44

Sulfur dioxide was liberated when the sodium hydroxide treatment solutions were acidified with sulfuric acid. A similar observation was made when cuprammonium solutions of chlorocellulose were acidified. These observations indicated that the residual sulfur in chlorocelluloses was probably present in the same form as the sulfur which had been removed by the reagents employed in the washing operation. The residual sulfur, however, was possibly present in the less accessible regions of the chlorocelluloses; the swelling and dispersing action of the concentrated sodium hydroxide solution upon chlorocelluloses may have rendered the sulfur groups in these regions accessible to reaction with alkali.

It was evident that chlorocelluloses had undergone considerable alteration during the concentrated sodium hydroxide solution treatment at elevated temperature. The solubility of these caustic-treated products in dilute alkali and their insolubility in dilute acid indicated that the products were probably acidic in nature. Acidic organic products may have been formed by an alkaline oxidation process since air was present during the concentrated sodium hydroxide treatment of chlorocelluloses.

HYDROLYSIS OF CHLOROCELLULOSES

Chlorocelluloses were hydrolyzed with sulfuric acid according to the procedure described in Institute Method 428. Accurately weighed samples (0.1 to 0.15 gram) of unpurified products 1, 2, 7, 8, 9, and 10 were treated with 2 ml. of 72% sulfuric acid which had been previously cooled to 12 to 15°C. Hydrolysis with concentrated acid was continued for two hours at 18

to 22°C., except in the case of product 9, which was treated for four hours; during each hydrolysis the odor of sulfur dioxide was detected. Each product dissolved completely in 72% sulfuric acid; the color of the concentrated solutions ranged from the very light amber of hydrolyzate 1 to the dark brown of hydrolyzate 9.

Each solution was diluted to 3% sulfuric acid by the addition of 75 ml. of water. Dilution of the concentrated hydrolyzates resulted in the precipitation of various amounts of material from solution. Hydrolyzates 1 and 2 were clear upon dilution; very small amounts of a gelatinous precipitate were formed upon the dilution of hydrolyzate 8; successively greater amounts of precipitate were formed upon the dilution of hydrolyzates 7, 10, and 9, respectively. The insoluble material was still present in appreciable quantity after each diluted hydrolyzate had been boiled under a reflux for four hours.

Each hydrolyzate was cooled and filtered through a coarse fritted-glass filtration tube. The insoluble materials in hydrolyzates 7, 8, and 10 were present in very small quantities; it was impossible to remove these insolubles from the filters. Hydrolyzate 9, however, contained a much greater quantity of insoluble material. These insolubles were washed with water, removed from the filter, dried in vacuo at 44 to 46°C., and analyzed for chlorine.

After filtration, sulfuric acid was neutralized to the litmus paper end point by gently heating each hydrolyzate with an excess of barium

carbonate. The neutralized hydrolyzate was then cooled and filtered free of barium sulfate and barium carbonate.

Only the very slightest trace of silver chloride was observed after a portion of each filtered hydrolyzate had been treated with nitric acid and silver nitrate solution.

Each neutralized, filtered hydrolyzate was acidified to the litmus paper end point with a few drops of 10% acetic acid and concentrated to thick sirup (0.1 to 0.2 ml.) in vacuo at a temperature not exceeding 50°C. A portion of each hydrolyzate was filtered through an asbestos mat in a medicine dropper tube; the filtrate and washings (about 10 ml.) were evaporated to dryness over calcium chloride in a vacuum desiccator. Each dried sirup was then dried to constant weight in vacuo at 44 to 46°C. and analyzed for chlorine.

Products 13, 14, and 15 were hydrolyzed quantitatively in the same manner but in much larger quantities (5 grams, oven-dry basis). The hydrolyzate of product 13 was a clear, light amber-colored solution; hydrolyzate 14 contained a sizeable quantity of gelatinous insoluble material; hydrolyzate 15 contained an even greater quantity of insolubles. These insolubles were separated by centrifugation. After each hydrolyzate had been decanted, the insolubles were washed with water, dried in vacuo at 44 to 46°C., and analyzed for chlorine.

After neutralization with barium carbonate, hydrolyzates 13, 14, and 15 were filtered and acidified to the litmus paper end point with 1.75, 2.25, and 1.75 ml. of glacial acetic acid, respectively.

Portions of each hydrolyzate which had been treated with nitric acid and silver nitrate solution exhibited only the very slightest tendency to form silver chloride.

Each hydrolyzate (5 to 6 liters) was concentrated to about 20 ml. in vacuo at a temperature not exceeding 50°C. Several filtrations were required during the course of each evaporation and at the end of each evaporation to remove material which had precipitated from solution. After the addition of 0.20 ml. of 0.10% phenylmercuric acetate preservative, aliquot samples of each hydrolyzate were taken for decolorization experiments and for yield and chlorine determinations; the remainder of each hydrolyzate was concentrated to a thick sirup over calcium chloride in a vacuum desiccator.

The portion of each hydrolyzate, which had been withdrawn for decolorization treatment, was diluted with water and allowed to stand at room temperature with decolorizing carbon. Each decolorized hydrolyzate was then filtered free of carbon, treated with 0.10 ml. of 0.10% phenylmercuric acetate preservative, and evaporated to a thick sirup over calcium chloride in a vacuum desiccator. The color of each hydrolyzate was noticeably reduced by this treatment.

The sample of each hydrolyzate, which had been set aside for yield determination and chlorine analysis, was evaporated to dryness over calcium chloride in a vacuum desiccator. Each dried hydrolyzate was crushed to a powder, dried to constant weight in vacuo at 44 to 46°C.,

and analyzed for chlorine. During each chlorine analysis, barium carbonate, which was formed by the peroxide oxidation of the barium acetate contained in each hydrolyzate, was observed in the alkaline melt solution. Upon acidification with nitric acid, the white solid dissolved completely with the evolution of carbon dioxide. The fact that the solid dissolved completely revealed that barium sulfate was absent. This signified that sulfur was no longer present in the hydrolyzate.

