# PREPARATIONS AND PROPERTIES
# OF
# METHYL ALLYL CELLULOSE ETHERS

A Thesis

by

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# Preparations and Properties of Methyl Allyl Cellulose Ethers

In special rocket propellants, burning of the nitrocellulose-nitroglycerine (cordite) tube must be completely restricted to the inside surface of the cordite by applying suitable coatings to the outside surface. Various methyl allyl celluloses containing about 0.5 to 1.5 allyl groups per glucose unit have been prepared from an alkali soluble methylcellulose. Three studied in detail contained 0.70 methyl and 0.79 allyl, or 0.59 methyl and 0.95 allyl and 0.59 methyl and 1.47 allyl groups. The solubilities and properties of these substances, together with the acetate and dibromide of the latter, were noted. Methods for estimating the degree of unsaturation of these compounds were worked out including a modified bromide-bromate method.

A study of the changes in physical properties of methyl allyl cellulose films, cross-linked by polymerization of the allyl groups, indicated that polymerization decreased their solubility, flexibility, elongation at break, and moisture vapour permeability, while their tensile strength remained almost constant. Films of the more highly allylated derivative, when polymerized, satisfied the standard test for nitroglycerine barriers.

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# GENERAL INTRODUCTION

In special rocket propellants, burning of the nitrocellulose-nitroglycerine (cordite) tube must be completely restricted to the inside surface of the cordite by applying suitable coatings to the other surfaces. A suitable coating usually consists of a nitroglycerine barrier, a fireproof paint (like Glyptal Red 1201) and an adhesive tape carrying a rubber base cement. The main war purpose of this research is to find out whether or not unsaturated ethers of starch and cellulose might form suitable coatings for inhibiting the diffusion of nitroglycerine.

Nitroglycerine diffusion will cause the coating to burn almost as easily as the propellant, exposing more burning surfaces and producing too high pressures in the rocket. In order to eliminate burning irregularities as completely as possible, a coating must fulfil the following requirements:

(a) adhere sufficiently tightly to the cordite so that no burning can occur between the coating and the cordite.

(b) resist the diffusion of nitroglycerine for any length of time and at any temperature up to 65°.

(c) have a temperature coefficient of expansion similar to that of cordite, so that the coating-cordite union can withstand cycling between -40° and 60°, the extreme conditions likely to be encountered in military or naval operations.

Preliminary work consisted of preparing a number of allyl starches in various ways. Generally, these allyl starches formed films that adhered tightly to the cordite, prevented nitroglycerine diffusion, but on exposure to air were easily oxidized, polymerized and became extremely brittle. This relative ease of polymerization in air made physical tests on the unpolymerized films very difficult. For these reasons the work on allyl starches was diverted to work on allyl cellulose ethers. These ethers, derived from the linear macromolecules of cellulose, should form much stronger films than the corresponding branch chain molecules of starch. Moreover, the lack of branching in cellulose derivatives made it less difficult to assess any effect that subsequent cross linking, caused by polymerization of allyl groups, might have on the diffusion of nitroglycerine.

Since cellulose ethers were generally more stable and possessed greater film strength than cellulose esters, the former type of compound was chosen. The main purpose in the preparation of methyl allyl celluloses was to produce unsaturated ethers of maximum solubility in some common solvent or mixture of solvents, with minimum degradation of the cellulose chain, and adapted to form strong, clear, uniform films. After an examination of the available literature on allyl cellulose and related compounds, no clear, concise method of preparing a product with the above characteristics was found. Consequently, the first part of the research consisted of preparing such derivatives. In order to carry out the allylation in a homogeneous medium with minimum degradation, an alkali-soluble, stable methylcellulose ether was used as a starting material.

The second part of the research consisted of converting the methyl allyl celluloses into transparent films and then deciding by suitable physical tests whether or not these films offered promise as nitroglycerine barriers. These tests, which included measurements of tensile strength, elongation or stretch, Mullen burst test, flexibility, moisture vapour permeability, and nitroglycerine diffusion were performed on methyl allyl cellulose films both in the unpolymerized and polymerized states.

# HISTORICAL INTRODUCTION

## I. STRUCTURE OF CELLULOSE.

Proof of the structure of cellulose has now been well established and can be found in scores of relevent references in any of the modern technical books or reviews on the subject (1, 2, 3).

Today cellulose is considered to be a linear macromolecule composed of $\beta$-glucopyranose units, each of which is depicted (Fig. 1) with five carbon atoms in the plane of the paper, with the oxygen atom completing the ring not in this plane. When viewed in perspective, the hydroxyl groups and the glucosidic group are arranged above and below the plane of the paper so that their distribution is "trans". When the glucose units are linked in chains, the glucopyranose ring alternates in respect to the side that is uppermost. This conclusion is supported by X-ray data. The 1, 4-glucosidic linkages between the cellulose chains are limited in their free rotation by certain stereochemical restrictions (4). From this structure, both terminal glucose residues are distinguished from the other glucose units in the body of the chain; the right hand terminal unit by the presence of a reducing hemiacetal group, and the left hand unit by the presence of an extra hydroxyl group.

The glucose residues in the cellulose chain are held together by primary valence force of about 50,000 calories per mole. According to the Astbury micellar fringe theory, the very long cellulose chains form amorphous and crystalline regions each of X-ray dimensions. The crystalline portions of the cellulose chains adhere to their neighbours by hydrogen bonding of approximately 15,000 calories per mole in strength.

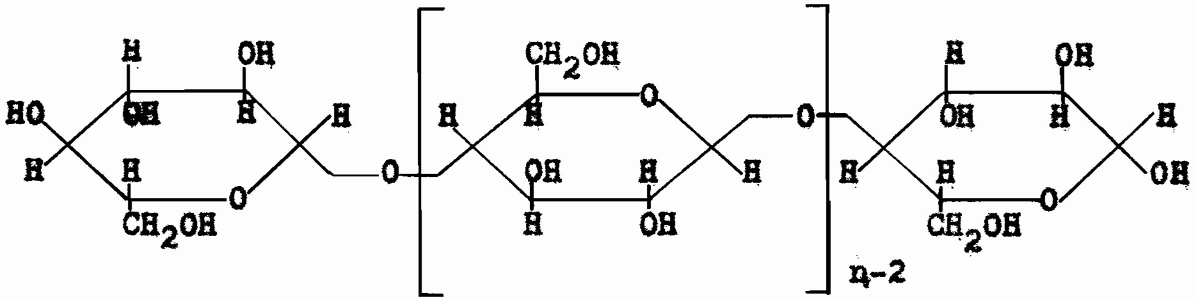


Fig. 1

Cellulose Macromolecule of n glucose units

Because of the organized, cumulative strength of the crystal forces, the crystalline portions are much less accessible to most chemical reagents than the amorphous portions. For this reason, reactions carried out on fibrous cellulose often change the amorphous portions greatly while the crystalline portions are affected only to a minor extent.

Inspection of Fig. 1 shows that each of the $\beta$-glucopyranose residues possesses two secondary and one primary hydroxyl groups. The primary hydroxyls in position 6 generally react more rapidly than the two kinds of secondary hydroxyls in positions 2 and 3. For example, Purves and his collaborators have shown the relative rates for the esterification of positions 2, 3 and 6 to be 2.3, 0.07 and 15 (5) for ethylcellulose and 2.2, 0.11 and 23 for cellulose acetate (6), respectively. In these cellulose derivatives at least one of the secondary positions was already substituted with ethoxyl or acetate groups, and so the relatively low reactivity of the other secondary hydroxyls may be caused by some repulsive effect of an electrical or steric nature. Cellulose dispersed in quaternary bases alkylates in the primary positions with a rate equal to the sum of the rates of the two secondary positions (5). Also, when cellulose is swollen in alkali, the secondary positions react more rapidly, and the relative rate of alkylation in the secondary positions increases as the alkali concentration increases (5). Spurlin (7) has fully discussed the rates of reaction of the various hydroxyl groups, and so detailed mention of the subject here seems unwarranted.

These hydroxyl groups react according to the laws of chance (7) and the arrangement of the substituents in the cellulose derivatives depends largely upon whether the reaction is carried out in homogeneous medium or not.

## II. STRUCTURE OF STARCH

The structure of a starch molecule (8) differs from that of the cellulose molecule in several ways. In the first place, the starch molecule is regarded as a coiled macromolecule, composed of $\alpha$-glucopyranose residues. Secondly, the starch consists of two different polysaccharides, water soluble amylose and less soluble, paste-forming amylopectin. The amylose consists mainly of a homogeneous mixture of linear, or nearly linear, polymers in which 100 to 700 glucose residues are united in the $\alpha$-1:4-glucosidic arrangement (See Fig. 2).

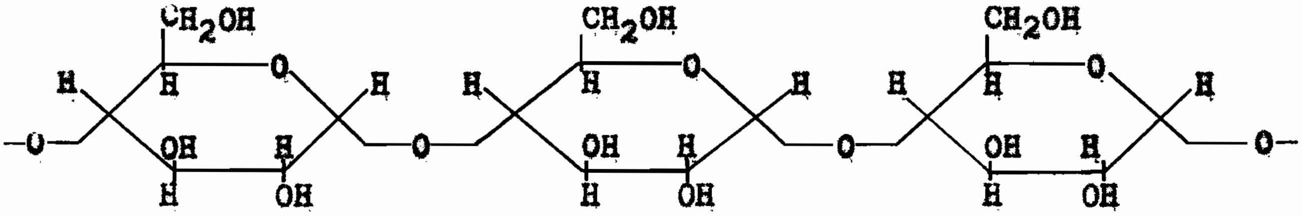


Fig. 2

Section of Amylose Chain

The amylopectin fraction consists of large, branch-chained molecules, each containing 500 to more than 2000 glucose residues in which the branching occurs on the average at every twenty-fifth glucose unit. The branching is supposed to originate at primary alcohol units. (See Fig. 3)

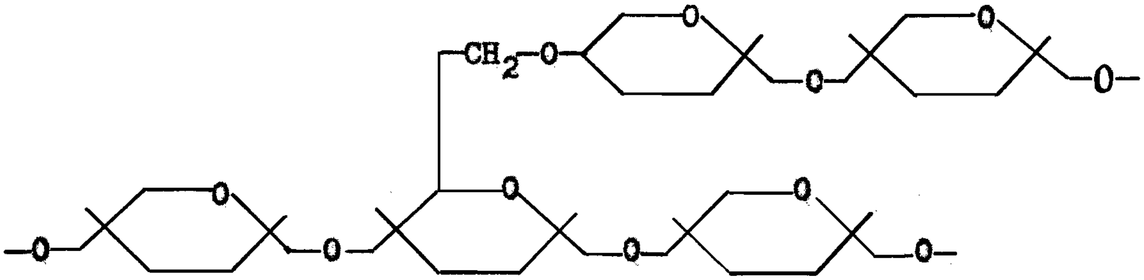


Fig. 3.
Branch Point of Amylopectin

Whistler and Hilbert (9) have found wide variations in the mechanical properties of films made from the acetates of amylose, amylopectin and whole starch. In general, amylose triacetate and trimethyl amylose form good films, while the same derivatives produce very poor films when based on the amylopectin portion of the starch granule. No studies of the relative reactivity of the three kinds of hydroxyl groups in the starch macromolecule have hitherto been made.

## III ADVANTAGES OF CELLULOSE ETHERS OVER CELLULOSE ESTERS

The decision to prepare unsaturated ethers instead of unsaturated esters of cellulose was based mainly on the fact that cellulose ethers possess greater stability than cellulose esters to heat, light, water, alkali and even dilute acids. Cellulose ethers are not hydrolyzed by water at 170° for many days, and their desirable physical properties are unaffected by a 25 per cent solution of potassium hydroxide. Demarest, Moeller and Cash (10) observed that cellulose acetate and cellulose butyrate plastics are badly distorted when exposed to a temperature of 90° and a relative humidity of 100 per cent for twenty-four hours, while an ethyl cellulose plastic was unaffected. On exposure to ultra-violet light, most cellulose ether films and coatings are not discoloured. Unplasticized cellulose ester films are hard and brittle, while those of unplasticized ethyl cellulose films are softer, tougher and more elastic. The tensile strengths of unplasticized cellulose acetate and ethyl cellulose films are much the same, but the plasticized ether film is many times stronger than the similar ester film. Finally, cellulose ethers are relatively less flammable than those of cellulose esters. The only disadvantage of cellulose ethers is the high cost of the etherifying agents (11).

## IV. UNSATURATED ESTERS OF CELLULOSE

Even though this work deals with unsaturated ethers rather than unsaturated esters of cellulose, it seems advisable briefly to review the pertinent literature concerning the latter, with the object of being able to note later on similarities in their properties and film-forming characteristics.

In general, the preparation of unsaturated esters is similar to that of the saturated esters of cellulose, except in cases where the unsaturated linkage may complicate the behaviour of the esterifying agent. For example, acrylic acid polymerizes during the esterification so is not a satisfactory esterifying agent. The general methods of preparing lower (12, 13, 14), higher (15, 16) and mixed (17, 18) unsaturated esters are fully discussed in many patents; and since we are not directly concerned with such esters in this research, further details will not be given.

The freshly prepared lower substituted, unsaturated cellulose esters are soluble in a wide range of common organic solvents. For example, cellulose tricrotonate is soluble in acetic acid, acetone, chloroform, benzene and in mixtures of solvents, such as benzene-alcohol. The higher unsaturated esters of oleic, linoleic, ricinoleic and similar acids are usually insoluble in all solvents unless care is taken to prepare them in inert atmospheres, such as carbon dioxide or nitrogen (19). The lower unsaturated cellulose esters of such acids as crotonic form transparent (17), flexible (16) films, which are oxidized very slowly in the air, or more quickly by heat or ultra-violet light, into products almost completely unaffected by most organic solvents and impermeable and resistant to moisture. The higher unsaturated esters are very resistant to moisture, form flexible films and are converted upon drying at room temperature into insoluble products.

Malm and Fordyce (20) in their patent claim that their unplasticized unsaturated cellulose ester films are polymerized by five hours of exposure to intense ultra-violet light, or by twenty-four hours of heat at approximately 100° , into tough, transparent, very flexible films, insoluble in common solvents and of improved resistance to moisture. The moisture impermeability of the film is increased three or four fold from the original value before polymerization. However, Hagedorn and Moller (21) pointed out that the unsaturated cellulose esters with a short carbon chain (cellulose crotonate) give brittle masses with little strength or elasticity. They also mentioned that cellulose linoleate ignites spontaneously in air unless kept in a moistened condition.

## V. UNSATURATED ETHERS OF SIMPLE CARBOHYDRATES

Since this research deals briefly with allyl starches, and in more detail with methyl allyl cellulose and its derivatives, it seems advisable to discuss these compounds' simpler analogues in order to obtain as clear a picture as possible of probable methods of preparation and of the probable properties of the macromolecular materials.

The first simple allyl carbohydrate derivatives, allyl tetraacetyl $\alpha$-D-glucoside and allyl $\alpha$- and $\beta$-glucoside, were prepared by Fischer and Strauss (22) and Bourquelot and Bridel (23), respectively, in 1912. Twenty-one years later Tomecko and Adams (24) produced various unsaturated ethers, such as methyl tetraallyl $\alpha$-glucoside and pentaallyl sucrose. These papers and others produced little exact information regarding the properties of these allyl carbohydrates. However, recently Nichols and Yanovsky have completely discussed this type of compound in a series of excellent papers.