In as much as each hydrolyzate contained an appreciable quantity of barium acetate, barium determinations were carried out. The filtrate from each chlorine analysis was collected quantitatively, treated with an excess of sodium chloride, and filtered to remove the silver chloride. The filtrate was neutralized to the methyl orange end point with sodium hydroxide solution, reacidified with 1 ml. of N hydrochloric acid, and treated with an excess of potassium sulfate to precipitate barium sulfate. Barium sulfate was determined gravimetrically in the conventional manner. The barium content of each hydrolyzate was calculated as follows:

$$\text{Barium, \%} = \frac{58.85 \text{ (grams BaSO}_4\text{)}}{\text{(grams oven-dry sample)}}$$

The chlorine content of each hydrolyzate was corrected for the presence of barium acetate in the following manner.

$$\text{Corrected chlorine, \%} = \frac{100 \text{ (chlorine, \%)}}{100 - 1.860 \text{ (barium, \%)}} \quad .$$

The experimental yield of oven-dry hydrolyzate, corrected for the presence of barium acetate, was compared with the calculated theoretical yield of hydrolyzate to determine the percentage of the theoretical yield

actually obtained. The experimental yield of hydrolyzate was corrected for the presence of barium acetate as follows:

$$\text{Experimental yield, grams} = \frac{100 (\text{grams oven-dry hydrolyzate})}{100 - 1.860 (\text{barium, \%})}$$

The theoretical amount of hydrolyzate produced was calculated from the following equation:

$$\text{Theoretical yield, grams} = \frac{(180.2 + 18.45y)(\text{grams chlorocellulose})}{(162.1 + 46.06x + 18.45y)}$$

where y and x represent the degrees of substitution of chlorine and sulfurous acid ester in chlorocellulose, respectively.

An approximate yield of insoluble material from the hydrolysis, expressed on the basis of the original chlorocellulose, was also calculated. These values may be slightly in error because of the difficulty encountered in collecting and washing this material.

A material balance over the chlorine contents of chlorocelluloses before hydrolysis and the end products after hydrolysis could not be prepared because varying, unknown amounts of material precipitated from solution during the concentration of each hydrolyzate.

The data obtained in the course of the hydrolysis study are presented in Table XV.

Chlorine analyses of the oven-dry hydrolyzates revealed that considerable amounts of chlorine were present. After hydrolyzates 13 and 14 had been corrected for the presence of barium acetate, the degree of chlorine substitution of the carbohydrate portion of each hydrolyzate

TABLE XV

HYDROLYSIS OF CHLOROCCELLULOSES

Product	Yield, %	Cl, %	Ba, %	Cl Corrected for Barium Acetate, %	D.S. of Cl	D.S. of Cl in Original Product
1	--	4.2	--	--	0.22	0.22
7	--	10.8	--	--	0.58	0.64
8	--	6.95	--	--	0.37	0.45
9	--	21	--	--	1.2	1.30
9In	22.0	24.1	--	--	1.40	1.30
					1.26 ^c	
10	--	11.6	--	--	0.63	1.07
13	97.3 ^a	3.59	21.2	5.92	0.31	0.29
14	--	5.76	28.5	12.3	0.67	0.66
14In	4.9	15.3	--	--	0.84	0.66
					0.76 ^c	
15	47.0 ^a	6.72	31.46	16.2	0.90	1.04
15In ^b	8.3	20.74	--	--	1.18	1.04
					1.06 ^c	

In - Designates the portion of the product which was soluble in 72% sulfuric acid, but which was insoluble upon dilution to 3% acid and boiling under reflux for four hours. The yield value was based upon the original weight of the product.

- a. The yield of hydrolyzate was expressed as a percentage of the theoretical yield.
- b. This yield value may be slightly high and the percentage of chlorine slightly low because of impurities picked up when the centrifuge bottle shattered during washing.
- c. These values were calculated on a cellulose basis: Chlorine, % = $3546\bar{y} / 162.1 + 18.45\bar{y}$.

closely approached that of the original product. The degrees of chlorine substitution of hydrolyzate 15 and product 15 did not exhibit the same close agreement; the discrepancy may have been caused by the presence of fairly large amounts of rather highly chlorinated insoluble materials which were encountered during hydrolysis and during evaporation of the hydrolyzate. The degrees of chlorine substitution of hydrolyzates 1, 7, 8, 9, and 10 and the respective products generally exhibited poor agreement; this disagreement was caused, no doubt, by the presence of undetermined barium acetate.

The fact that the soluble organic chlorides, which were contained in each hydrolyzate, formed only the very slightest traces of silver chloride when treated with silver nitrate signified that chlorine was bound firmly within hydrolyzed chlorocelluloses. The observation also substantiated the conclusion drawn in the 18% sodium hydroxide treatment study; the reactive chlorine in the sodium hydroxide treatment solutions was probably caused by the presence of chloride ions rather than by the presence of soluble, reactive organic chlorides. This conclusion may also be extended to the cuprammonium solubility study; in several instances, reactive chlorine was found to be present in the cuprammonium treatment solutions.

When the degree of chlorine substitution of hydrolysis insolubles was calculated on the basis of substituted sugar units (chlorine, % = $3546\bar{y} / 180.2 + 18.45\bar{y}$), it was evident that the recoverable hydrolysis insolubles of products 9, 14, and 15 were more highly substituted than the original chlorocelluloses. These differences were not as apparent when the degrees of chlorine substitution of the insolubles were calculated on the basis of substituted cellulose chains (chlorine, % = $3546\bar{y} / 162.1 + 18.45\bar{y}$). Since the degrees of polymerization of the hydrolysis insolubles were, in all probability,

somewhere between those of the respective chlorocelluloses and one, it was assumed that the hydrolysis insolubles were somewhat more highly substituted than the original chlorocelluloses.

It was observed that the quantity of hydrolysis insolubles increased as the chlorine content of the chlorocelluloses increased. Product 13, which contained only 6.12% chlorine, produced a hydrolyzate which contained no insoluble material. Successively greater amounts of hydrolysis insolubles were obtained from products 14 and 15, respectively. Product 9, which contained 23.43% chlorine, produced the largest quantity of hydrolysis insolubles (22.0% insoluble on the basis of the original product). It was also observed that the hydrolyzate yield, which was expressed as a percentage of the theoretical yield, decreased as the chlorine content of the original chlorocelluloses increased. These trends, together with the finding that the hydrolysis insolubles were somewhat more highly substituted than the original chlorocelluloses, signified that resistance to hydrolysis increased as the chlorine content of chlorocelluloses increased. Resistance to hydrolysis could be expected since it is generally known that chlorinated compounds exhibit a lower affinity for polar reagents than do the corresponding hydroxy compounds. Barham, Stickley, and Caldwell (21), in their study of the phosphorus pentachloride chlorination of starch, reported that pentachlorostarch was unaffected by a 50% sulfuric acid hydrolytic treatment.

Sulfur dioxide was liberated when chlorocelluloses were treated with 72% sulfuric acid or 85% phosphoric acid. This indicated that the residual sulfur in chlorocelluloses was probably present in the same type

of linkage as the sulfur which has been removed during the washing operation. Dissolution of chlorocelluloses in sulfuric acid probably rendered the sulfur in the less accessible regions of chlorocelluloses accessible to chemical attack.

PRELIMINARY CHROMATOGRAPHIC STUDY

The concentrated hydrolyzates, which were prepared in the course of the hydrolysis study, were subjected to a paper partition chromatographic study. Oven drying of the developed, aniline hydrogen phthalate-treated chromatograms resulted in a reaction of the aniline hydrogen phthalate with the reducing groups in the hydrolyzate constituents to form reddish-brown colored spots. In many instances these colored spots were distinctly visible in ordinary light, but some of the spots were weak and could be distinguished only when the chromatograms were viewed under ultraviolet light. For the sake of convenience an arbitrary ranking of spot intensities is presented in Table XVI. This nomenclature will be employed in all future descriptions of paper partition chromatographic spot intensities.

In a number of instances it was possible to calculate the distances traveled by the separated spots relative to the distance traveled by the developer solution (R_f value) (42). Whenever possible, R_f values were employed to designate the various spots formed.

TABLE XVI
QUALITATIVE RANKING OF PAPER PARTITION
CHROMATOGRAPHIC SPOT INTENSITIES

Spot Intensity Rank	Qualitative Description of Spot Intensity
7	Very strongly visible.
6	Strongly visible.
5	Visible.
4 ^a	Faintly visible.
3 ^a	Strongly visible under ultraviolet light.
2	Visible under ultraviolet light.
1	Barely visible under ultraviolet light. Questionable.

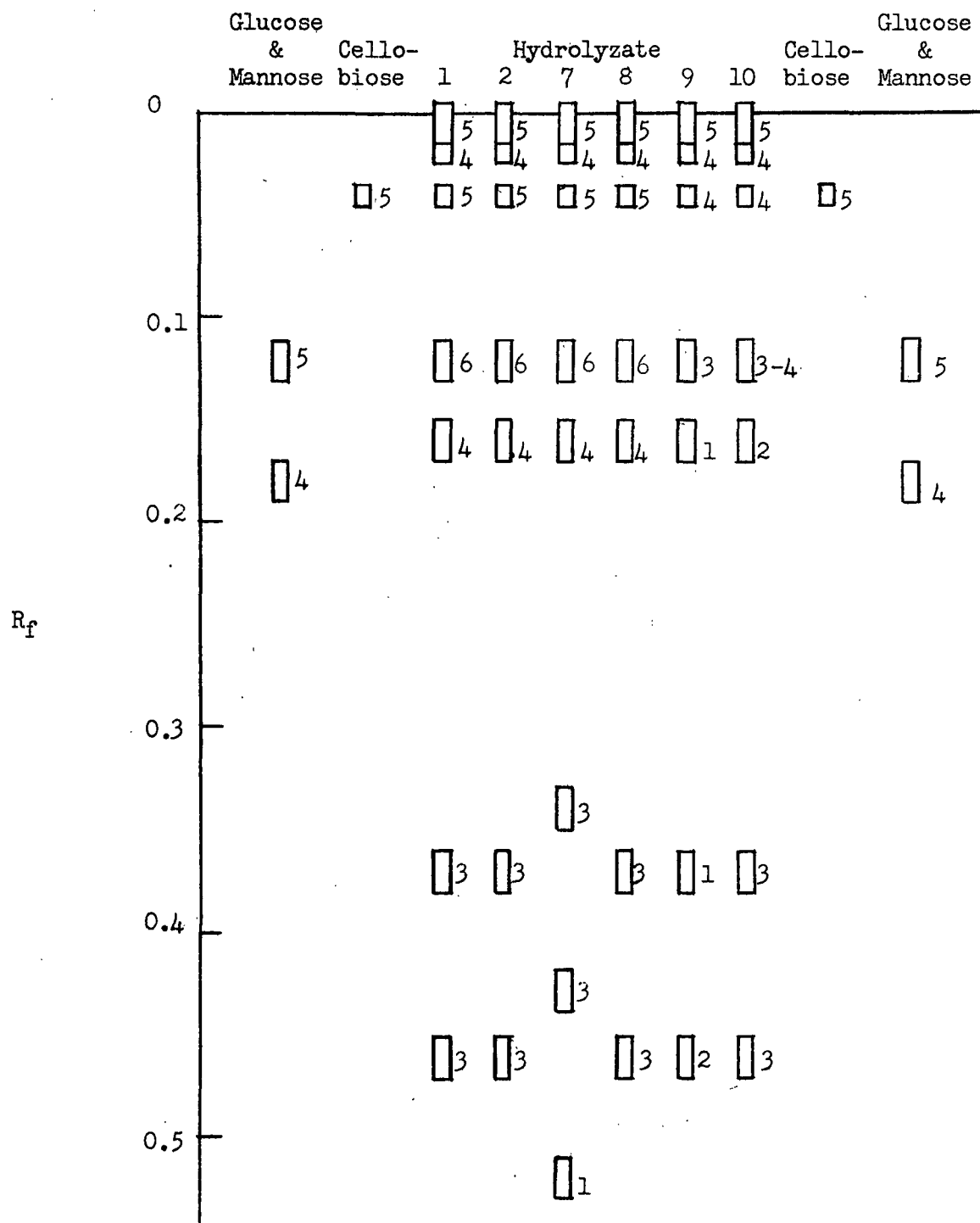
^aThese values may overlap on occasions.

The components of the hydrolyzates of products 1, 2, 7, 8, 9, and 10 were chromatographically separated on paper together with a known solution of cellobiose and a known mixture of glucose and mannose. The results are illustrated in Figure 1 in the form of a chromatogram.

The paper partition chromatographic study revealed that each hydrolyzate produced a spot which corresponded with known cellobiose spots ($R_f = 0.04$). Each hydrolyzate also produced spots which traveled smaller distances than cellobiose. The spots near the starting line ($R_f = 0.00$ to 0.01) indicated that each hydrolyzate probably contained material which possessed a greater degree of polymerization than cellobiose; these spots and the presence of spots in the cellobiose region signified that the contents of each hydrolyzate probably were not completely hydrolyzed to

FIGURE 1

CHROMATOGRAM OF CHLOROCELLULOSE HYDROLYZATES



The number at the side of each spot represents the spot intensity rank.

monomer units. The white spots ($R_f = 0.02$) above cellobiose were formed by the barium acetate contained in each hydrolyzate.