Nichols and Yanovsky have prepared in good yields a series of allyl ethers from non-reducing carbohydrates (25,26) such as methyl $\alpha$-glucoside, sucrose and sorbitol by treating them with 50 per cent aqueous caustic soda and allyl bromide at the reflux temperature of allyl bromide for four to five hours. The resulting oils of high boiling-point were not completely substituted and so were given a further treatment with sodium, forming sodium alcoholates. These alcoholates were again heated under reflux with more allyl bromide for two hours, and there resulted in most cases completely, or almost completely, substituted allyl carbohydrate derivatives. In another paper (27) they succeeded in allylating reducing carbohydrates, such as glucose, by first forming the allyl $\alpha$-glucoside according to the standard Fischer method. That is, dry hydrogen chloride gas was dissolved in dry allyl alcohol and stirred with anhydrous glucose. The resulting glucosides, being stable in alkali, were almost completely allylated in the manner already described for non-reducing carbohydrates.

Nichols and Yanovsky found that these oily carbohydrates polymerized in air and in oxygen, especially at higher temperatures, into insoluble, infusible, colourless, transparent, brittle, thermosetting resins. In order to obtain a possible mechanism for the apparent polymerization of these allyl ethers, the following series of experiments were performed. Firstly, from a rate of polymerization study, the necessity of oxygen throughout the polymerization was observed. The rate of polymerization curves were obtained by passing oxygen at a uniform rate over the oily allyl ethers at 97° and measuring their increase in viscosity at various times. In an atmosphere of carbon dioxide instead of oxygen, the viscosity remained practically constant. It also was noted that if polymerization was carried to a certain point and then heating was continued in the absence of oxygen, in every case polymerization proceeded normally for a short time and then appeared to stop. It followed that heat alone would not convert the oils into hard, brittle resins. The actual amount of oxygen combined was observed by combustion analysis (See Table I) on samples that had been heated at 97° in a constant stream of oxygen for various lengths of time.

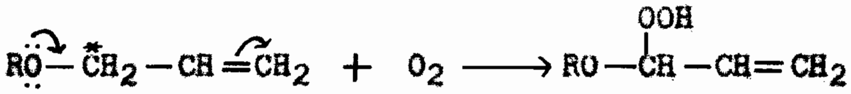
TABLE I

Oxygen Combined in Polymerization of Methyl Tetraallyl α-Glucoside

| Time (hours) | Carbon % | Hydrogen % | Combined Atoms of oxygen per Molecule |
|---|---|---|---|
| 0 | 63.92 | 8.11 | 0 |
| 3½ | 59.90 | 7.50 | 1.7 |
| 5½ | 58.50 | 7.20 | 2.2 |

Secondly, tests during polymerization of these allyl ethers indicated the formation of peroxides. Finally, a strong odour of acrolein always accompanied oxidation and polymerization of all allyl ethers. In the case of allyl mannitol, acrolein was collected during the oxidation and identified by means of its 2-4 dinitrophenylhydrazone and the Schiff's aldehyde test. With this evidence they suggested the following mechanism for oxidation and polymerization of all allyl ethers of simple carbohydrates.

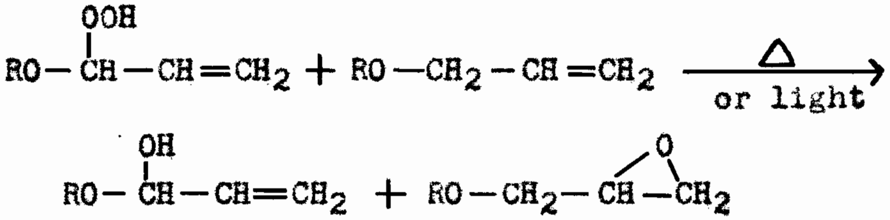
(a) Formation of hydroperoxide at the α-methylenic carbon atom, which is reactive, since it is adjacent to an ether oxygen containing unshared pairs of electrons and in α-position to a double bond.



$$RO-CH_2-CH=CH_2 + O_2 \longrightarrow RO-\overset{OOH}{\overset{|}{CH}}-CH=CH_2$$

peroxide

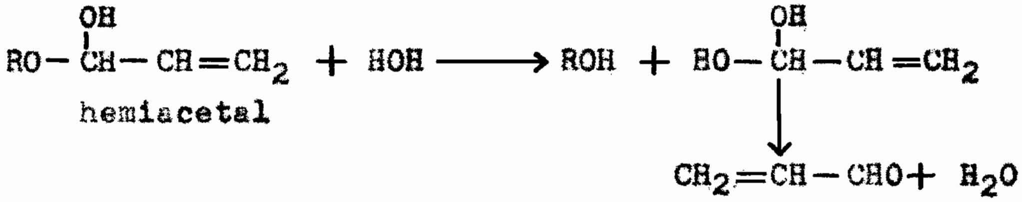
(b) Decomposition of the Peroxide. In the presence of heat or light the double bond is oxidized with the formation of an epoxy compound.



hemiacetal

epoxy compound

(c) Hydrolysis of the Hemiacetal into Acrolein. A trace of water, which should be formed during oxidation of this type, would readily hydrolyze the hemiacetal into acrolein.

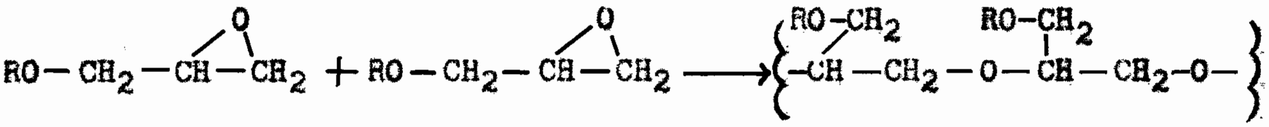


$$RO-\overset{OH}{\overset{|}{CH}}-CH=CH_2 + HOH \longrightarrow ROH + HO-\overset{OH}{\overset{|}{CH}}-CH=CH_2 \;\downarrow\; CH_2=CH-CHO + H_2O$$

hemiacetal

acrolein

(d) Epoxy Compounds easily Polymerized by cross linking into three dimensional networks.



## VI. UNSATURATED ETHERS OF STARCH AND CELLULOSE

Many hundreds of patents and papers have been written concerning cellulose ethers ever since Suida (28) first prepared one in 1905. However, in this extensive literature, very little exact information concerning the preparation and properties of unsaturated cellulose ethers, completely soluble in common solvents, appears. This statement also was true of unsaturated starch ethers until just recently when Nichols, Hamilton, Smith and Yanovsky (29) published their work on certain allyl starches. It, therefore, seems desirable to review the general methods available for etherification, and then to discuss the preparation and properties of the unsaturated ethers.

### (1) Methods and Mechanism of Etherification.

The etherification of the alcohol groups in polymolecular carbohydrates is usually brought about by the action of alkyl sulphates in the presence of an alkali; by alkyl halides and pyridine; and by alkyl halides and alkali. The last of these methods is most general, the first being applied only to methylation and ethylation, and the second being limited to reactions with very labile halides. Special methods (30, 31) recently have used sodium or sodamide in liquid ammonia to form the sodium cellulosate and then have carried out the alkylation with lower alkyl halides soluble in liquid ammonia. Diazomethane and ethylene oxide and its homologs are sometimes used as etherifying agents. The former methylates the cellulose, while the latter adds directly to the cellulose to form hydroxyalkyl ethers.

Further details on the various starch and cellulose ethers that have been prepared in these general ways seem unnecessary, in view of the many fine books and reviews now available on the subject (11, 32, 33, 34, 35, 36).

### (a) Etherifications with Alkyl Halides and Alkali

The reaction is probably represented by the following general equations, only one of the three kinds of hydroxyls in the cellulose or starch being indicated, and RX being any alkyl halide.

$$C_6H_9O_4-OH + NaOH \rightleftharpoons C_6H_9O_4-ONa + H_2O \qquad (1)$$

$$C_6H_9O_4-ONa + RX \longrightarrow C_6H_9O_4-OR + NaX \qquad (2)$$

Bock (37) has shown that etherification by an alkyl halide or sulphate carried out in a homogeneous medium (i.e. cellulose dissolved in a quaternary ammonium hydroxide) produces ethers that are soluble in water although such ethers contain only 0.6 to 0.7 methyl or ethyl groups. The introduction of 1.2 to 1.7 groups is usually necessary in order to produce a water soluble ether in the regular heterogeneous alkali cellulose process. Bock's explanation for this difference is that a more even distribution of alkyl groups along the macromolecules is obtained when cellulose is alkylated in solution. Purves and Mahoney (38) have confirmed this explanation in the case of an ethylated cellulose. Since this thesis is principally concerned with homogeneous etherification, it is hardly necessary to consider the additional factors of importance in heterogeneous processes. These factors, including the function of water and alkali in swelling the fibrous cellulose, are discussed elsewhere (39).

### (b) Side Reactions

A number of possible side reactions can take place during etherification owing to alkaline hydrolysis of the alkyl halide to an alcohol, an ether or an unsaturated olefin.

$$RX + NaOH \longrightarrow ROH + NaX \qquad (3)$$

$$ROH + RX + NaOH \longrightarrow R_2O + NaX + H_2O \qquad (4)$$

$$R\cdot CH_2\cdot CH_2X + NaOH \longrightarrow RCH{=}CH_2 + NaX + H_2O \qquad (5)$$

At high alkali concentrations the alcohol primarily produced will react with more alkyl halide to form the corresponding ether. Lorand (40) has found that the amount of hydrolysis of benzyl chloride to the corresponding alcohol and ether increased with increase in temperature, rate of stirring and time; and decreased with increase in the benzyl chloride-caustic soda ratio. Also the hydrolysis increased at first with an increase in the caustic soda concentration and reached a maximum at about 20 per cent alkali; it then fell off rapidly. Smith et al (29) showed that when equal volumes of allyl bromide and sodium hydroxide were mixed and stirred for three hours at 80°, about 23 per cent of allyl bromide was hydrolyzed with alkali concentrations up to 10 per cent; about 9 per cent with 20 to 30 per cent alkali; and only about 2.5 per cent with 40 to 50 per cent alkali. Consequently, the amount of etherifying agent going to side reactions will be considerable, unless all the above factors, particularly alkali concentration, are properly adjusted.

### (c) Function of Alkali in Homogeneous Solution

The alkali probably reacts with the hydroxy groups in the polymolecular carbohydrate to form either a molecular complex (equation 6) or a true alcoholate (equation 7).

$$xC_6H_9O_4{-}OH + yNaOH \rightleftharpoons (C_6H_9O_4{-}OH)_x \cdot (NaOH)_y \qquad (6)$$

$$C_6H_9O_4{-}OH + NaOH \rightleftharpoons C_6H_9O_4{-}ONa + H_2O \qquad (7)$$

Most of the evidence for a molecular complex formation comes from work on heterogeneous alkali cellulose. For example, numerous workers from different kinds of evidence (41) have suggested that in alkali concentrations of 12 to 18 per cent, a complex, $(C_6H_{10}O_5)_2 \cdot NaOH$, is probably formed and in 20 to 40 per cent alkali another with the composition , $C_6H_{10}O_5 \cdot NaOH$. X-ray data strongly support a new crystal structure for cellulose, and compound formation, in alkali of about 21 per cent concentration. Also, the fact that cellulose forms soluble complexes with cuprammonium and with the analogous diamine compounds, lends further support to equation 6. The majority of investigators in this field prefer the molecular complex type of structure (equation 6) to the alcoholate (equation 7) in the presence of water, since the latter compound is readily hydrolyzed by water.

On the other hand, a considerable amount of evidence seems to indicate that cellulose, like the simple alcohols and certain polyhydric compounds, forms a true alcoholate. Various metallic alcoholates of cellulose have been prepared. Scherer and Hussey (42), for example, obtained a trisodium alcoholate by treating cotton with metallic sodium in liquid ammonia. The resulting product possessed the properties of a normally prepared alkali cellulose and formed an xanthate with carbon disulphide. They showed that the hydrogen evolved from a definite amount of sodium reacting with cellulose corresponded to the reaction of an alcohol with sodium.

$$ROH + Na \longrightarrow RONa + \tfrac{1}{2}H_2 \qquad (8)$$

Harris and Purves (43) also showed that thallous ethylate (a strong base like its sodium analog), dissolved in ether or benzene, forms an insoluble thallium cellulosate as follows:

$$C_6H_9O_4-OH + TlOC_2H_5 \rightleftharpoons C_6H_9O_4-OTl + C_2H_5OH \qquad (9)$$

This reaction does not proceed to completion as the large thallium atoms cannot enter the crystalline portion of the cellulose structure, so that only the surface hydroxyl groups are available for reaction.

Further indications of the formation of an alcoholate are obtained from the chemical reactions of alkali cellulose. Alkali cellulose reacts similarly to sodium ethylate, in that it forms an xanthate with carbon disulphide, ethers with alkyl halides, and esters with acidic anhydrides.

Most likely the mechanism is a combination of equation 6 and 7. That is, an addition compound is first formed, which loses water forming the alcoholate.

$$\begin{tikzcd} C_6H_9O_4{-}OH + NaOH \arrow[r, rightleftharpoons] & C_6H_9O_4{-}OH\cdot NaOH \arrow[d, rightleftharpoons] \\ & C_6H_9O_4\cdot ONa + H_2O \end{tikzcd} \qquad (10)$$

This mechanism is possibly correct since the degree of etherification depends upon the factors likely to govern the above equilibrium, such as, concentration of alkali, water, cellulose and temperature. It is found that on increasing the sodium hydroxide-water ratio and decreasing the water-cellulose ratio, the degree of substitution is increased. Lorand (40), for example, has increased the ethoxyl content of a commercial ethyl cellulose by increasing the concentration of the sodium hydroxide at the end of the reaction, thus forcing the equilibrium to the right.

### (d) Function of Etherifying Agent

In choosing an etherifying agent, many factors must be considered; such as its activity, molecular size, solubility in alkali, and the nature of its alkyl radical, in order to obtain a cellulose ether with certain required properties.

For example, a water-soluble or an alkali-soluble ether may be prepared by slightly etherifying (0.5 to 0.7 groups) of the alkali cellulose with methyl or ethyl halides and not with long chain alkyl halides.

An alkyl iodideis more reactive than an alkyl bromide, or chloride, but, owing to its slow diffusion rate, is largely converted into by-products, and so is rarely used as an etherifying agent. Ball (44) quotes the relative reactivities of ethyl chloride and allyl bromide on the basis that normal butyl chloride is unity as two and eighty, respectively. These ratios explain why allylation proceeds more easily than ethylation (45).

The alkyl halides used in etherification are generally only slightly soluble in the aqueous hydroxide. Their solubilities decrease with the size and kind of alkyl groups and with the caustic concentration. Allyl bromide is less soluble in aqueous alkali than methyl or ethyl bromide and the inability to obtain fully allylated products (45) may be connected with this fact.