The probability that glucose was contained in each hydrolyzate was evidenced by the fact that each hydrolyzate produced a spot which corresponded with known glucose spots ($R_f = 0.12$). These spots were prominent in the case of hydrolyzates 1, 2, 7, and 8, and became progressively fainter in the case of hydrolyzates 10 and 9, respectively. A qualitative trend of this nature was to be expected, since the amount of glucose present in the hydrolyzate theoretically would tend to decrease as the chlorine content of the chlorocellulose increased.

The remaining spots on the chromatogram were unknown. Spots ($R_f = 0.16$) were observed between the known glucose and mannose spots. In addition, two series of unknown spots ($R_f = 0.37$ and 0.46) were observed far below the known glucose spots. The presence of these unknown spots was undoubtedly caused by the hydrolyzed portions of celluloses which had reacted with thionyl chloride.

Hydrolyzate 9 produced only very faint spots with R_f values greater than that of glucose; these spots were much fainter in intensity than the corresponding spots produced by the other hydrolyzates. This denoted that the material in hydrolyzate 9 was probably incompletely hydrolyzed to monomer units; this was in agreement with the observation that highly chlorinated cellulose was resistant to hydrolytic action.

For some unaccountable reason the spots formed by hydrolyzate 7 seemed to have somewhat smaller R_f values than the spots produced by the other hydrolyzates. The spot ($R_f = 0.52$) presumably formed by hydrolyzate 7 was so faint that its presence was questionable.

Hydrolyzates and decolorized hydrolyzates 13, 14, and 15 were chromatographed in the same manner. The spots formed by each hydrolyzate were the same as those illustrated in Figure 1. Each spot traveled the same relative distance, in respect to the distance traveled by the solution, as the corresponding spots in Figure 1. The formation of the same spots by both the original and the decolorized hydrolyzates qualitatively revealed that decolorization with carbon did not remove reducing material from the hydrolyzates.

CELLULOSE COLUMN CHROMATOGRAPHIC STUDY

The hydrolyzate of unpurified product 13 was subjected to a large-scale, quantitative chromatographic study in order to investigate more fully the unknown hydrolyzate constituents observed during the preliminary chromatographic study.

A sample of hydrolyzate 13 was distributed evenly over the one-half water-saturated n-butanol soaked cellulose powder at the top of the column. The sample (7.371 grams) contained 3.870 grams of oven-dry solids, of which 1.52 grams consisted of barium acetate. The chromatogram was developed by allowing one-half saturated n-butanol to flow through the column. In order to accelerate the separation, the first 700 ml. of

developer solution were allowed to flow through the column without restriction. This initial effluent did not contain any hydrolyzate component. The capillary tip was then fastened to the bottom of the column and the automatic fraction collector was started.

After the glucose fraction of hydrolyzate 13 had been collected completely, the column was washed by allowing 1200 ml. of 50% ethanol to flow through the column. The fractions obtained from the cellulose column are listed in Table XVII.

TABLE XVII
CHROMATOGRAPHIC FRACTIONATION OF HYDROLYZATE 13

Fraction	From Test Tubes No.
--	1 - 50 (no material present)
A	51 - 83
B	84 - 136
C	137 - 215
D	216 - 297
E	298 - 470
F	471 - 1096
G	Column washings

The large fractions of hydrolyzate 13 were evaporated to hard, brown, glassy sirups in a tared flask in vacuo at a temperature not exceeding 50°C. The sirups were dried to constant weight to determine the quantity of material in each fraction. Fractions A, B, C, and D were readily soluble in absolute ethanol. An attempt was made to dissolve fraction E

in water, but only a portion (fraction E-1) dissolved; the remaining material (fraction E-2) was dissolved in absolute ethanol. Fraction F was also only partially soluble in water (fraction F-1); the remainder (fraction F-2) was dissolved in ethyl acetate. Fraction G was readily soluble in water. Each solution was then filtered into a small volumetric flask through celite and decolorizing carbon and diluted to volume. All the foregoing operations were performed quantitatively. A portion of each solution was placed in a two decimeter polarimeter tube and examined for optical activity.

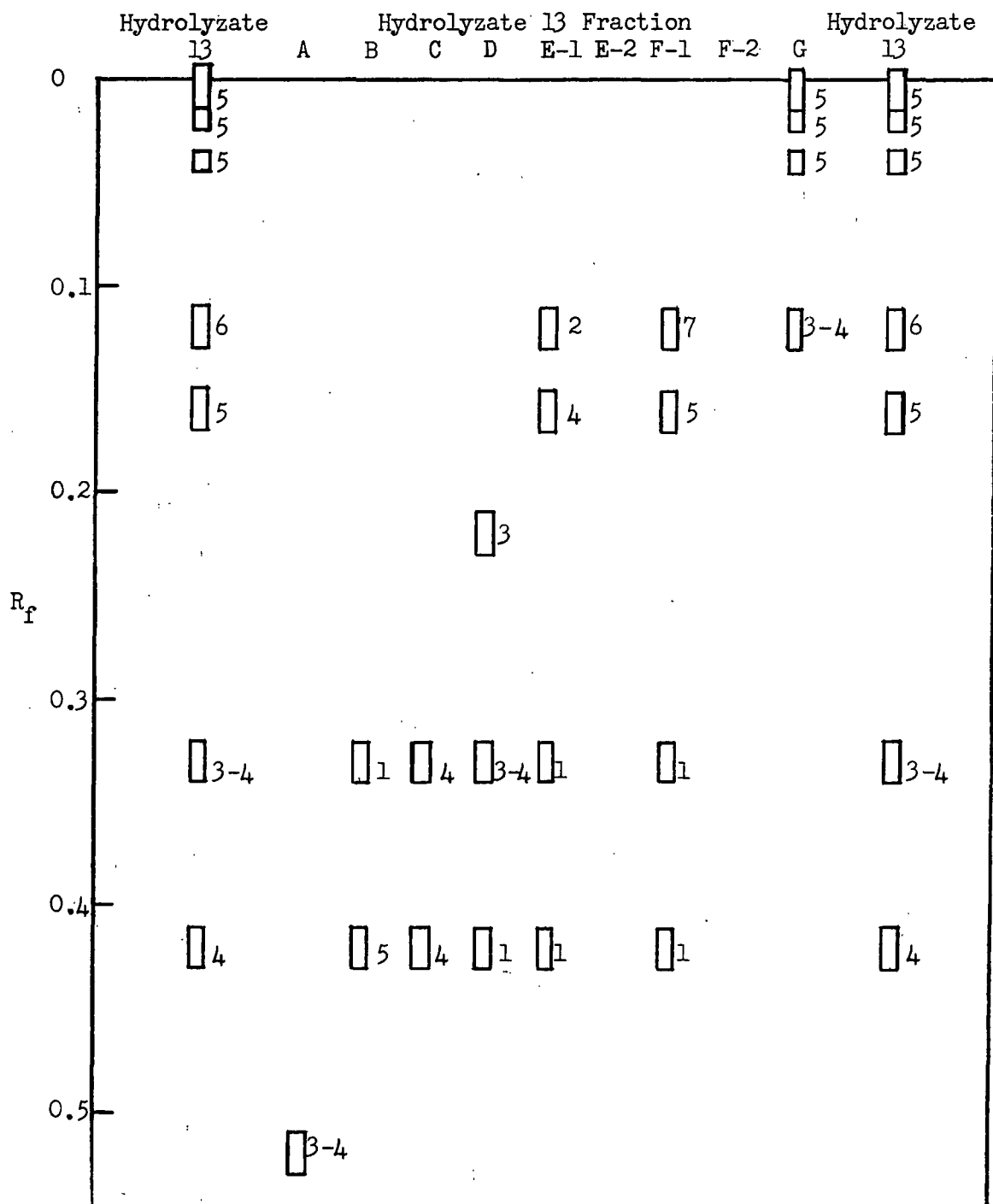
A portion of each fraction was evaporated to a thick sirup and spotted on a paper partition chromatogram which was developed overnight with a solution of pyridine, n-butanol, and water. The chromatogram is illustrated in Figure 2.