Primarily alkyl groups containing three or more carbon atoms, benzyl groups and others, are hydrophobic in character. Consequently, when they react with the alkali cellulose they form an increasingly hydrophobic etherified cellulose, which naturally hinders the access of fresh aqueous alkali to the reaction zone. Therefore, in order to get the same degree of subsitution, an ether containing more hydrophobic radicals must undergo much more drastic reaction conditions than an ether such as methyl containing less hydrophobic radicals. The more drastic the reaction conditions, the more degraded (low viscosity) the product is likely to be.

### (e) The Rate of the Etherification Reaction

The rate of etherification increases with an increase in the sodium hydroxide:water and the etherifying agent:cellulose ratios. Increase in temperature or rate of stirring always increases the velocity of the reaction. An inert solvent, while often improving the homogenity of the reaction mixture, usually lowers the reaction speed (40, 46) possibly by diluting the reactants.

## (2) Preparations and Properties of Unsaturated Ethers

### (a) Allyl Starches

Tomecko and Adams (24) in 1923 prepared what they called a "monoallyl starch" by mixing starch, 10 per cent aqueous potassium hydroxide and allyl bromide. This product, which contained 0.5 allyl groups per glucose unit, according to combustion analysis, was a white amorphous powder of low solubility. The low substitution was probably connected with extensive hydrolysis of the allyl bromide in the presence of alkali so dilute as 10 per cent.

The Eastern Regional Research Laboratory (29) recently prepared soluble allyl ethers of starch by direct alkylation of various starches with allyl chloride and 50 per cent aqueous sodium hydroxide. Allyl bromide, the 50 per cent alkali and acetone-soluble starch acetates were also used. Their yields were around 90 to 98 per cent of theory in all cases and their products from various starches had an allyl content of 30.0 to 37.5 per cent, as estimated by the Wijs method for double bonds. These percentages correspond to 1.7 to 2.4 allyl groups per glucose unit.

Allyl starch prepared by their method was a soft, gummy, but not tacky, substance. It was soluble in most organic solvents but not in aliphatic hydrocarbons. Solutions of allyl starch in acetone, alcohol, and other solvents were stable and even in 30 per cent concentration had a low viscosity. Films of allyl starch, on exposure to the air, gradually polymerized and became insoluble, the process being 13 to 73 per cent complete after a week. This process of insolubilization was catalyzed by heat, chemical agents such as cobalt naphthenate, infrared and ultra-violet radiation. The authors list several possible industrial applications ofthese allyl starches, including lacquers, varnishes, adhesives, and plastics.

### (b). Unsaturated Cellulose Ethers

#### (1). Vinyl Cellulose

The first member of this series, vinyl cellulose, was recently isolated and studied by Favorskiĭ and collaborators, (47, 48). Cotton linters was heated in the presence of alkali with acetylene under pressure and in an autoclave at 120° to 150° for four to forty-eight hours. The resulting product had a carbon content of 49.1 to 58.3 per cent, and a hydrogen content of 6.2 to 6.6 per cent, corresponding to the formation of divinyl and some trivinyl ether of cellulose. This product was partly soluble in dioxane, ethyl acetate, glycol chlorohydrin and dichloroethylene, also in Schweitzer's reagent. Although this new method of obtaining vinyl cellulose ethers is interesting, the mixture of unreacted cellulose, monovinyl, divinyl and trivinyl ether produced is still of restricted value because it is only partly soluble.

### (ii) Allyl Cellulose

A completely insoluble and possibly impure allyl cellulose was prepared by Tomecko and Adams (24) in 1923 by treating cellulose reprecipitated from cuprammonium hydroxide solution with allyl bromide and potassium hydroxide. Combustion analysis gave a carbon content of 45.15 per cent and a hydrogen content of 6.44 per cent values which proved the product was mainly cellulose.

In 1929 Sakurada (49) obtained a snow-white mixture of diallyl and triallyl ethers of cellulose in one operation by suspending shredded cotton paper in 40 to 50 per cent sodium hydroxide and subjecting the resulting alkali cellulose to the action of allyl bromide. This etherification proceeded relatively easily. Combustion and halogen adsorption analyses agreed, showing that the double bonds had remained intact.

A tetrabromide corresponding to that from a diallyl ether also was obtained.

All allyl cellulose ethers prepared by Sakurada were only partly soluble in ethyl alcohol, benzene and carbon tetrachloride, possibly because of the heterogeneous manner in which the etherification was carried out. Although the purified ether was stable to heat, its low solubility appeared to render it undesirable for present purposes. Moreover, its alcohol soluble fraction most probably had a low degree of polymerization.

In 1941 Haller and Heckendorn (50) were able to facilitate further substitution by allylating alkali cellulose in the presence of xylene, which exerts a swelling effect on the partly substituted ether.

Several patents were taken out by Dreyfus in 1931 (51) on the production of allyl celluloses. Seymour (52) claimed to have prepared unsaturated cellulose ethers, including allyl cellulose, more or less soluble in toluene, xylene, benzene, acetone, ether or alcohol, and readily soluble in alcohol-benzene. These products on exposure to ultra-violet light became insoluble in all common organic solvents. Other patents, a few of which are quoted here (53, 54, 55), claimed improvement in the dyeing properties of cellulose materials by converting them completely, or partially, into allyl cellulose. However, in most patents details of the preparations are missing or vague.

### (iii) Crotonyl and Higher Unsaturated Celluloses

Preparations of crotonyl cellulose and other higher unsaturated ethers were patented by the British Celanese Limited (56). Etherification was effected in the presence of a base, either in an aqueous medium or in an organic solvent, such as benzene and toluene. These ethers could be made into films that were easily polymerized to insoluble products on exposure to light or heat. Halogenation yielded products of reduced inflammability. Dykstra (57) also rendered crotonyl cellulose films insoluble by ultra-violet light and driers, such as cobalt oleate (cf. allyl starch p. 24).

Other unsaturated mixed ethers, such as chlorobutenyl or ethyl chlorobutenyl cellulose and benzyl cinnamyl cellulose, were described in patents by Ellsworth (58) and others.

A British patent (59) claimed to have produced a halogenated unsaturated cellulose ether by employing such etherifying agents as 1-3 dibromo-2-butene and 1-2-3 trichloropropene. These halogenated ethers of cellulose had a low inflammability.

Very recently, Ushakov (60) prepared a mixed ether, ethyl allyl cellulose, by heating alkali cellulose with a mixture of ethyl chloride and allyl bromide in an autoclave. This product is stated to have "copolymerized with sulphur dioxide", but exact details of the properties of the product are not yet available.

## VII HALOGENATION METHODS FOR DETERMINING UNSATURATION OF ORGANIC COMPOUNDS

A great number of quantitative methods can be found in the literature for determining the unsaturation of organic compounds. The easiest and perhaps best methods involve the use of halogen or iodine monohalides. Of the three halogens, bromine is the most useful since chlorine, being very reactive, is likely to undergo substitution as well as addition reactions; and iodine, being very inactive, adds to very few ethylenic linkages. Buckwater and Wagner (61) subdivided halogenation methods into three main types based upon the nature of the agent and the medium; they are as follows:

(a) Iodine-halide method, such as thoseof Hübl, Wijs and Hanus, conducted in non-aqueous solvents (62,63,64).

(b) Bromination in non-aqueous solvent, especially carbon tetrachloride (61,70).

(c) Bromide-bromate method conducted in the presence of water (65, 66) and catalysts (67).

The Hübl, Wijs and Hanus methods probably use the least severe halogenating agents, especially the iodine halides, and so are used in analysis of fats, oils and unsaturated hydrocarbons where the possibility of substitution, as well as addition, to the double bond is likely to take place. The second method of bromination in non-aqueous solvents (61,64) is useful, since the extent of substitution can be measured by titrating the hydrogen bromide formed during the reaction, as well as the double bonds. These two methods are relatively slow and great care has to be taken to make sure all reagents are free of water.

The bromide-bromate method can be conducted in the presence of water and is relatively quick. However, if substitution is possible, as in the case of unsaturated fats, oils and hydrocarbons, great care must be taken not to have a large excess of bromine present. Lewis and Bradstreet (66) titrated unsaturated aliphatic hydrocarbons with a bromide-bromate solution in such a way as to reduce possible substitution to almost zero.

Caldwell and Pointkowski (68) showed that Hanus's method on unsaturated compounds, such as allyl alcohol and cinnamic acid, gave low or indefinite results. However, Cortese (69) pointed out that the bromide-bromate method of Francis (65) gave practically complete halogenation of allyl bromide and allyl alcohol (results - 0.97 and 0.96 double bonds, respectively). Also, in a very fine paper, Frognier and Goetsenhoven (70) determined the extent of unsaturation in many unsaturated compounds, such as vinylacetic-nitrile, ethyl vinylacetate and crotonic acid, by the bromide-bromate method, and claimed the method accurate and reproducible to about 0.2 per cent. They showed that the reaction was considerably faster in an ionizing medium, such as water and acetic acid, than in non-ionizing media, such as carbon tetrachloride and chloroform. For example, in a non-ionizing medium (carbon tetrachloride) crotonic acid was 6 per cent brominated in twenty hours, while in an ionizing medium (carbon tetrachloride and water) its bromination was complete in five minutes. They proved that temperature changes from 0° to 30° had very little effect on the amount of bromine absorbed in the case of crotonic nitrile. Finally, they found that light increased the rate of bromination.

A considerable amount of information is available on the proximity of negative groups retarding the addition of bromine, on the difficulty of halogenating conjugated systems and so forth, but in simple ethylenic compounds where substitution is unlikely, the bromide-bromate method should give good results. To understand fully any possible weaknesses of the method, a brief discussion of the mechanism of addition of halogens to ethylenic double bonds is desirable.

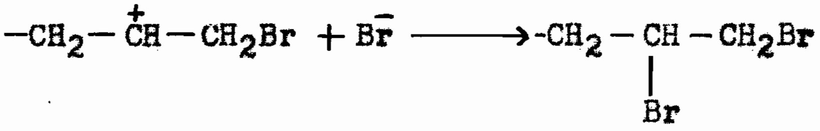
According to Ingold(71), Frognier and Goetsenhoven (70) and others (72), bromine's positive ion first adds to the double bond forming the positive carbonium ion as follows:

$$Br_2 \rightleftharpoons Br^+ + Br^- \qquad (11)$$

$$-CH_2-CH=CH_2+Br^+ \longrightarrow -CH_2-\overset{+}{C}H-CH_2Br \qquad (12)$$

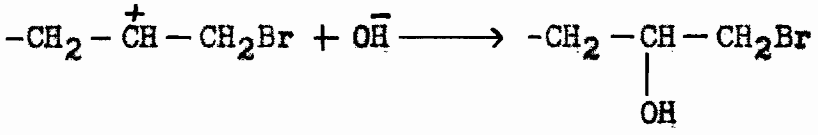
Now in the presence of water, either a negative bromine ion or a hydroxyl ion could add:

$$Br_2 + HOH \rightleftharpoons \overset{+}{H} + \overset{-}{Br} + BrOH \qquad (13)$$



$$-CH_2-\overset{+}{C}H-CH_2Br + \overset{-}{Br} \longrightarrow -CH_2-\underset{\displaystyle Br}{\underset{|}{CH}}-CH_2Br \qquad (14)$$

a dibromide



$$-CH_2-\overset{+}{C}H-CH_2Br + \overset{-}{OH} \longrightarrow -CH_2-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_2Br \qquad (15)$$

a bromohydrin

or

$$-CH_2-CH=CH_2 + Br(H_2O)^{+} \longrightarrow -CH_2-CHBr-CH_2OH + H^{+}$$

The amount of bromohydrin (equation 15) formed can be reduced by carrying out the reaction in a large excess of potassium bromide or an acid (70), which would not only repress the equilibrium reaction (equation 13), but also reduce the activity of the bromine (equation 11). However, the relative brominating activities of HOBr, Br and $\overline{Br}$ are given as 0.12, 80, and 110,000, respectively (73) and so the formation of the bromohydrin should be slight. Even if the bromohydrin does form, it will not interfere with the estimation of double bonds, since the bromide from the hypobromous acid will be immobilized as hydrobromic acid.

Sakurada (49) and the Eastern Regional Laboratories (29) used Wijs's method for determining the degree of unsaturation of allyl celluloses and allyl starches, respectively.

Sakurada showed that hydrocellulose treated with Wijs solution for forty-eight hours absorbed no halogens. The allyl celluloses he obtained were not soluble in the carbon tetrachloride and Wijs solution, but were swollen enough so that he was able to obtain satisfactory iodine numbers.

## VIII NITROGLYCERINE DIFFUSION

Hofer and Lumry (74), of the Explosives Research Laboratories at Bruceton, Pennsylvania, tried to eliminate nitroglycerine diffusion through coatings applied to double base propellant surfaces by electroplating with copper or silver. The metal coatings were completely impervious to nitroglycerine, but owing to the large difference in temperature coefficients of expansion between the plated metal and the powder grain, the two would not adhere sufficiently tightly to the cordite. Since this type of coating was unsuccessful, they next investigated extruded cellulose tubing as a possible nitroglycerine barrier.

This very dense flexible viscose cellulose sheath was plasticized with glycerine, which is completely insoluble in nitroglycerine, contained a preservative to prevent bacterial decay, and some other additants. After immersion in nitroglycerine for sixteen days, the sheath was not pulped, and its flexibility and thickness remained constant. However, 7.8 per cent of the sheath was soluble in the nitroglycerine, although no apparent change in its appearance was observed. Work carried out in the Dupont laboratories (74) showed that no common substance other than water, together with aqueous solutions and very finely divided suspensions passed through this sheath even under drastic conditions. It was pointed out that the glycerine in the pores of the sheath would possibly be removed after sufficiently prolonged warming and thereby cause a slight diffusion of the highly viscous nitroglycerine. They suggested that if desirable an increase in the density and thickness of the sheath would improve its value as a nitroglycerine barrier. The remainder of their report dealt with methods of coating the cordite SC grains with the cellulose sheaths. This mechanical problem was not completely solved.

In this introduction, an attempt has been made to produce as complete a picture as possible of the relevant information concerning starch, cellulose and unsaturated derivatives of simple and polymolecular carbohydrates. It is obvious from this discussion that the etherification of polymolecular carbohydrates to completely soluble derivatives with a reasonable degree of polymerization is still, to a large extent, an art learned only by experience. The preparation of products with the properties desired can only be based upon a detailed familiarity with all the reaction variables.

# EXPERIMENTAL PROCEDURES

## I. ALLYL STARCHES

A commercially available cornstarch was used for the preparations, in all of which the method of allylation recently published by the Eastern Regional Laboratory (29) was used. Starch acetate (10 g. air dry basis) was dissolved or highly swollen in a sufficient amount (25 - 225 cc.) of a suitable solvent (dioxane or acetone) and mixed in a flask with 50 per cent sodium hydroxide (25 g.) and allyl bromide (30 cc.). This flask was attached through a ground glass joint to a condenser and the contents were agitated for three and one half hours at the reflux temperature of allyl bromide by a stirrer placed down the centre of the inner tube of the condenser. The organic solvent was omitted when starch itself was used, the starch merely being suspended in the caustic soda. The excess alkali in the reaction mixture was neutralized with 5 per cent acetic acid and any unreacted allyl bromide and by-products, such as allyl alcohol and allyl ether, were removed by steam distillation. The allyl starches isolated when insoluble were thoroughly washed with water, when soluble were dissolved in a suitable solvent and reprecipitated. They were dried in air.