The chromatogram clearly indicated that a complete fractionation of hydrolyzate 13 had not been attained. It was observed that very few clear-cut fractions were obtained; practically every fraction was contaminated with at least traces of one or more of the other fractions. Fractions A and D contained hydrolyzate components ($R_F = 0.52$ and 0.22 , respectively) which were not clearly observed in any of the chromatograms prepared previously.

A sample (10 to 30 mg.) of fractions A, B, C, D, E-1, E-2, and F-2 was gently evaporated to dryness on a steam bath and then dried to constant weight in vacuo at 44 to 46°C. Each dried sirup was quantitatively dissolved in ethanol, water, or ethyl acetate, transferred to a Parr bomb

FIGURE 2

CHROMATOGRAPHIC SEPARATION OF THE
COMPONENTS OF HYDROLYZATE 13



The number at the side of each spot represents the spot intensity rank.

cup, and gently evaporated to dryness; the sirup was carefully distributed over the sides and bottom of the cup. Each sirup was then analyzed for chlorine. Fractions F-1 and G were analyzed in the usual manner.

The data obtained in the course of the chromatographic study are presented in Table XVIII.

All the fractions of hydrolyzate 13 were found to contain chlorine in at least small amounts. The presence of chlorine in all the fractions was another indication that complete separation of the hydrolyzate components had not been attained. Of the nine fractions collected, only four contained appreciable quantities of chlorine; the four highly chlorinated fractions (fractions A, B, C, and D) exhibited chlorine contents between 11.2 and 13.5%, but this was still far below the theoretical chlorine content (17.85%) required for a monochlorohexose. The total quantity of material in fractions A through D amounted to 0.2545 gram or 10.8% of the carbohydrate material which was originally placed on the column. These fractions contained a total of 0.0302 gram of chlorine or 21.7% of the chlorine which was originally present in the hydrolyzate.

Fractions A through F represented that portion of hydrolyzate 13 which had probably been converted to monomer units. The total quantity of material in these fractions was 1.666 grams or 70.9% of the carbohydrate material which was originally present in the hydrolyzate. The chlorine contained in these fractions amounted to 0.0523 gram or 37.6% of the original chlorine. The glucose fraction (fraction F-1) contained 47.2%

TABLE XVIII

FRACTIONATION OF HYDROLYZATE 13 WITH A
CELLULOSE CHROMATOGRAPHIC COLUMN

Frac- tion	R_f^3	Dried Frac- tion, g.	Specific [α] _D ²⁵ , °	Rotation ⁴ Solvent	Cl, %	Cl in Frac- tion, g.
A	0.52	0.0163	0	EtOH	13	0.0021
B	0.42	0.1303	+41.0 ± 0.4	EtOH	11.7	0.0152
C	0.33	0.0677	+13 ± 1	EtOH	11.2	0.0075
D	0.22	0.0402	+ 2 ± 1	EtOH	13.5	0.0054
E-1	0.16	0.0803	-41 ± 1	H ₂ O	4.9	0.0039
E-2	0.16	0.0154	- 3 ± 3	EtOH	6.4	0.0010
F-1	0.12	1.1086	+40.2 ± 0.4	H ₂ O	1.48	0.0164
F-2	0.12	0.2071	0	AcOEt	0.4	0.0008
G	0.04-0.01	<u>1.6104</u>	+2.9 ± 0.1	H ₂ O	2.12	<u>0.0341</u>
Total		3.2763			--	0.0864
Residual ¹		<u>0.594</u>			8.9	<u>0.053</u>
Original ²		3.870			3.59	0.139

¹This represents the quantity (calculated by difference) of material which was not removed by washing the column.

²The original hydrolyzate 13 contained 39.4% barium acetate; hence, the 3.870 grams of material placed on the column contained 1.52 grams of barium acetate and only 2.35 grams of hydrolyzed product 13.

³This R_f value represents the R_f value of the principal component which appeared in the fraction.

⁴Optical rotations were measured using each entire fraction. All the solutions, except those of fractions F-1 and G, were 3 ml. in volume. The solution of fraction F-1 was 25 ml. The solution of fraction G was 10.00 ml.

of the original carbohydrate. A large glucose fraction was expected since the degree of chlorine substitution of product 13 was only 0.29. If the unsubstituted anhydroglucose units in the chlorocellulose had been destroyed by thionyl chloride treatments, glucose could not be expected to be present in the hydrolyzate. The fact that a large glucose fraction was present signified that many of the anhydroglucose units in the original cellulose were not affected by the thionyl chloride reaction.

The fractions which possessed R_f values between 0.00 and 0.04 represented the soluble portion of product 13 which had not been completely hydrolyzed to monomer units. A washing of the column with 50% ethanol did not result in the complete removal of this material. The data in Table XVIII revealed that considerable quantities of residual material were still contained within the column. The total relatively incompletely hydrolyzed material (fraction G plus the residual material in the column) contained 1.52 grams of barium acetate, 0.68 gram or 29% of the carbohydrate portion of hydrolyzate 13, and 0.087 gram or 63% of the chlorine which was originally present in the hydrolyzate. The fact that the greatest portion of the original chlorine resided within the relatively incompletely hydrolyzed material agreed with earlier observations that the presence of combined chlorine in cellulose tended to increase the resistance of the chlorocellulose to hydrolytic attack.