Table II summarizes the conditions for a few typical experiments. The properties of these allyl ethers (Table II) are discussed later. Product (a) was prepared by direct allylation of the starch, while product (b) was made by first degrading the starch in ethyl alcohol containing 0.5 per cent hydrochloric acid (75) and then allylating. The next three starch ethers (c), (d) and (e) were made by first preparing the acetate, by Mullen and Pacsu's pyridine-acetic anhydride method (76) from the undegraded starch, and from starches that had been slightly degraded by boiling with 5 per cent aqueous acetic acid for half an hour and three hours respectively. The last two acetates (f) and (g) were prepared by carrying out the acetylation in the presence of 0.1 per cent (77) and 5.0 per cent (78) concentrated sulphuric acid, respectively, which is a degrading catalyst. These acetates were completely soluble in the acetone solvent while (d) and (e) were only partially soluble. Allylation was carried out in the usual manner (29), the acetyl groups being simultaneously hydrolyzed by the 50 per cent alkali.

## TABLE II

## Experimental Conditions for Allylation of Starch

| Preparation | Weight Starting Material (grams) | Pretreatment of Starch | Aqueous NaOH (by weight) | Allyl Bromide (cc.) | Solvent (cc.) | Reaction Time (hours) | Appearance |
|---|---|---|---|---|---|---|---|
| (a) | Cornstarch 5 g. | none | 50 g. of 10% | 12 | - | 1 | White amorphous powder |
| (b) | Degraded cornstarch 2.5 g. | Boil ½ hr. with EtOH & 0.5% HCl | 12.5 g. of 20% | 17 | - | 3 | White and gummy |
| (c) | Undegraded starch acetate 10 g. | none | 25 g. of 50% | 40 | 100 dioxane | 14 | Yellow brown, soft and gummy |
| (d) | Slightly degraded starch acetate 10 g. | Boil ½ hr. with 5% HOAc | 25 g. of 50% | 30 | 225 acetone | 3½ | Straw white and flaky |
| (e) | Somewhat degraded starch acetate 10 g. | Boil 3 hrs. with 5% HOAc | 25 g. of 50% | 30 | 100 acetone | 3½ | Yellow-brown powder |
| (f) | Degraded starch acetate 10 g. | none | 25 g. of 50% | 30 | 25 acetone | 3½ | White and gummy |
| (g) | Very degraded starch acetate 10 g. | none | 25 g. of 50% | 30 | 25 acetone | 3½ | Light brown, gummy and sticky |

**NOTE:** The air dried commercial starch had a moisture content of 11.0% (approximately).

## II METHYL ALLYL CELLULOSES

### 1. Characteristics and Purification of Starting Materials

The methyl cellulose was a high grade commercial material prepared by a heterogeneous reaction from alkali cellulose. The batches used in this research had the characteristics listed in Table III.

### TABLE III

### Characteristics of Methyl Cellulose[(a)]

| Lot Number | Viscosity in 2% aqueous NaOH at 20° | Approximate Moisture Content % | Ash Content | Methoxyl Content % | Methoxyl Content Groups per Glucose Unit |
|---|---|---|---|---|---|
| MX-261 | 25 cps. | 7.9 | - | 12.64 | 0.70 |
| MX- 0 | 21 cps. | 7.0 | 0.18 | 10.13 | 0.55 |
| MX-267 | 34 cps. | 9.6 | 0.19 | 10.74 | 0.59 |

The allyl bromide was freshly redistilled before use - b.p. 70.8° to 71.3°. It was obtained from Eastman Kodak or prepared from allyl alcohol (79).

The commercial dioxane was purified by acid hydrolysis from any glycol acetal impurities, was neutralized with potassium hydroxide, dried and heated under reflux over sodium

(a) These methyl celluloses (Methocel) were kindly given us by Dr. S. H. Bass of the Dow Chemical Company.

to remove peroxides (80). It was later found that high grade commercial dioxane (containing a trace of peroxides) appeared to have no detrimental effects on the reaction (See P. 82).

The commercial glacial acetic acid was purified by boiling under reflux with a small amount of chromium trioxide for three hours and then by distilling (81).

## 2. Preparation and Properties of "Lower" Substituted Methyl Allyl Celluloses

### (a) Preparation

Methylcellulose (12.5 g. air dry basis) was completely dissolved in a 10 per cent (by weight) aqueous solution of C.P. sodium hydroxide (187.5 g.) by stirring or shaking for a few hours. The resulting frothy solution was mixed with a large excess of allyl bromide (37.5 cc.) in a three-necked one litre flask. The flask was then connected through ground glass joints to a condenser, a mercury seal stirrer and a thermometer, and was heated on a water bath to 65° with gentle agitation. After fifteen minutes to half an hour, the main reaction started and frothing occurred so that the original volume of the mixture was more than doubled. At this stage in the reaction, it was advisable to remove the water bath and to stir vigorously until the frothing started to subside. A white, spongy, fibrous precipitate was formed when the stirring was not very vigorous, or a white powdery, partly fibrous product if the stirring was vigorous at the time when methyl allyl cellulose was separating. If the allyl bromide was added slowly from a dropping funnel with normal agitation, a powdery product was always formed. The heterogeneous mixture was heated at the reflux temperature of allyl bromide with efficient stirring for about another hour (total reaction time two hours) and cooled to room temperature.

### (b) Purification

#### Method A

The powder or the disintegrated fibrous mass was recovered by filtration and washed with hot water until free of alkali, or was first neutralized with 5 per cent aqueous acetic acid then filtered and washed free of the resulting sodium acetate with hot water. A rapid steam distillation then removed excess allyl bromide and the by-products, allyl alcohol and allyl ether. The steam distillation was continued until the distillate gave no double bond test with very dilute bromine water (0.01 N). Finally, the product was filtered, washed with hot distilled water and dried in air or over calcium chloride *in vacuo* at room temperature.

The dried methyl allyl cellulose was redissolved in 90 per cent aqueous acetic acid (2.5 per cent solution by weight) by shaking for several hours. The resulting viscous solution was filtered several times through Whatman No. 1 filter paper, using a Büchner funnel, and reprecipitated into rapidly stirred hot distilled water (ratio of one part of solution to fifteen parts of water). The reprecipitated, snow white, fluffy, fibrous product was recovered, washed with hot distilled water until free of acid and dried over calcium chloride *in vacuo* at room temperature to a constant weight. The hard lumpy product sometimes obtained could easily be pulverized in a mortar.

## Method B
## Benzene Purification Method

This method was used in place of Method A for crude, originally powdery products that formed hard plastic lumps on drying from water, and so could not be easily pulverized. The method also was necessary when handling products of allylation lower than about 0.7 allyl groups per glucose unit since these derivatives were partly soluble in water and frothed vigorously during the steam distillation.

After the two hours' allylation, excess alkali in the reaction mixture was neutralized with 5 per cent aqueous acid and the suspension was heated to 90 - 95° on a water bath in order to coagulate the fine precipitate of methyl allyl cellulose. This operation was done under a hood and the operator wore a gas mask. The precipitate was then immediately recovered by filtration on a steam-jacketed Büchner funnel, washed free of soluble salts with hot distilled water and as much water removed as possible by suction.

Now the fine powdery precipitate was added to stock benzene (200 cc.), shaken and the benzene removed by distillation on a water bath. This process was repeated adding more benzene from time to time until the distillate attained the boiling point of the stock benzene. Sodium-dried benzene (200 cc.) was then added, the mixture heated under reflux for half an hour and the benzene again removed by distillation. The operation was repeated until the distillate came over at the boiling point of pure benzene (80.2°). The product was dried several days in a vacuum desiccator containing phosphorus pentoxide and paraffin wax under a vacuum of 25 mm. pressure, until it was free of benzene. The resulting product even if in lumps was now easily broken up into a fine powder.

Yield for a product containing 0.80 to 1.00 allyl groups per glucose unit varied from 88 to 95 per cent (12.32 to 13.16 g.) of theory. Lower allylated products were recovered in lower yields because a portion was soluble in cold water and was lost.

(1) Anal. Calcd. for cellulose with 0.79 alloxyl and 0.70 methoxyl groups per glucose unit: (from MX-261) allyl, 15.94; C, 53.5; H, 7.16. Found: allyl, 16.00 (average); C, 53.1, 53.3; H, 7.54, 7.45.

(2) Anal. Calcd. for cellulose with 0.95 alloxyl and 0.59 methoxyl groups per glucose unit: (from MX-267) allyl, 18.71. Found: allyl, 18.71, 18.72.

## (c) Properties

Low substituted methyl allyl cellulose was a white, fibrous, flaky product or a powder, which, in the air dry condition, had a moisture content of about 2.9 per cent, and an ash content of 0.4 per cent. In the bone dry condition it was hygroscopic. Only a very small portion was soluble or highly swollen by cold water, and heating the solution or gel caused coagulation. Very few solvents, or mixtures of solvents, dissolved all of the material. A list of its range of solubilities in various solvents is given in Table IV.

### TABLE IV

Solubilities of "Lower" Substituted Methyl Allyl Cellulose

| Solvent | Results of Solubility Tests |
|---|---|
| Acetic acid (glacial) | Partly soluble & highly swollen |
| Acetone | Insoluble |
| Benzene | Swollen and transparent |
| Carbon tetrachloride | Slightly swollen |
| Chloroform | Swollen |
| Diethyl ether | Insoluble |
| Dioxane | Highly swollen transparent gel |
| Ethyl alcohol | Insoluble |
| Ethyl acetate | Insoluble |
| Methylene chloride | Slightly swollen |
| Methyl alcohol | Swollen |
| Morpholine | Soluble |
| Pyridine | Highly swollen |
| 10% Sodium hydroxide | Insoluble |
| Acetic acid:water (9:1) | Soluble |
| (a) Acetic acid:chloroform (1:1) | Almost completely soluble |
| (a) Acetic acid:methylene chloride (1:1) | Almost completely soluble |
| Methanol:chloroform (4:1) | Partly soluble & swollen |
| Methanol:acetylene chloride (1:1) | Almost completely soluble |
| Methanol:dioxane (3:1) | Almost completely soluble |
| (b) Methanol:carbon tetrachloride (1:1) | Partly soluble & highly swollen |
| Dioxane:ethanol (1:1) | Partly soluble & highly swollen |
| Dioxane:water (4:1) | Partly soluble and highly swollen |

(a) A trace of water or methanol in these solvent mixtures assists solvation.

(b) Methylene chloride, benzene or acetic acid can be used in place of carbon tetrachloride.

Excellent, clear, transparent, odourless films were made by dissolving this allyl ether in 85 to 90 per cent aqueous acetic acid and then removing the solvent by evaporation. The physical properties of these films will be discussed in Part IV (See P. 93).

On standing in a bakelite stoppered bottle for a year, the methyl allyl cellulose did not dissolve in a 90 per cent aqueous acetic acid solution. Swelling and gel formation did, however, occur.

## 3. Preparation and Properties of "Higher" Substituted Methyl Allyl Cellulose and Derivatives

### (a) Higher Methyl Allyl cellulose

#### (i) Preparation from Methylcellulose

Methylcellulose (12.5 g. air dry basis) was dissolved in a 10 per cent (by weight) aqueous solution of C.P. sodium hydroxide (300 g.) by shaking for about fifteen hours. The resulting clear solution was placed in a three-necked one-litre flask to which a reflux condenser, a mercury seal stirrer, and a U-tube were attached through ground glass joints. The

U-tube, in turn, was joined through ground glass to two dropping funnels containing 50 per cent (by weight) aqueous solution of C.P. sodium hydroxide (300 g.) and allyl bromide (75 cc.). The flask was heated on a water bath to about 70°, and then the allyl bromide and the 50 per cent sodium hydroxide were added, at approximate rates of 50 grams and 7.5 cc., respectively, every ten minutes. In a very short time the clear solution became milky, and then within half an hour precipitation occurred, accompanied usually by vigorous foaming of the solution. Now dioxane (250 cc.) was slowly added through the condenser. The dioxane reduced the foaming and dissolved the precipitated cellulose derivative, thereby enabling the allylation to continue in an almost homogeneous solution. The 50 per cent sodium hydroxide was then added at an increased rate of about one-quarter of its total volume every ten minutes. After all the chemicals were added, the resulting thick jelly was heated, at the reflux temperature of allyl bromide, with efficient stirring for another hour (total reaction time two hours) and then cooled to about 30°.

The final, milky white and partly transparent jelly was added slowly, in a fine stream, to rapidly stirred distilled water (about 15 l.) containing enough acetic acid to neutralize the excess alkali. The fine, white, fibrous precipitate was filtered, washed and triturated with distilled water to remove soluble salts. Then the product was steam-distilled until the distillate gave no double bond test with a very dilute bromine water (0.01 N). This distillation removed excess allyl bromide, and any by-products such as allyl alcohol and allyl ether formed during the reaction. Finally, the fibrous product was filtered, washed with distilled water, and dried over calcium chloride in vacuo at room temperature. The yield of the crude product varied from 95 to 98 per cent of the theoretical.

The dried product was redissolved in purified acetic acid (2.5 per cent solution by weight), filtered first through linen and then several times through one to five layers of Whatman No. 1 filter paper, and reprecipitated into rapidly stirred distilled water (ratio of one part of solution to fifteen parts of water). The reprecipitated, finely divided, fibrous mass was again filtered, triturated, and washed with distilled water until free of acid. Then it was dried over calcium chloride and finally over phosphorus pentoxide in vacuo at room temperature to a constant weight.

The overall yield varied from 90 to 96 per cent (13.7 to 14.6 g.) of the theoretical.

Anal. Calcd. for cellulose with 1.47 alloxyl and 0.59 methoxyl groups per glucose unit: (from MX-267) allyl, 26.33; C, 57.6; H, 7.5. Found: allyl, 26.36, 26.31; C, 57.2, 57.1; H, 7.65, 7.68.

### (ii) Reallylation of "Lower" Methyl Allyl Cellulose

Methyl allyl cellulose (from MX-261, 5 g.) containing 16.64 per cent allyl (0.83 allyl groups per glucose unit) was partially dissolved and partially highly swollen when shaken mechanically for forty-eight hours with 100 cc. of 85 per cent (by volume) aqueous stock dioxane. The excess dioxane was pressed out and the resulting very highly swollen gel was mixed in a flask with 45 per cent (by weight) aqueous hydroxide solution (55 g.) and allyl bromide (20 cc.). The flask was attached through ground glass joints to a condenser and the contents were agitated by a stirrer placed down the centre of the inner tube of the condenser. After heating on a water bath at 75 - 80° for one and one half hours, a light straw-coloured solution was formed. The solution was neutralized with aqueous acetic acid and the product was isolated and purified by the "benzene purification method" (P. 41).

The yield was 80 per cent of the theoretical (5.14 g.). Anal. Calcd. for cellulose with 1.40 alloxyl and 0.70 methoxyl groups per glucose unit: allyl, 25.20. Found: allyl, 25.30, 25.19.

### (iii) Properties

A methyl allyl cellulose with 0.59 methoxyl, 1.47 alloxyl and, by difference, 0.94 hydroxyl groups per glucose unit was a fluffy, fibrous, snow-white substance, which in the air dry condition had a moisture content of one to two per cent. Its range of solubilities in various common solvents is given in Table V.

### TABLE V

### Solubilities of a Methyl Allyl Cellulose ("Higher" Substituted)

| Solvent | Results of Solubility Tests |
|---|---|
| Acetic acid (glacial) | Soluble |
| Acetone | Highly swollen |
| Benzene | Transparent and glassy |
| Carbon tetrachloride | Slightly swollen |
| Chloroform | Soluble |
| Diethyl ether | Insoluble |
| Dioxane | Soluble |
| Ethyl alcohol | Insoluble |
| Methylene chloride | Soluble |
| Methyl alcohol | Swollen |
| Morpholine | Soluble |
| Pyridine | Soluble |
| 10% Sodium hydroxide | Insoluble |
| Water | Insoluble |
| Benzene:ethyl alcohol (1:2) | Soluble |

From preliminary tests this methyl allyl cellulose was a thermosetting plastic. It was moulded into a translucent, dark grey, hard plastic when subjected to temperature between 145° and 160° and pressures between 4,000 and 5,000 lbs./sq. in. for fifteen minutes. The density of the plastic varied between 1.11 and 1.14 depending on the pressure applied. Excellent, clear, transparent, odourless, water-proof films were made by dissolving the snow-white, fibrous cellulose ether in glacial acetic acid, glacial acetic acid-benzene mixtures or in pyridine, and then removing the solvent by evaporation. (P. 65).

In air the fibrous methyl allyl cellulose slowly polymerized to a product of reduced solubility in all the organic solvents for the original ether (Table V) and the allyl content simultaneously decreased. For example, a sample of fibrous methyl allyl cellulose was 100 per cent soluble in glacial acetic acid and contained 1.32 allyl groups per glucose unit. After being kept in air for five months its solubility was greatly reduced and its allyl content was found in separate estimations to be 0.51, 0.55, 0.64 and 0.74 groups per glucose unit. The reproducibility of the allyl estimation in a heterogeneous system was low.

In order to preserve methyl allyl cellulose for any length of time, it was necessary to keep it *in vacuo*, in solution, or in a dark glass bottle in an atmosphere of nitrogen (Table VI). The decrease in solubility and in allyl content could be greatly accelerated by heat and ultra-violet light (P.97).

Although the allyl groups readily polymerized in the presence of oxygen, they were surprisingly stable toward hydrogenation. Table VII summarizes experiments with Raney nickel and platinum catalysts from which it appears that only slight cleavage or hydrogenation of the allyl group occurred.

## TABLE VI

### Stability of Methyl Allyl Cellulose during Storage

| Number of days in Vacuum of 1-2 cm. (a) | % Allyl | Allyl Groups per Glucose Unit | Soluble in Glacial HAc % |
|---|---|---|---|
| 28 | 26.33 | 1.470 | 100 |
| 68 | 26.36 | 1.472 | 100 |
| 83 | 26.31 | 1.468 | 100 |
| 98 | 26.06 | 1.449 | 100 |
| 124 | 25.86 | 1.435 | 100 |

(a) - In a vacuum desiccator only opened in order to remove samples.

## TABLE VII

### Hydrogenation of Methyl Allyl Cellulose

| | Catalyst | Temperature | Pressure lbs./sq. in. | Time (hours) | Yield % | % Allyl |
|---|---|---|---|---|---|---|
| (1) | - | - | - | - | - | 26.31 |
| (2) | RaNi | 90 - 100 | 1720 - 1780 | 6 | 76 | 25.46 |
| (3) | RaNi | 135 - 165 | 1750 - 2000 | 12 | 55 | 22.06 |
| (4) | Pt | 25 | slightly positive | 24 | - | 21.45 |

(2) Methyl allyl cellulose, 2 g., in 150 cc. of dioxane with 0.3 g. of catalyst.

(3) Methyl allyl cellulose, 1 g., in 100 cc. of dioxane with 0.2 g. of catalyst.

(4) Methyl allyl cellulose, 0.2 g., in 25 cc. of glacial acetic acid with 0.01 g. of catalyst.

**NOTE:** Raney nickel prepared by method of Cavert, Adkins (82) and platinum according to Adams, Voorhees and Shriner's method (83).

## (b) Methyl Allyl Cellulose Acetate

### (i) Starting Materials

High grade pyridine was dried over barium oxide and freshly redistilled before use (b.p. 114.5 - 115.2° @ 1 atm.).

Commercial acetic anhydride was purified by passing it through an efficient fractionating column, collecting the fraction that boiled between 139.6 to 140° under a pressure of one atmosphere.

### (ii) Method of Preparation and Purification

Methyl allyl cellulose (2 g., from above preparation containing 1.47 alloxyl and 0.59 methoxyl groups per glucose unit - P. 46) was dissolved in pyridine (50 cc.) and thoroughly mixed with acetic anhydride (20 cc.) in a nitrogen atmosphere. This mixture was acetylated in a black coated flask for several days at room temperature and for forty-eight hours in a water bath at about 45°. The resulting dark orange solution, after concentrating under a vacuum, was precipitated in rapidly stirred distilled water (2½ l.). The precipitate was filtered, thoroughly washed until free of any odour of pyridine, and then washed with more distilled water (2 l.). The white fibrous material was dried over phosphorus pentoxide *in vacuo* at room temperature.

The acetate was further purified by dissolving it either in acetone or dioxane, filtering and reprecipitating into rapidly stirred distilled water. The reprecipitated product was again filtered, washed with distilled water and dried over phosphorus pentoxide _in vacuo_ at room temperature to a constant weight.

A yield of approximately 90 to 93 per cent (2.1 to 2.2 g.) of theory was obtained, the yield being based on complete acetylation of the free hydroxyl groups in the methyl allyl cellulose.

Anal. Calcd. for cellulose with 1.47 alloxyl, 0.59 methoxyl and 0.94 acetyl groups per glucose unit: allyl, 22.46; acetyl, 14.7. Found: allyl, 22.31, 22.40; acetyl, 14.21, 14.38, 14.45, 14.47 (Saponification Method, P. 62), 14.30, 14.03 (Chromic Oxidation Method, P. 63).

### (iii) Properties

Methyl allyl cellulose acetate was a white, fibrous substance. Its wide range of solubilities in various common solvents is given in Table VIII.

Clear, transparent films of acceptable strength were prepared from acetone and ether-acetone (20:1) solutions of this acetate. The latter solution formed a clear film in fifteen minutes under a vacuum of one centimeter.

# TABLE VIII

## Solubilities of a "Higher" Substituted Methyl Allyl Cellulose Acetate

| Solvent | Results of Solubility Tests |
|---|---|
| Acetic acid (glacial) | Soluble |
| Acetone | Soluble |
| Benzene | Soluble |
| Chloroform | Soluble |
| Carbon tetrachloride | Partly soluble & highly swollen |
| Diethyl ether | Almost completely soluble |
| Dioxane | Soluble |
| Ethyl alcohol | Slightly swollen |
| Methyl alcohol | Slightly swollen |
| Methylene chloride | Soluble |
| Morpholine | Soluble |
| Pyridine | Soluble |
| 10% Sodium hydroxide | Insoluble |
| Water | Insoluble |

## (c) Methyl Allyl Cellulose Dibromide

### (i) Method of Preparation and Purification

Methyl allyl cellulose (0.5 g. from above preparation containing 1.47 alloxyl and 0.59 methoxyl groups per glucose unit - P.46) was dissolved in glacial acetic acid (200 cc.), treated with an excess of 2 N potassium bromide-potassium bromate solution (2.16 g. of potassium bromide and 0.56 g. of potassium bromate dissolved in 10 cc. of water) and allowed to stand overnight. The mixture was added to rapidly stirred distilled water (2 l.) and enough formic acid was added to destroy the excess bromine. Then the bromide was recovered by filtration, washed well with a sodium thiosulphate solution and with distilled water, and dried in a desiccator over calcium chloride.

The yield was about 96 per cent (0.98 g.) of the theoretical.

Anal. Calcd. for cellulose with 0.59 methoxyl and 1.47 allyl dibromide groups per glucose unit: Br, 50.61.

Found: Br, 46.35, 46.17.

Bromine was estimated by the wet combustion method of Carius (84).

### (ii) Properties

Methyl allyl cellulose dibromide was usually a snow-white, powdery substance, but occurred in a fibrous state when it was precipitated quickly from solution. Its small range of solubilities is given in Table IX.

### TABLE IX

### Solubilities of a Methyl Allyl Cellulose Dibromide

| Solvent | Results of Solubility Tests |
|---|---|
| Acetic acid (glacial) | Slightly swollen |
| Acetone | Slightly swollen colloidal particles |
| Benzene | Slightly swollen |
| Chloroform | Slightly swollen colloidal particles |
| Diethyl ether | Insoluble |
| Dioxane | Partly soluble and colloidal |
| Ethyl alcohol | Insoluble |
| Methyl alcohol | Slightly swollen |
| Methylene chloride | Slightly swollen |
| Morpholine | Partly soluble and highly swollen |
| Pyridine | Soluble |
| Water | Insoluble |

The dibromide did not burn freely like other cellulose derivatives, but shrivelled up and decomposed on exposure to a flame.

## III ANALYTICAL PROCEDURES FOR ALLYL ETHERS OF CARBOHYDRATES

### 1. Drying of Allyl Derivatives - Moisture Determination

All allyl ethers for analytical work were dried *in vacuo* over phosphorus pentoxide at room temperature until the surface of the phosphorus pentoxide appeared to remain unchanged. Drying in an Abderhalden at 60° was inadvisable, particularly with the higher substituted allyl ethers, since they were oxidized and polymerized by the heat.

### 2. Solubilities in Common Solvents

Solubility Tables IV, V, VIII and IX were obtained by allowing 0.05 gram (0.10 g. in Table IV) samples of the allyl cellulose ethers, either to stand for several days, or to be shaken for twelve hours in the presence of 10 cc. of the solvent.

### 3. Attempted Determination of Allyl plus Methoxyl

Alkoxyl determinations were made by the Viebock and Schwappach method, as modified by Clark (85) in which the alkoxyl group is liberated as volatile alkyl iodide by heating the substance with hydriodic acid. The alkyl iodide is trapped by bromine in acetic acid-potassium acetate solution and the amount corresponds in the final titration to six equivalents of sodium thiosulphate. The methyl allyl cellulose contained 0.59 methoxyl and 1.47 allyl groups per glucose unit, the latter being determined by the bromine titration method. These values correspond to percentages of 7.98 and 26.33 respectively.

In a typical estimation, a 0.04768 g. sample yielded alkyl iodide equivalent to 38.8 cc. of 0.0499 N sodium thiosulphate. Of this amount, the volume V equivalent to the methoxyl content was obtained from the following equation:

$$\%\ OCH_3 = 7.98 = \frac{V \times 0.0499 \times 31 \times 100}{6 \times 1000 \times 0.04768}$$

whence $V = 14.75$ cc.

The volume of thiosulphate corresponding to the allyl groups was therefore $(38.8 - 14.75) = 24.05$ cc., whence allyl = 17.23 per cent. A duplicate estimation in the same apparatus gave the value $CH_2{=}CH{-}CH_2{-}$, 17.22 per cent, and in duplicate equipment the results were 17.43 and 17.45 per cent. There was therefore a variation of 0.2 per cent between the results obtained in the two pieces of equipment.

Although samples were treated with the constant boiling hydroiodic acid for periods varying from one to four hours, and sample weights were varied from 0.017 g. to 0.047 g., the results remained close to 17.3 per cent . Since the allyl content was known to be 26.33 per cent, it was concluded that the Viebock estimation, although reproducible, was of no value in determining the methoxyl or allyl substitution in methyl allyl celluloses.

## 4. Determination of Unsaturation

### (a) Samples of Allyl Carbohydrates Completely Soluble in Glacial or Aqueous Acetic Acid

At least two samples of an allyl ether (dried over phosphorus pentoxide) weighing between 0.04 and 0.07 g. each were placed in ground glass stoppered iodine flasks (250 cc.). To each flask was added 30 cc. of redistilled glacial acetic acid, or some aqueous acetic acid solution, depending upon which solvent completely dissolved the unsaturated ether. The flasks were stoppered and left to stand with intermittent, gentle shaking until the allyl ether had completely dissolved (this time varied from two or three minutes to six hours depending on the particular allyl ether and its physical state).

### (b) Samples of Allyl Carbohydrates Partially Soluble in Glacial Acetic Acid

A definite weight (2 g.) of an allyl ether was accurately weighed out and placed in a ground-glass flask to which pure glacial acetic acid (100 cc.) was added. The mixture was shaken until saturation was reached (about twelve hours), centrifuged for about 0.5 hour and then the resulting clear solution was removed by filtration or decantation (if the gel remained). At least three 5 cc. samples of the solution were run from a 50 cc. burette into iodine flasks and each was diluted with glacial acetic acid (25 cc. to 50 cc.).

The dry weight of the sample was obtained by running a definite volume (usually 10 cc.) into a tared ground-glass weighing bottle and removing the solvent by evaporation at room temperature under an efficient vacuum. The residue was then dried to a constant weight over phosphorus pentoxide _in vacuo._ The weight of the sample was the average of the best two out of three samples dried in this manner.

### (c) Bromination

An excess of potassium bromide-potassium bromate solution(1) (usually 2 to 5 cc. of 0.25 N approximately) was added quickly from a micro-burette to the clear solutions from (a) and (b) contained in iodine flasks, which were constantly rotated during the addition. If the solutions contained much water, it was necessary to add 5 cc. of 10 per cent sulphuric acid in order to release the bromine from the bromide-bromate solution. The flasks were immediately stoppered and a few cubic centimeters of 10 per cent potassium iodide solution was placed on the curved shaped top to prevent the evaporation of any halogen. After three to five minutes

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(1) The 0.25 N potassium bromide-potassium bromate solution was prepared by dissolving 25 g. of C.P. potassium bromide and 7 g. of C.P. potassium bromate in one litre of distilled water (65).

the stopper of the flask was carefully removed and 10 cc. of 10 per cent potassium iodide solution, 100 cc. of distilled water and 5 cc. of 10 per cent sulphuric acid, if not already in the solution, were immediately added. The liberated iodine was titrated with a sodium thiosulphate solution (0.1 N approximately), using near the end-point 10 drops of freshly prepared starch as an indicator. A reagent blank was run with every determination and the temperature was kept as near as possible to 25° throughout the estimation.

If the blank and the titration corresponded to x cc. and y cc., respectively, of normal thiosulphate, the percentage of allyl was given by the equation:

$$\% \ CH_2{=}CH{-}CH_2{-} = \frac{(x-y)}{2000} \times 41.07 \times \frac{100}{\text{sample}}$$

The most important factor in the determination was to dissolve the sample in sufficient glacial acetic acid so that the allyl carbohydrate remained in solution or in a very finely dispersed condition during the bromination. Then, if all the aqueous reagents were added with constant swirling, a soft, bulky, highly swollen methyl allyl cellulose dibromide separated. This precipitate did not tend to absorb any bromine or iodine and the end point in the titration was usually very sharp. However, if the suspension was allowed to stand for an hour before back titrating with sodium thiosulphate, the precipitate usually coagulated and the mixture had to be vigorously shaken near the end point in order to assist the diffusion of all absorbed halogen.