It was observed that fraction E-1 exhibited a very highly negative specific rotation $[\alpha]_D^{25} = -41^\circ \pm 1$). Fraction E-1 contained small amounts of highly chlorinated material which belonged primarily to fractions B

and C ($R_f = 0.42$ and 0.33 , respectively); the relatively small chlorine content of fraction E-1 was probably caused by the presence of these contaminants and, hence, the bulk of fraction E-1 most probably was unsubstituted with chlorine. The presence of these contaminants could not possibly account for the high negative rotation of fraction E-1 because these materials exhibited positive rotations. Carbon and hydrogen analyses of purified chlorocelluloses indicated the possibility of the presence of anhydro or carbonyl groupings in chlorocelluloses; anhydro groupings on carbon atoms two and three may have been formed by the removal of sulfurous acid ester groupings from the chlorocelluloses (12). The negative rotation of fraction E-1 may have been caused by the presence of carbonyl or anhydro groupings alone; the presence of groupings similar to anhydro linkages (isopropylidene linkages between adjacent hydroxyl groups) in glucose and in other sugars, which have a configuration similar to that of glucose (mannose and xylose), apparently tend to make the rotations of these sugars more negative (43).

During the acidic hydrolysis of the chlorocellulose anhydro linkages may have been broken, with the accompaniment of Walden inversion, to form sugars (mannose, allose, or altrose) which possess the same configuration as glucose except for the hydroxyl groups on carbon atoms two and three (12, 44, 45). However, when fraction E-1 was chromatographed on paper together with D-mannose, D-allose, and D-altrose, the spot formed by fraction E-1 ($R_f = 0.16$) corresponded most closely with the spot produced by mannose ($R_f = 0.16$), which does not possess a negative rotation (43). This indicated that perhaps the anhydro linkages were not attacked during

acidic hydrolysis. However, no additional experimental work has been performed to ascertain the presence of carbonyl groupings, anhydro groupings, or the occurrence of configurational changes.

Small samples of each fraction were gently evaporated to dryness and treated with Fehling solution. Each fraction, except fractions E-2 and F-2, reacted rapidly to form a red precipitate of cuprous oxide. Fraction F-2 reacted only slightly; the precipitated, water-washed cuprous oxide could be detected only upon the application of the phosphomolybdic acid test. Fraction E-2 produced negative results. The fact that most of the fractions exhibited high reducing powers contributed some evidence to the effect that these fractions were carbohydrate in nature.

The lack of reducing power exhibited by fractions E-2 and F-2 explained the lack of spots on the paper partition chromatogram. These two fractions exhibited at the most only slight optical activity; the small negative rotation of fraction E-2 may have been caused by the presence of small amounts of fraction E-1. The lack of reducing power and the small rotations exhibited by fractions E-2 and F-2 gave an indication that perhaps these fractions were degradation products and of a noncarbohydrate nature; however, no additional experimental work has been carried out to determine this. Fractions E-2 and F-2 together contained 0.2225 gram or 9.48% of the original carbohydrate material and only 0.0018 gram or 1.3% of the original chlorine in the hydrolyzate.

Small samples of each fraction, which had been evaporated to dryness, were dissolved in 0.25 ml. of water and treated with 0.1 N silver nitrate

solution. Silver chloride was either absent or present in only faint traces in all the fractions except D and G. Fractions D and G produced appreciable quantities of silver chloride. This observation did not necessarily conflict with the observation that silver chloride was formed only in the very slightest traces upon the treatment of the hydrolyzates of chlorocelluloses with silver nitrate. Since the solubility of silver chloride in water is 0.00191 gram per liter at room temperature (46) and the portion of hydrolyzate 13, which was tested with silver nitrate, was withdrawn from a volume of approximately six liters of hydrolyzate, a maximum of only 0.0115 gram of silver chloride could have been in solution. This quantity of silver chloride is equivalent to 0.00284 gram of chlorine which is only 0.0568% chlorine on the basis of the original chlorocellulose or 0.928% of the chlorine content of the original chlorocellulose. If this amount of reactive chlorine was assumed to be concentrated within fractions D and G, relatively large amounts of silver chloride would be expected to form, since the silver nitrate test was carried out on very small volumes of solutions of these fractions. The quantity of reactive chlorine in these fractions, however, was not determined. Since the portion of hydrolyzate 13 which was tested with silver nitrate was also treated with nitric acid, the amount of silver chloride in solution may have been less than the amount calculated above because an excess of nitrate ion tends to reduce the solubility of silver chloride (47).

A portion of fraction F-1 was evaporated in vacuo at 50°C. to approximately 60% concentration, decolorized with carbon, and filtered. The clear, colorless filtrate was evaporated in vacuo at 50°C. to approximately

80 to 90% concentration, seeded with a grain of anhydrous glucose, and allowed to stand several hours at 50°C. After crystallization had started, the sirup was allowed to stand overnight at room temperature. The crystals were then washed with absolute ethanol and dried to constant weight. The compound exhibited a sharp melting point at 145°C. The phenylosazone was prepared by treating 0.02 gram of the compound with 0.04 gram of phenylhydrazine hydrochloride, 0.06 gram of anhydrous sodium acetate, and 0.4 ml. of water, and heating the mixture in a boiling water bath. The yellow phenylosazone started to precipitate in four minutes; it exhibited a melting point between 204 and 205°C. The remainder of the compound (0.1751 gram) was dissolved in water, diluted to 10.00 ml., placed in a 2-decimeter polarimeter tube, and examined for optical rotation. The specific rotation was found to be $+52 \pm 1^\circ$. Glucose melts at 146°C. and has a specific rotation of $+52.7^\circ$; its phenylosazone melts at 208°C. (43). When the compound was mixed with glucose, it melted at 145°C. When the compound was chromatographed on paper along with glucose, the spots produced by each possessed identical R_f values (0.12). The presence of glucose in fraction F-1 was therefore definitely established.

Only portions of dried fractions B, C, and D were found to be soluble in hot ethyl acetate. These portions were quantitatively dissolved, cooled, filtered through celite and decolorizing carbon, and evaporated to small volumes (2 to 4 ml.). Each ethyl acetate solution was then treated with petroleum ether (30 to 60°C.) to the point of incipient precipitation and allowed to stand at room temperature. At intervals, a few drops of petroleum ether were added to readjust each solution to the point of incipient precipitation. Over a period of several weeks, small amounts of fractions C and D gradually

came out of solution in the form of sticky, unidentified sirups. In the case of fraction B, however, the ethyl acetate and petroleum ether solution contained a hard, white solid. When this solid was shattered and viewed under a polarization microscope, the fragments were found to be crystalline in nature.

Crystalline fraction B was washed with a solution of ethyl acetate and petroleum ether (volume ratio of one to three, respectively) and finally with petroleum ether alone. Several much smaller crops of crystalline fraction B were obtained by seeding the evaporated mother liquor with a fragment of the crystals; fraction B crystallized very readily in the form of fine needles after seed crystals were available. The substance was obtained in a yield of 65.6% of the original fraction B.

Crystalline fraction B was found to exhibit a sharp melting point at 134 to 135°C. The compound reacted rapidly with Fehling solution to form a precipitate of cuprous oxide. When the compound stood overnight at room temperature in silver nitrate solution, only small amounts of silver chloride were formed, even though the compound produced a strong Beilstein test for chlorine. A sample of 0.0160 gram of the compound in a 3 ml. absolute ethanol solution produced a specific rotation of $+100 \pm 3^\circ$. Another sample of 0.0156 gram of the compound in a 3 ml. aqueous solution exhibited some evidence of mutarotation. The first measurement produced a specific rotation of $+50 \pm 3^\circ$ but, because of experimental complications, this value was not obtained until 1.33 hours after the solution

had been prepared. The equilibrium specific rotation was observed to be $+43 \pm 3^\circ$; no change was noted in the specific rotation after four hours had elapsed.

Samples of crystalline fraction B were analyzed for chlorine, carbon, and hydrogen. A determination of the molecular weight was also performed by dissolving the compound in cyclohexanol and measuring the freezing point depression (48). These data are listed in Table XIX along with the theoretical values required for a monochlorohexose ($C_6H_{11}O_5Cl$) and an anhydro monochlorohexose ($C_6H_9O_4Cl$).

TABLE XIX
ANALYSIS OF CRYSTALLINE FRACTION B

	Fraction B	Monochlorohexose ($C_6H_{11}O_5Cl$)	Anhydro Monochloro- hexose ($C_6H_9O_4Cl$)
Chlorine, %	18.66	17.85	19.64
Carbon, %	36.82	36.28	39.90
Hydrogen, %	5.85	5.58	5.02
Molecular weight	246	198.61	180.59

These data indicated that crystalline fraction B was a monochlorohexose. A paper partition chromatogram revealed that the compound produced the spot which had previously identified fraction B.

Helferich and Brederick (49) prepared 6-chloroglucose and established the melting point of this compound to be 135 to 136°C. The specific rotation of 6-chloroglucose was reported to be $+78.3^\circ$ immediately after

solution in water; the specific rotation finally attained an equilibrium value of $+35.0^\circ$. Fehling solution was reported to be rapidly reduced by this compound. Since the melting point and the specific rotation of the monochlorohexose which was obtained from fraction B approached the respective values exhibited by 6-chloroglucose, crystalline fraction B was, in all probability, 6-chloroglucose.

The isolation of a chlorinated sugar from the hydrolyzate of a chlorocellulose established that chlorine had entered the cellulose chain by the replacement of hydroxyl groups to form a stable chlorine derivative of cellulose.

The chlorohexose isolated from fraction B was obtained with a practically quantitative recovery of chlorine. The chlorine content of fraction B, which was corrected for the yield of the chlorohexose, indicated that the chlorohexose contained $11.7 / 0.656 = 17.8\%$ chlorine; the actual chlorine content of the chlorohexose was 18.7% and the theoretical chlorine content of a chlorohexose is 17.8% (Table XIX). Since the chlorohexose was isolated from a highly chlorinated fraction with a practically quantitative recovery of chlorine, it was possible that other unidentified chlorohexoses were present in the other highly chlorinated fractions. Since the 6-chloroglucose prepared by Helferich and Brederick (49) exhibited a specific rotation of $+35.0^\circ$ and the 3-chloroglucose prepared by Newth, Overend, and Wiggins (50) exhibited a rotation of 64.1° , it might be expected, by an analogy with methylated glucoses (43), that other chloroglucoses would produce positive rotations. Fraction C ($11.2\% \text{ Cl}$) produced a fairly high specific rotation ($+13 \pm 1^\circ$)

and may have contained a chlorinated sugar. Fraction D (13.5% Cl) possessed a low specific rotation ($+2 \pm 1^\circ$), but may have been contaminated with fraction E-1 which possessed a very highly negative rotation; hence, it was also possible that fraction D contained a chlorinated sugar. Fraction A (13% Cl) did not exhibit any optical activity; this fraction, therefore, may have contained highly chlorinated degradation products or noncarbohydrate material.

SUMMARY AND CONCLUSIONS

Chlorocellulose, which is prepared by treating mercerized cellulose with thionyl chloride in a pyridine medium, is a fibrous, tan to dark brown-colored material which contains sulfur as well as chlorine. The color of chlorocellulose darkens with both increased reaction temperature and reaction time; the color is probably caused by the presence of an unidentified dark solid material which is formed in side reactions between thionyl chloride and pyridine. The color of chlorocellulose does not seem to be appreciably reduced by washes with water, sodium bicarbonate solution, or dilute sodium hydroxide solution.

The chlorine content of chlorocellulose increases with both increased reaction temperature and reaction time. Excessive temperatures of reaction, however, may result in the formation of black, gritty, non-fibrous materials. In this study, a chlorocellulose which possesses a degree of chlorine substitution as high as 1.30 has been prepared. Fairly reproducible degrees of chlorine substitution are attained when thionyl chloride treatments are carried out under the same reaction conditions. Reactions which are terminated in anhydrous media (absolute methanol) produce chlorocelluloses which appear to contain somewhat more chlorine than do chlorocelluloses which have been washed with water and aqueous solutions of sodium bicarbonate or sodium hydroxide.

The sulfur content of chlorocellulose which has been washed with water and sodium bicarbonate or dilute sodium hydroxide solutions is relatively low and exhibits no trend with either reaction temperature or

reaction time. The sulfur content of chlorocellulose which has been produced under anhydrous conditions, however, is very high and increases with reaction time.