## 5. Acetyl Determination

### (a) Saponification Method

A modified Malm, Genung, Williams and Pile method (86) was used. It consisted of weighing out 0.1 to 0.2 gram samples of methyl allyl cellulose acetate and dissolving each of them in freshly redistilled pyridine (25 cc.) in Erlenmeyer flasks. Then to each sample and the blanks was added 0.6 N sodium hydroxide (5 cc.) and the homogeneous solutions were mixed and allowed to stand overnight. Distilled water (100 cc.) was added, five to six drops of phenolphthalein, and the solution was titrated with 0.05 N hydrochloric acid until the indicator changed. If a thick curdy precipitate formed, an excess of acid was added and the mixture allowed to stand for one hour with occasional shaking in order to leach out all sodium hydroxide in the precipitate. The acid was then back titrated with 0.05 N sodium hydroxide.

If the blank and the titration corresponded to x cc. and y cc., respectively, of normal hydrochloric acid, the percentage of acetyl was given by the equation:

$$\% \ CH_3CO— = \frac{(x-y)}{1000} \times 43.04 \times \frac{100}{\text{weight}}$$

Slightly less accuracy was obtained than by Malm et al through using the smaller weight of sample.

### (b) Chromic Oxidation Method

Lemieux (87) has recently developed in this laboratory a chromic oxidation method for the estimation of acetyl. This method involved the addition of 30 per cent (by weight) aqueous chromium trioxide to a dry sample of methyl allyl cellulose acetate (0.05 g. approximately). The flask containing the mixture was joined through ground glass to a special head consisting of a graduate (A), whereby water was added to the flask, a tube (B) that delivered nitrogen gas below the surface of the solution in order to sweep the acetic acid formed out through a side arm (C). The side arm (C) was then connected to a water condenser. After the apparatus was assembled as described, the flask and contents were heated up to about 150° on an oil bath and the distillate that passed over was collected in a 50 cc. graduate (D). Small volumes of water (5 cc.) were added from (A) from time to time after a similar volume had been collected in (D). This process was continued until a total of 55 cc. of distillate had been collected. The contents of the graduate were now transferred to an Erlenmeyer (250 cc.) flask, the condenser was washed with distilled water, and the washwater added to the flask. This solution, containing the liberated acetic acid, was titrated with 0.02 N sodium hydroxide until the first appearance of colour, using phenolphthalein as indicator. Then the solution was boiled to remove dissolved carbon dioxide, cooled to room temperature and the titration continued to the first permanent pink colour. Finally, any chromic acid that had been carried into the distillate was estimated by adding a little bicarbonate, potassium iodide (1 g.) and 10 per cent sulphuric acid (10 cc.). After the mixture had stood in a stoppered flask for a few minutes, the liberated iodine was titrated with 0.02 N sodium thiosulphate, using a starch solution as an indicator. A blank was always run on the methyl allyl cellulose.

In calculating the result, the normality of the chromic acid, as found iodometrically, was subtracted from the total acid normality as found in the titration. The difference was attributed to acetic acid derived from the acetyl content of the sample. The apparent acetyl value was reduced by the amount of acetyl registered in the blank with methyl allyl cellulose (about 1.65 per cent).

This method with methyl allyl cellulose acetate had an accuracy of ±2 per cent at best. Experimental conditions had to be closely controlled in order to obtain a fairly constant blank and hence good checks.

# IV POLYMERIZATION OF ALLYL STARCH AND METHYL ALLYL CELLULOSE FILMS

## 1. Method of Preparing Films

### (a) Methyl Allyl Cellulose Films

Solutions of methyl allyl cellulose in pure glacial acetic acid (2.5 to 4 per cent) were mixed with an equal volume of purified benzene in order to increase the rate of evaporation to near that of the benzene-glacial acetic acid azeotrope (b.p. 80°). Each solution before use was filtered several times with slight suction through several thicknesses of Whatman No. 1 filter paper and was then poured carefully into a scrupulously clean plate glass - Plaster of Paris mould. This mould was made by gluing (with commercial animal glue) Plaster of Paris moulding all around the rim of an ordinary piece of high grade window plate glass. The mould, measuring 6½ x 5½ inches, containing the solution, was floated on mercury, in order to obtain films of as uniform a thickness as possible, and the whole was contained in a desiccator. The desiccator, which also contained moist potassium hydroxide pellets, was either evacuated for about twelve hours over a 15 mm. vacuum, or for two to three days over 9-10 cm. vacuum, in order to remove the solvents by slow evaporation. The solvents were not recovered, but commercially recovery would be possible.

The dried film, no longer smelling of acetic acid, was cut away from the Plaster of Paris mould to which it adhered, and which had enabled it to dry under tension. All films were kept in vacuo until ready for use, since the oxygen of the air slowly polymerized them.

### (b) Allyl Starch Films

The allyl starch films adhered very tightly to glass surfaces and could not be removed from them without damage. Consequently, allyl starch films were prepared by pouring a freshly filtered, uniform 12 per cent allyl starch-acetone solution on to a clean mercury surface in a round dish measuring 9½ inches in diameter. The dish containing the solution was placed in a desiccator and the solvent was removed under vacuum of 10 - 15 cm. The dried film, when strong enough to support itself without damage (slightly polymerized), was cut away from the edges of the glass dish to which it adhered, and kept in vacuo until ready for use.

## 2. Measurement of Physical Properties of Films

### (a) Tensile Strength and Elongation

Tensile strengths and elongations were carried out on the Louis-Schopper (Leipzig) Tensile Tester in a constant temperature and humidity room according to TAPPI paper standards (88).

Test strips, 15 mm. by 60 mm., were cut from single sheets 5½ inches by 6½ inches (P. 65), always in the same direction, and were thoroughly mixed to minimize geometric variables. The maximum thickness variation across a single sheet was a thousanth of an inch and across a single test strip was 0.2 to 0.8 thousanth of an inch. The thickness of every test strip was determined by averaging ten readings across the strip. It should be noted that the brittle, polymerized films when breaking usually shattered, and the middle portion between the two clamps fell free. This test may not be considered a true tensile test! Also brittle films may be damaged by the clamping device on the apparatus, although great care was taken to avoid this source of uncertainty.

In general, the accuracy of this test was better than ±10 per cent. In order to increase this accuracy, a much larger number of strips would have to be taken for each test and would have to be made from a much larger uniform sheet. The requisite size was impracticable in this laboratory. However, the approximate values obtained in Table XX seem to indicate the effect of polymerization on these unsaturated cellulose ether films.

### (b) Moisture Vapour Permeability

Moisture vapour permeability tests were carried out according to TAPPI paper standards (89). After completion of the test on the unpolymerized films, they were carefully removed from the testing container and placed under ultra-violet light, usually for twenty-four hours. They were then carefully replaced on the testing container with the same surfaces exposed to the water vapour as in the previous test. In general, the accuracy of this test was better than ±6 per cent.

### (c) Relative Rate of Polymerization

Strips of methyl allyl cellulose film, prepared as above (P. 65), were heated in a Fischer's Freas oven at a definite temperature (within ±2°) for various lengths of time. Polymerization by means of ultra-violet radiation was brought about by means of a General Electric S-4 Sun-lamp from which in most experiments the outer glass casing had been removed. This casing prevented emission of light of wave length shorter than 2800 Å.

Each strip, as it was removed from the oven, was weighed, placed in an Erlenmeyer flask (125 cc.) and purified glacial acetic acid (50 cc.) was added. The flasks were cork-stoppered and agitated for twenty-four hours or longer. The insoluble portion of the film was either filtered into a coarse tared fritted glass filter, or, in the case of a gel that blocked the filter, the gel was removed by centrifuging in tared centrifuge cups. The fritted glass filters or centrifuge cups, containing the insoluble portion of the films, were washed with pure glacial acetic acid and dried under reduced pressures to a constant weight. The accuracy of this method was approximately ±1.0 per cent if reasonable care was taken. However, the gel from partially polymerized films, being fluffy and light, was very difficult to handle; it not only was impossible to filter, but would not cohere into a mass of jelly on centrifuging.

The clear filtrates or decanted solutions were each filtered twice through Whatman No. 1 filter paper and the percentage of allyl groups remaining in the soluble portion of the film were determined by the titration for double bonds (P. 59). A blank was run.

The decrease in solubility and in the unsaturation of the soluble portion of the films was taken as a qualitative measure of the degree of polymerization. The results are in Table XIX.

### (d) Nitroglycerine Diffusion(i)

A freshly filtered 2.5 per cent solution of methyl allyl cellulose in acetic acid (10 cc.) was poured into a very clean saucer-shaped glass container (25 cc.). The solvent was removed by evaporation under a vacuum of 1 cm. and the resulting

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(i) This test was kindly carried out by Dr. C.H. Findlay of the Canadian Industries Limited (Explosive Division).

film, moulded to the shape of the container, was further dried over potassium pentoxide _in vacuo_. The dry film was now carefully removed from the container, weighed to the nearest milligram and the thickness of its base determined to the nearest thousanth of an inch. The moulded films were then either polymerized under a quartz ultra-violet light or else stored _in vacuo_ until ready to test.

The film was again weighed, supported in the neck of a wide mouthed Erlenmeyer flask and the depression in the film was filled with the regular grade of nitroglycerine. The film and nitroglycerine was allowed to stand for sixteen days at room temperature, being examined daily for the appearance of any nitroglycerine on the under side. At the end of the sixteen day test period the nitroglycerine was poured off and the top washed with acetone, care being taken not to allow any solution to come in contact with the under side of the film. If any droplets were observed on the under side, they were wiped off with a piece of filter paper and tested to ascertain if they consisted of nitroglycerine. The films were then dried, weighed, and the under side tested qualitatively for nitroglycerine by the diphenylamine reagent.

In the case of allyl starch, and sometimes with methyl allyl cellulose films, the depression was made in the film by the air pressure of a Mullen tester. This method, of course, stretched the film and was a much more severe test of its impermeability.

If the films were to be plasticized by glycerine, the latter was added to the 2.5 per cent solution and thoroughly mixed before removal of the solvent by evaporation. Glycerine was a good plasticizer for the lower substituted methyl allyl cellulose in all proportions. However, with the higher substituted product, it was not very compatible,possibly because the glycerine, which naturally absorbs a little water from the atmosphere, was repelled by the larger number of hydrophobic allyl groups in the cellulose ether.

## RESULTS AND DISCUSSION

### I ALLYL STARCHES

The work done on allyl starches was only of a preliminary nature and had the object of preparing completely soluble samples from which thin films could be made. Table II summarizes the conditions employed in several experiments and the properties of the corresponding products are listed in Table X. It quickly became apparent that the direct allylation of undegraded starch, preparation (a), or undegraded starch acetate (c), yielded insoluble or partly soluble allyl ethers. A considerable amount of previous degradation by mineral acid was necessary for 100 per cent solubility of the allyl ether in acetic acid (preparations b, f, g). This degradation was probably necessary to break up the branch-chain starch macromolecules and render the fragments more accessible to the allylating agents. The degree of allyl substitution did not in itself determine the solubility, for the products (c), (e) and (g) had practically the same substitution (2.3 to 2.5) but ranged in solubility from 52 to 100 per cent.

The branched chain structure of the original starch and the fact that soluble film-forming allyl ethers were highly degraded probably explains the low mechanical strength of the films. Exposure for a few weeks to the atmosphere caused the allyl groups in such films to polymerize and the products became very brittle. These undesirable properties made them of little promise as practical barriers against the diffusion of nitroglycerine. Moreover, the rate of polymerization was great enough to render such films of little value for an academic study of the effect of polymerization on the diffusion of nitroglycerine, or, for that matter, of water vapour. Permeability tests may last for as long as seven days at elevated temperatures during which time the degree of polymerization would have radically changed.

The work with allyl starch was discontinued after a sample kindly given by Dr. L. I. Smith, behaved similarly to the preparations just discussed.

## TABLE X

### Analyses and Properties of Allylated Starches (a)

| Preparation | Weight Starting Material (grams) | Portion of Allyl Starch soluble in Glacial Acetic Acid | | | Solubility in some Common Solvents | Film Properties |
|---|---|---|---|---|---|---|
| | | % Soluble | % Allyl | Allyl Groups per Glucose Unit | | |
| (a) | Cornstarch 5 g. | 0 | - | - | Slightly soluble in water | None |
| (b) | Degraded cornstarch 2.5 g. | 100 | - | - | Soluble in ethanol, acetone, acetic acid | Brittle and crumbly |
| (c) | Undegraded starch acetate 10 g. | 52 | 38.9 | 2.48 | Partially soluble in acetic acid, dioxane. Swells in ethanol and acetone | Plastic and weak |
| (d) | Slightly degraded starch acetate 10 g. | 24 | 18.0 | 0.86 | Swells in ethanol and acetone | Weak and crumbly |
| (e) | Somewhat degraded starch acetate 10 g. | 81.0 | 37.0 | 2.30 | Swells in ethanol and acetone | Brittle, weak and crumbly |
| (f) | Degraded starch acetate 10 g. | 100 | 33.8 | 2.00 | Soluble in acetone, acetic acid | Flexible, transparent, plastic and weak |
| (g) | Very degraded starch acetate 10 g. | 100 | 37.3 | 2.32 | Soluble in acetone, acetic acid, ethanol | Flexible, weak and sticky |

(a) See Table II

**NOTE:** Method (65) used here to determine degree of unsaturation is possibly high (approximately 5%) owing to the heterogeneous condition of bromination. An improved method of determining unsaturation was later developed in the research (P.59).

## II METHYL ALLYL CELLULOSE

### 1. "Lower" Substituted (substitution: 0.70 methyl, 0.79 allyl groups per glucose unit)

The preliminary work on the allylation of undegraded starch and starch acetates strongly suggested that the inaccessibility of much of the starch to the reagents, operating in a heterogeneous system, rendered the reaction incomplete and the product insoluble or only partly soluble. These difficulties diminished when severely degraded starch was allylated. Sakurada's (49) attempts to allylate cellulose encountered the same difficulties. The problem of preparing allyl cellulose ethers of adequate solubility and of adequate chain length therefore seemed to resolve itself into discovering methods of keeping the cellulose in solution, or at least in a very finely dispersed form, during allylation. With these considerations in mind, an alkali-soluble and alkali stable, low substituted technical methyl cellulose was chosen as a starting material. Unfortunately, this methyl ether was only soluble in alkali of low concentration (4 to 10 per cent) and from an examination of the usual mechanism of etherification of cellulose (see Introduction), a high alkali concentration during the reaction is necessary in order to obtain a product of maximum substitution and to reduce side reactions to a minimum. There was, however, no evidence that maximum substitution in an allyl cellulose was necessary, or even desirable, for the preparation of polymerized films.

Methylcellulose was completely dissolved in a large excess of 10 per cent alkali and treated with allyl bromide for various times after the initial reaction had taken place. Table XI shows that little alkali remained after the first half hour and that the soluble portion of the product had nearly reached its final allyl content. Side reactions, as expected, were rapid with caustic soda as dilute as 10 per cent and the final allyl substitution of the soluble product was low.