Most of the sulfur in chlorocellulose is readily removed in the form of sulfur dioxide by treatments with water, sodium bicarbonate solution, and dilute alkali. The ease of the removal of sulfur groups by these media and the quantitative sodium hydroxide consumption of absolute methanol-washed chlorocellulose indicate that sulfur is present in the form of unstable sulfurous acid ester linkages. The residual sulfur in chlorocellulose is probably present in the inaccessible regions of chlorocellulose; this sulfur is also removed in the form of sulfur dioxide when chlorocellulose is swelled or dispersed in cuprammonium solution, 18% sodium hydroxide solution, 72% sulfuric acid, or 85% phosphoric acid. The exact type of sulfurous acid ester linkage and the cellulosic hydroxyl groups involved, however, have not been determined.

Chlorocellulose is not dissolved by any common organic solvent. In addition, extraction of chlorocellulose with organic solvents does not appear to result in an appreciable removal of colored material. Chlorocellulose does dissolve in hot 60% ethylenediamine but cannot be regenerated from solution by acidification.

Treatment of chlorocellulose with an acidic aqueous sodium chlorite solution results in the removal of considerable amounts of color; purified chlorocellulose is fibrous in nature and ranges from white to lemon yellow in color. The chlorine content of chlorited chlorocellulose attains

a constant value when the color of the purified product is no longer appreciably altered by subsequent chlorite treatments. An appreciable loss of chlorine is incurred during sodium chlorite purification, but the degree of chlorine substitution of purified chlorocellulose is not appreciably different from that of unpurified chlorocellulose; this indicates that the material removed during purification possesses approximately the same chlorine content as chlorocellulose. Sulfur is also lost during the sodium chlorite purification of chlorocellulose, but the residual sulfur still seems to be present in the form of a sulfurous acid ester. The yield of purified chlorocellulose (on the basis of the original chlorocellulose) exhibits a tendency to decrease as the chlorine content of chlorocellulose increases and as its color deepens.

The fact that chlorine is stably bound within chlorocellulose is evidenced by a number of observations. The degrees of chlorine substitution of chlorocellulose and chlorocellulose which has been regenerated from cuprammonium solution generally agree quite closely. The hydrolyzate of chlorocellulose contains only slight traces of chlorine which react with silver nitrate. A chlorine analysis of the dried hydrolyzate reveals that the degrees of chlorine substitution of chlorocellulose and hydrolyzed chlorocellulose are in fairly close agreement. In addition, a chromatographic separation of the components of a hydrolyzate indicated that high concentrations of chlorine are present in some fractions. Finally, a crystalline monochlorohexose was isolated from a hydrolyzate component and identified. The isolation of a monochlorohexose (probably

6-chloroglucose) indicates that chlorine enters the cellulose chain by the replacement of hydroxyl groups.

Chlorocellulose is largely dissolved by cuprammonium solution. The solubility tends to decrease as the chlorine content of chlorocellulose increases. The low qualitative viscosities of cuprammonium solutions of chlorocellulose and the low yields of regenerated chlorocellulose indicate that degradation of the cellulose chain probably occurs during the thionyl chloride reaction. The cuprammonium reaction liquors of some of the more highly substituted chlorocelluloses contain small but appreciable quantities of reactive chlorine.

The chlorine atoms in chlorocellulose are relatively stable under conditions of dilute alkalinity. A treatment of chlorocellulose with 18% sodium hydroxide, however, results in appreciable losses of chlorine; at elevated temperatures the chlorine loss is even greater. The yield of 18% sodium hydroxide-treated chlorocellulose is low. Considerable amounts of reactive chlorine are contained in all the concentrated sodium hydroxide treatment liquors; there is an indication, however, that unreactive organic chlorides are present in the reaction liquor obtained during the 18% sodium hydroxide treatment of chlorocellulose at room temperature.

The fact that only slight traces of reactive chlorine are present in the hydrolyzates of chlorocellulose indicates that the reactive chlorine in the cuprammonium and sodium hydroxide treatment liquors is probably not caused by the presence of reactive organic chlorides but rather by the presence of chloride ion.

The resistance of chlorocellulose to sulfuric acid hydrolysis increases as the chlorine content of chlorocellulose increases. Smaller yields of hydrolyzate and greater quantities of hydrolysis insolubles, which contain a somewhat higher degree of chlorine substitution than the original chlorocellulose, are produced as the chlorine content of chlorocellulose increases. In addition, during the quantitative chromatographic separation of the components of a hydrolyzate, a large portion of the hydrolyzate exhibited R_f values equal to and less than the R_f value of cellobiose. This portion contains most of the chlorine which was originally present in the hydrolyzate.

Glucose has been definitely established to be the main constituent of one of the large, chromatographically separated fractions of a hydrolyzate of chlorocellulose. This fraction contains 47.2% of the original hydrolyzate. The isolation of a large glucose fraction signifies that a large portion of the anhydroglucose units in the original cellulose did not react with thionyl chloride. Paper partition chromatograms qualitatively disclose that the quantity of glucose contained within the hydrolyzates of chlorocellulose decreases as the chlorine content of chlorocellulose increases.

The quantitative chromatographic separation of the components of a hydrolyzate resulted in the collection of some materials which have no reducing power or optical activity; these substances may be noncarbohydrate in nature, but this has not been experimentally verified.

Four fractions of a quantitatively chromatographed hydrolyzate, which was obtained from an incompletely purified product, possess chlorine contents ranging between 11.2 and 13.5% chlorine. These fractions contain 10.8% of the material originally present in the hydrolyzate and 21.7% of the original chlorine. Since a monochlorohexose (probably 6-chloroglucose) has been isolated from one of these fractions, it is conceivable that other unidentified chlorosugars are contained within the other highly chlorinated fractions.

Two of the chromatographically separated components of a hydrolyzate react with silver nitrate to form silver chloride. This does not conflict with the previous observation that the hydrolyzates yield only faint traces of silver chloride when treated with silver nitrate. The solubility of silver chloride offers a satisfactory explanation; the hydrolyzates which have been tested were present in dilute solutions, whereas the fractions which have been tested were present in concentrated solutions.

Carbon and hydrogen analyses of purified chlorocellulose indicate that there is an excess of oxygen atoms above and beyond the number required to combine with hydrogen atoms to form hydroxyl groups. It is possible that these excess oxygen atoms are present in the form of anhydro or carbonyl linkages. One of the fractions obtained from a quantitatively chromatographed hydrolyzate exhibits a very highly negative specific rotation; most of the fractions have substantial positive rotations. The presence of a negatively rotatory fraction may

be caused by material which contains carbonyl groupings or anhydro linkages. The negative rotation may also be caused by the rupture of the anhydro groupings, with the occurrence of Walden inversion, to form sugars whose configuration has been altered. However, no experimental work has been performed to verify the possible presence of carbonyl groupings, anhydro linkages, or changes in structural configuration.

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