### TABLE XI

### Decrease in Alkali Concentration with Time(a)

| Reaction Time (hours) | Alkali Concentration % | Portion Soluble in HOAc | |
|---|---|---|---|
| | | % Allyl | Allyl Groups per Glucose Unit |
| 0 | 10 | 0 | 0 |
| ½ | 2.2 | 13.4 | 0.64 |
| 2 | 0.6 | 16.89 | 0.85 |
| 5 | 0 | 16.50 | 0.81 |

(a) 25 g. methylcellulose, 375 g. of 10 per cent NaOH and 75 cc. allyl bromide, Lot No. MX-261.

By using less allyl bromide, all other experimental conditions being the same, soluble products of lower substitution were obtained in lower yield (Table XII).

## TABLE XII

### Effect of Different Amounts of Allyl Bromide (a)

| Allyl Bromide (cc.) | Portion Soluble in 90% Acetic Acid | | |
|---|---|---|---|
| | % Soluble | % Allyl | Allyl Groups per Glucose Unit |
| 50 | 82 | 12.24 | 0.58 |
| 50 | 80 | 12.06 | 0.57 |
| 75 | 100 | 16.00 | 0.79 |

(a) 25 g. methylcellulose and 375 g. of 10% NaOH in each case. Lot number MX-261.

When allylation proceeded with excess allyl bromide, a point was reached when the product separated as a coherent fibrous phase. Little further allylation occurred after this stage was reached even with high-speed stirring, presumably because the system was now very heterogeneous.

These methyl allyl celluloses tended to froth violently when attempts were made to remove by-products by steam distillation, and drying from water or alcohol converted them to insoluble hard grey masses. These difficulties led to the development of a method in which water, excess allyl bromide, allyl alcohol and allyl ether were removed by co-distillation with benzene. Benzene forms a series of azeotropic mixtures with the chief impurity allyl alcohol (b.p. 76.8°) and with water (b.p. 69.3°). Consequently, a water-free powdery product was obtained after the benzene had been removed by evaporation.

A point of interest was that on adding 50 per cent sodium hydroxide to the 10 per cent sodium hydroxide solution of methylcellulose, a hard, lumpy, abnormally highly swollen, fibrous gel with a "cabbage-like" structure formed which contained approximately twelve times as much caustic as methylcellulose (by weight). Allylation of this abnormally swollen material gave a product partially soluble in alcohol, glacial acetic acid and acetone. Further work on this highly swollen gel seemed desirable, because it might be made the starting material for a more highly allylated methylcellulose. The lead was not followed up because the same objective was reached by a different route. No detailed study of the allylation process was made although the variables could be easily predicted from a study of the mechanism of etherification (See P. 16 to 23). The main problem of the thesis was to study the effects of polymerization on films made from a soluble allyl cellulose derivative with suitable substitution and degree of polymerization.

## 2. "Higher" Substituted (substitution: 0.59 methyl and 1.47 allyl groups per glucose unit)

Attempts were made to prepare higher allylated cellulose ethers by allylation of methylcellulose in the presence of stronger alkali. The process was heterogeneous and in every case a product incompletely soluble in common solvents was obtained. After considering every factor known that tends to make a uniform product of high substitution (Mechanism of Etherification - P. 16 to 23) it was decided that the precipitation of partly allylated methylcellulose should be delayed as long as possible and that the concentration of alkali should be kept as high as possible. Since the original methylcellulose remained completely soluble only when the caustic soda concentration was not more than 10 per cent, allylation was commenced at that concentration. However, this preparation differs from that described for the low allylated product in that fresh 50 per cent alkali was added at such a rate as to maintain the alkali concentration during the first part of the reaction. Care was taken not to add this sodium hydroxide too quickly to the reaction mixture, otherwise the mixture would gel and become lumpy. Lorand (40) claims this low alkali concentration should make the initial etherification fast, and this was so, since in about half an hour a precipitation occurred. The combined effect of the methyl and allyl substituents, however, was now sufficient to render the material almost soluble in aqueous-dioxane containing caustic soda. The addition of dioxane therefore redissolved the precipitate. It was then possible to continue the addition of the 50 per cent caustic soda at a faster rate, together with further additions of allyl bromide, for sometime before the final coagulation occurred. In this way, the high alkali concentration necessary for high substitution was obtained, the presence of dioxane increased the solubility of allyl bromide in the reaction mixture, and thehomogeneous, or nearly homogeneous conditions yielded an almost completely soluble (97 to 100 per cent) methyl allyl cellulose.

In Table XIII the intrinsic viscosity data indicate that stock dioxane, containing a trace of peroxide, causes little, if any, degradation of the cellulose ether. The fact that the same intrinsic viscosities were observed with products allylated for two or three hours indicates the stability of the methyl allyl ether in the presence of alkali and during allylation. It should be emphasized that the conversion of these intrinsic viscosities into average chain lengths by the use of a Staudinger (90) or Kraemer and Lansing (91) numerical factor is unjustifiable. Such factors assume no cross linked molecules and this assumption is probably not quite true in the present case. The intrinsic viscosity of the allyl derivative was not compared with that of the original methylcellulose owing to the lack of a common solvent.

The reproducibility of the method from batch to batch is quite good (See Table XIII) and the slight gradual increase in allyl substitution is attributed mainly to a change in the drying techniques used later in the research. In Table XIII, batches 1 and 2 were air dried while batches 3, 4 and 5 were dried over calcium chloride _in vacuo_. The increase in allyl between batches 3 or 4 and 5 is possibly caused by improved analytical techniques or some change in the many variables, such as rate of stirring and rate of addition of alkali. Careful storage will reduce the loss of allyl by polymerization in the presence of traces of air, but when a vacuum desiccator has to be open and shut in order to remove samples, the methyl allyl cellulose gradually polymerizes (See Table VI).

The most undesirable features of this method are the high water-cellulose ratio and the large excesses of alkali and allyl bromide used (approximately 28 and 5.3 times the theoretical amounts, respectively). Since almost all of the allyl bromide was consumed in the reaction, a still larger excess would be necessary if an attempt were made to increase the degree of allylation.

# TABLE XIII

## Reproducibility of Methyl Allyl Cellulose Preparation

| Batch Number | Date of Preparation | Reaction Time (hrs.) | Allyl Groups per Glucose Unit (a) | Lim. $\frac{\eta_{sp}}{c\%} = [\eta]$ (c) |
|---|---|---|---|---|
| 1 | Sept. 14/45 | 3 | 1.32 (b) | 3.22 (stock dioxane) |
| 2 | Sept. 24/45 | 2 | 1.377 | 3.25 (peroxide<br>(free |
| | | 3 | 1.372 | 3.26 (dioxane |
| 3 | Jan. 3/46 | 2 | 1.44 | - |
| 4 | Jan. 11/46 | 3 | 1.44 | - |
| 5 | Jan. 20/46 | 2 | 1.47 | - |

(a) Methylcellulose (MX-267, 0.59 methyl groups per glucose unit) 12.5 g. (air dry); 300 g. of 10% and 300 g. of 50% NaOH; 75 cc. of allyl bromide and 250 cc. of dioxane.

(b) A large batch using 60 g. of methylcellulose, other reagents in proportions stated in (a).

(c) Intrinsic viscosity in glacial acetic acid at 25°.

## 3. Physical Properties

The physical form of these derivatives was markedly affected by the way in which they were precipitated from solution. When a one per cent solution in glacial acetic acid was poured into a large volume of water, the lower methyl allyl cellulose separated in a light, fluffy, fibrous state. A 5 per cent acetic acid solution yielded a much coarser and denser product. Precipitation of a lower substituted derivative with high speed stirring, as might be expected, tended to yield a powder.

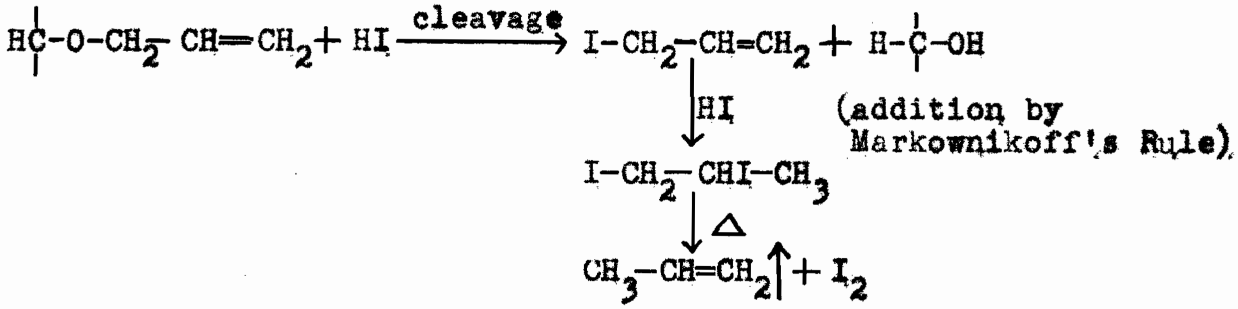
When air dried, the original methylcellulose, the "lower" and the "higher" allylated derivative retained about 9, 3 and 1 per cent, respectively, of moisture. Hygroscopicity therefore diminished, as is customary, with increasing substitution of hydrophobic hydrocarbon groups. The same increase in substitution altered solubilities in the direction described by Lorand (92) for the ethyl celluloses. Water or polar solvents, for example 90 per cent acetic acid, were constituents of solvents for the "lower" allylated product (Table IV); whereas the "higher" substituted methyl allyl cellulose dissolved in non-polar liquids like chloroform or dioxane or in the slightly polar glacial acetic acid (Table V). The introduction of acetyl groups improved the solubility in polar liquids considerably.

## III ANALYSES OF METHYL ALLYL CELLULOSE AND ITS DERIVATIVES

A great deal of effort throughout the research was devoted to determining the degree of substitution of the allylated derivatives. The methoxyl content could be assumed to be that of the particular methylcellulose used as starting material in the allylation, and, knowing this value, it appeared likely that a similar estimation on the product would give the sum of the methoxyl plus alloxyl substitutions. The boiling point of allyl iodide, 102°, is low enough for the compound to volatilize from the constant boiling hydroiodic acid used in the estimation.

Several standard alkoxyl determinations were carried out with various sample weights of a methyl allyl cellulose known to contain 7.98 per cent methoxyl and 26.33 per cent allyl groups per glucose unit, and the time of reflux was varied from one to four hours. When the recovery of methoxyl was assumed to be quantitative, that of allyl was always close to 17.3 per cent, instead of the proper value of 26.33 per cent. Therefore, although the method gave reproducible results, they were so low that they were of no value in determining the methoxyl and allyl content of the methyl allyl cellulose.

Sakurada (49) also found the alloxyl content of his diallyl cellulose ether was low (i.e., calculated, 47.2 per cent alloxyl; found, 41.27 per cent). He claimed that the hydrogen iodide of specific gravity 1.7 used in the estimation was not strong enough for complete cleavage of the ethers. However, it appears to the author that the formation is likely of unstable propylene iodide which readily decomposes evolving propylene (b.p. 47.0°) and leaving behind free iodine (b.p. 183°) in the reaction flask.

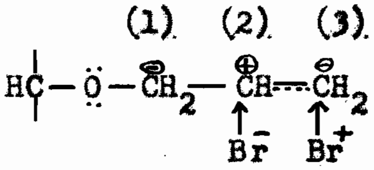


Although some of the propylene would be trapped in the scrubber or react with the excess bromine in the receiver, forming propylene dibromide, (b.p. 140°), most would pass through the system and be lost. No attempt was made to redesign the apparatus in order to estimate this propylene, because such a project was not a main objective of the work.

Another obvious method of estimating the allyl group was to titrate the unsaturated double bond it contained in some convenient way. Wijs's method employing iodine monochloride was used by Sakurada with degraded allyl celluloses of high substitution, but since the "lower" substituted methyl allyl cellulose in the present case was completely soluble only in aqueous acetic acid the iodine monochloride of Wijs's solution would be destroyed. The bromide-bromate method is free from this difficulty and as pointed out in the Introduction, is a much quicker and easier method than that of Wijs, provided care is taken to avoid loss of bromine and provided the compound does not undergo a substitution reaction.

Fuchs (93) has shown that bromine in carbon tetrachloride does not add to dry cellulose and Sakurada (49) noted that cellulose did not absorb the halogen of Wijs's solution. In the present work methylcellulose under the bromide-bromate experimental conditions (P. 59) was found not to consume any bromine. This fact and the experiments of Frognier and Goetsenhoven (70) and Cortese (69) on vinyl, allyl, and crotonyl derivatives are ample evidence to indicate that bromination of the methyl allyl cellulose should result only in addition to the double bond. Substitution is undoubtedly liable to take place when the allyl group is replaced by long unsaturated side chains, such as oleic and linoleic acids possess.

As shown in Table XIV the amount of bromine consumed by methyl allyl cellulose did not vary with the size of the sample taken, nor with the time (Table XV) or temperature (Table XVI) of bromination, which is a good indication that substitution is negligible unless it occurs instantaneously. Moreover, in the presence of glacial acetic acid the bromine is released quite slowly, and by agitation it is consumed by the double bonds as fast as it forms. Hence with the allyl carbon atoms (2) and (3) possessing very negative bromine atoms, substitution of the hydrogens on carbon atom (1) again seems unlikely.



$$\mathrm{H\overset{|}{\underset{|}{C}}}-\ddot{\underset{\cdot\cdot}{\mathrm{O}}}-\overset{(1)}{\overset{\ominus}{\mathrm{C}}\mathrm{H}_2}-\underset{\underset{\mathrm{Br}^-}{\uparrow}}{\overset{(2)}{\overset{\oplus}{\mathrm{C}}\mathrm{H}}}\cdots\underset{\underset{\mathrm{Br}^+}{\uparrow}}{\overset{(3)}{\overset{\ominus}{\mathrm{C}}\mathrm{H}_2}}$$

It is evident that absorption by the methyl allyl cellulose or a mechanical loss of bromine would give high values for allyl. This contingency is unlikely if the experimental procedure is followed closely.

## TABLE XIV

### Effect of Varying Sample Weight on Bromination

| Sample Weight (grams) | Volume of $KBrO_3$-KBr added (cc.) | Volume of $Na_2S_2O_3$ used (cc.) | % Allyl |
|---|---|---|---|
| 0.02468 | 3 | 4.19 | 25.97 |
| 0.05650 | 5 | 5.12 | 26.07 |
| 0.10041 | 8 | 6.98 | 26.09 |
| 0.19937 | 14 | 9.35 | 26.12 |

## TABLE XV

### Effect of Time on Bromination

| Time (minutes) | % Allyl | Allyl Groups per Glucose Unit |
|---|---|---|
| 3 | 26.21 | 1.461 |
| 3 | 26.36 | 1.471 |
| 5 | 26.31 | 1.468 |
| 5 | 26.25 | 1.464 |
| 60 | 26.38 | 1.473 |
| 60 | 26.44 | 1.478 |

## TABLE XVI

### Effect of Temperature on Bromination

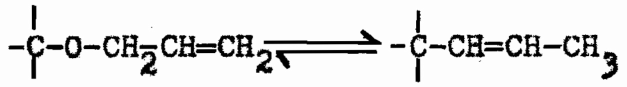
| Temperature | % Allyl |
|---|---|
| 20 | 25.80 |
| 30 | 25.87 |
| 40 | 25.91 |

Several larger scale brominations were carried out in order to check the mechanism of the reaction. The resulting methyl allyl cellulose dibromides were consistently low in bromine content, the highest value observed being 46.3 per cent, whereas the figure calculated from the bromide-bromate titration was 50.6 per cent. The dibromide hydrolyzed in distilled water or very dilute acetic acid at room temperature, and the dry dibromide also evolved a pungent smelling gas when stored in a desiccator *in vacuo* for a week. These decomposition reactions were far too slow to explain the discrepancy between the calculated and observed bromine contents of the dibromide. Therefore, it was inferred that a small amount of hypobromous acid, as well as free bromine, had added to the allyl group to form the bromohydrin, $-\overset{|}{\underset{|}{C}}-O-CH_2-CH(OH)CH_2Br$. As explained in the Introduction, such addition would cause no inaccuracy in the bromide-bromate titration . The analysis of Sakurada's allyl cellulose dibromide (49) was also 3 per cent low.

Another possible method of estimating the allyl group involved the quantitative hydrogenation of the double bonds in methyl allyl cellulose. Preliminary hydrogenations summarized in Table VII made it clear that the allyl ether was reduced with great difficulty, as has been previously noted for allyl alcohol (94). More success was had in an estimation based on the fact that the complete allylation of cellulose increases the carbon content from 44.4 to 63.8

per cent. The results of sufficiently accurate combustion analysis therefore in theory determined the allyl substitution. In practice, however, the carbon analyses were variable and uniformly lower than the values calculated from the bromide-bromate titration. It was eventually found that the rigorous exclusion of air while the methyl allyl cellulose was being dried and prepared for analysis resulted in good checks between the two methods of estimation. (P. 42 and 46). Adsorption of atmospheric oxygen, with the formation of peroxides, presumably occurred quickly enough to depress the carbon content of the methyl allyl cellulose. The concordance between the carbon and bromide-bromate estimations suggested that the latter probably gave the allyl content correctly to one part in a hundred, or to about 0.02 allyl groups per glucose unit.

When thoroughly acetylated with acetic anhydride and pyridine, the methyl allyl cellulose gave a white, fibrous soluble acetyl derivative. This derivative was analyzed for acetyl by a standard saponification with alkali (86) and also by a new, unpublished method just devised by Mr. R. U. Lemieux. Control experiments, carried out by Mr. Lemieux, showed that the acetyl groups in cellulose acetate, or the ethyl groups in ethyl cellulose, could be quantitatively recovered as acetic acid by distilling the samples with aqueous chromium trioxide. Blank values were obtained with methylcellulose and the results with the mixed esters, cellulose acetate-butyrate and acetate propionate, were non-quantitative . Although the results with methyl allyl cellulose acetate were high, it was found that methyl allyl cellulose itself recorded an apparent acetyl value of 1.65 per cent. This unexpected circumstance might have originated in a slight shift of the double bond in the allyl group under the conditions of the estimation, giving rise to a $CH_3CH{=}$ unit readily oxidized to acetic acid.



$$-\overset{|}{\underset{|}{C}}-O-CH_2CH{=}CH_2 \rightleftharpoons -\overset{|}{\underset{|}{C}}-CH{=}CH-CH_3$$

98.35%     1.65%

With this correction, acetyl values obtained by both methods came into fair agreement.

## TABLE XVII

### Comparison of Acetyl Values[(a)] by Two Methods

| Saponification<br>% | $CrO_3$ Method<br>% | $CrO_3$ Method Corrected<br>% |
|---|---|---|
| 14.21 | 15.41 | 14.03 |
| 14.38 | 15.68 | 14.30 |

(a) On methyl allyl cellulose acetate (See P. 53)

The value of acetyl 14.3 per cent was accepted as correct and allyl groups amounted to 22.4 per cent as found by the bromide-bromate titration. Since the substance originated in a methylcellulose of substitution 0.59 and base molecular weight of 170.4, the following simultaneous equations revealed the substitutions, x and y of the acetyl and allyl groups, respectively.

$$\%\ \text{Acetyl} = \frac{4300x}{170.4 + 42x + 40y}$$

$$\%\ \text{Allyl} = \frac{4100y}{170.4 + 42x + 40y}$$

Solution of these equations gave substitutions of 0.89 and 1.45 for acetyl and allyl, respectively. These values, together with that of 0.59 for the methyl groups, amounted to a total substitution of 2.93; whereas 3.00 was that required by theory. This discrepancy of 0.07 groups may be caused by the different analytical manipulations, but most likely results from slight polymerization during the preparation of the methyl allyl cellulose. The slightly low carbon values obtained support this latter view (See P. 42, 46). However, this satisfactory agreement was the final indication that allyl groups were estimated with reasonable accuracy by the bromination method as modified during the present work.

## IV PHYSICAL PROPERTIES OF UNPLASTICIZED CLEAR FILMS OF METHYL ALLYL CELLULOSES

### 1. Unpolymerized Films

The unpolymerized and unplasticized films of methyl allyl celluloses formed as described in the Experimental portion (P. 65), were water-white in colour, very clear, transparent, odourless and tasteless. The surfaces of all these films had a slight uniform mottle caused possibly by local strains although the Fischer Strainoscope indicated no gross strains were present. This mottle was more pronounced if the films were dried quickly. Some physical properties of these films are given in Table XVIII.

It is clear from the Table XVIII that the "lower" substituted product had a higher tensile strength and higher Mullen burst value, perhaps because the weaker alkali used during its preparation had caused less degradation, or more likely, because there were more unsubstituted hydroxyl groups. In this case the strength of the film decreased as more and more polar hydroxyl groups were replaced by allyl groups whose mutual attraction is very low (98).

The tensile strength of the "higher" substituted methyl allyl cellulose, which had an intrinsic viscosity of 3.25, was similar to the tensile strength of benzyl cellulose films with the same intrinsic viscosity prepared by Okada (46). It may be that benzyl and unpolymerized allyl groups behave in

# TABLE XVIII

## Physical Properties of Unpolymerized Methyl Allyl Cellulose Films

| Property | Lower Substituted ($0.95$ allyl, $0.59$ $OCH_3$ and $1.46$ $OH$) | Higher Substituted ($1.44$ allyl, $0.59$ $OCH_3$ and $0.97$ $OH$) |
|---|---|---|
| 1. Specific Gravity (a) | 1.10 - 1.14 | 1.05 - 1.07 |
| 2. Tensile Strength (lb./sq. in) (dry) (b) | 8,200 ± 330 | 6,400 ± 500 |
| 3. Tensile Strength (kg./sq.cm.) (dry) (b) | 580 ± 20 | 450 ± 40 |
| 4. Elongation % (dry) (b) | 9 - 16 | 7 - 9 |
| 5. Moisture Vapour Permeability $g./cm.^2/0.01$ cm./hr. @ 37.5° (100° F.) (c) | $18.77 \times 10^{-4}$ | $17.74 \times 10^{-4}$ |
| 6. Mullen Burst Test (approx.) lbs./sq.in./0.01 in. (d) | 200 | 70 |
| 7. Air Porosity (e) | non-porous | non-porous |
| 8. Flexibility | Excellent | Good |

(a) Reference 95
(b) Reference 88
(c) Reference 89
(d) Reference 96
(e) Reference 97

a similar manner in cellulose. However, Okada's benzyl films had a greater elongation (22 per cent). The low elongation of these allyl films compared to methyl and benzyl celluloses suggests the possible existance of a few cross links even in the soluble allyl products.

## 2. Polymerized Films

The polymerization theory proposed by Nichols and Yanovsky (26) for simple allyl carbohydrates and described in the Introduction appears from certain qualitative observations to apply to methyl allyl celluloses. In the first place, polymerization of the cellulose ethers also requires oxygen. For example, a methyl allyl cellulose, after standing in air for five months, was only slightly soluble in glacial acetic acid, and its apparent allyl content had gone down from 1.32 to 0.61 allyl groups per glucose unit; while a similar sample, kept under a vacuum, was still 100 per cent soluble. In the second place, a strong acrid odour, possibly of acrolein, was observed whenever stoppered bottles containing purified methyl allyl cellulose were opened after they had stood undisturbed for a month or more. Table XIX shows the course of a polymerization accelerated by heating an unpolymerized film at 78° in air.

The relative rate of thermal polymerization of allyl ethers depends upon the temperature of polymerization (29). In the above example, a little more than twenty-four hours at 78° was required to render the film insoluble and much less time was necessary at 100°. It is interesting to note that the soluble portion (Table XIX) retains slightly fewer double bonds as polymerization proceeded. From this we can conclude that a certain small amount of cross linking is consistent with the retention of solubility.

## TABLE XIX

### Relative Rate of Thermal Polymerization of Films(a) in Air at 78° ± 2°

| Time in Oven (hours) | Insoluble Portion(b) % | Soluble Portion Allyl Groups/Glucose Unit |
|---|---|---|
| 0 | 0.9 | 1.44 |
| 1 | 1.5 | 1.42 |
| 6 | 9.7 | 1.37 |
| 12 | 22.2 | 1.34 |
| 24 | 70.0 | 1.29 |
| 48 | 100.0 | - |

(a) Cellulose substituted with 0.59 methyl and 1.44 allyl groups per glucose unit.

(b) In glacial acetic acid.

Although the "higher" substituted methyl allyl cellulose films polymerized very slowly in air at room temperature, the process was rapid under the influence of heat or ultra-violet light. Films that were rendered more than 50 per cent solvent resistant were generally less flexible and became quite brittle on prolonged treatment. Polymerization by heat treatment caused a slight yellowing of the colorless films.

Tables XX and XXI indicate that after polymerizing the elongation, solubilities and moisture vapour permeabilities of the films were reduced, while their tensile strengths usually remained approximately constant. Films polymerized under severe conditions showed decreased tensile strengths. The allyl starch films polymerized in air considerably quicker than the methyl allyl cellulose films (29).

## TABLE XX

### Physical Property Changes on Polymerization

| Film No. | Sample No. | Treatment | Nos. of Samples Tested | Tensile Strength (dry) | | Elongation (dry) % | Insoluble Portion % |
|---|---|---|---|---|---|---|---|
| | | | | lbs./sq.in. | kg./sq.mm. | | |
| **A. "Higher" Substituted Methyl Allyl Cellulose Films(a)** | | | | | | | |
| 1 | 1 | none | 10 | 5,290 ± 50 | 371 ± 3.5 | 11.4 ± 2.0 | 0.7 |
| 1 | 2 | 48 hrs. heat @ 100° | 9 | 5,300 ± 500 | 370 ± 35 | 3.0 ± 0.2 | 99.7 |
| 2 | 3 | 7 days in air @ 25° | 7 | 6,300 ± 300 | 440 ± 20 | 8.2 ± 1.0 | - |
| 2 | 4 | 21 " in air @ 25° | 4 | 6,400 ± 200 | 450 ± 14 | 4.5 ± 0.3 | - |
| 2 | 5 | 12 hrs. heat @ 100° | 6 | 4,500 ± 500 | 320 ± 35 | 3.0 ± 0.2 | 100.5 |
| 2 | 6 | 21 days in air and 24 hrs. ultra-violet | 3 | 4,300 ± 300 | 300 ± 20 | 2.1 ± 0.1 | 100 |
| 3 | 7 | none | 5 | 6,400 ± 580 | 450 ± 40 | 8.2 ± 0.8 | 0.45 |
| 3 | 8 | 6 hrs. ultra-violet | 5 | 6,500 ± 400 | 460 ± 30 | 5.0 ± 0.4 | 99 |
| 3 | 9 | 12 hrs. ultra-violet | 5 | 6,300 ± 500 | 440 ± 35 | 4.2 ± 0.8 | 100.2 |
| 3 | 10 | 24 hrs. ultra-violet | 5 | 4,500 ± 500 | 320 ± 35 | 2.3 ± 0.7 | 100.8 |
| **B. "Lower" Substituted Methyl Allyl Cellulose Films(a)** | | | | | | | |
| 4 | 11 | none | 10 | 8,210 ± 325 | 579 ± 18 | 13.1 ± 3.1 | |
| 4 | 12 | 12 hrs. under ultra-violet (>2800Å) | 5 | 7,750 ± 200 | 546 ± 14 | 10 ± 2.0 | |
| 4 | 13 | 24 hrs. under ultra-violet (12 hrs. >2800Å) | 5 | 6,960 ± 100 | 490 ± 6 | 3 ± 0.05 | |
| **C. Allyl Starch Films** | | | | | | | |
| 5 | 14 | 2 days in air | 6 | 374 ± 10 | 26 ± 1 | 72 ± 42.0 | - |
| 5 | 15 | 18 hrs. ultra-violet (>2800Å) | 5 | 2,770 ± 230 | 195 ± 16 | 2.8 ± 0.3 | 100 |

(a) See Table XVIII

## Notes on Table XX

(i) Rate of Loading Films - No. 1 - 13-16 Seconds
No. 2 - 13-20 "
No. 3 - 16-20 "
No. 4 - 13-21 "
No. 5 - 18-29 "

(ii) Width of all test specimens = 15 mm.
Length of all test specimens= 50 mm.

(iii) All samples were conditioned for 3 days at a constant temperature of 73° F.± 1° and 50 per cent humidity before testing.

(iv) Film 1 - dried in approximately 18 hours under reduced pressure of 1 cm.

Films 2, 3, 4 and 5 - dried in approximately 72 to 96 hours under reduced pressure of 9 cm.

(v) Average thickness of Film No. 1 - 0.0029± 0.0003 inches
No. 2 - 0.00275±0.00025 "
No. 3 - 0.0021±0.00010 "
No. 4 - 0.0020±0.0002 "
No. 5 - 0.0031±0.0001 "

(each hundred readings)

## TABLE XXI

### Moisture Vapour Permeability Changes on Polymerizing under Ultra-Violet Light

| Sample Number | Film Density | Composition of Film(a) | Moisture Vapour Permeability(b) gm/cm.$^2$/0.01 cm./hr. at 37.5° (100° F.) | | | |
|---|---|---|---|---|---|---|
| | | | Unpolymerised Film | Polymerised Film | | % Decrease |
| | | | | Time under Ultra-Violet | Permeability | |
| 1 | 1.100 | Methyl Allyl Cellulose (0.95 allyl groups per glucose unit) | $18.77 \times 10^{-4}$ | 12 hours(c) | $18.62 \times 10^{-4}$ | 0.8 |
| | | | | 24 hours | $16.01 \times 10^{-4}$ | 14.7 |
| 2 | 1.065 | Methyl Allyl Cellulose (1.44 allyl groups per glucose unit) | $17.50 \times 10^{-4}$ | 24 hours | $10.69 \times 10^{-4}$ | 38.9 |
| 3 | 1.053 | Methyl Allyl Cellulose (1.44 allyl groups per glucose unit) | $17.98 \times 10^{-4}$ | 24 hours | $11.96 \times 10^{-4}$ | 33.5 |
| 4 | - | Allyl Starch (~2.8 allyl groups per glucose unit) | - | 18 hours(c) | $6.42 \times 10^{-4}$ | - |

(a) Average thickness of films (average of 20 to 30 readings across sheet)
Film 1 - 0.0045cm; Film 2 - 0.0054cm; Film 3 - 0.0071 cm.; Film 4 - 0.0096 cm.

(b) Wax used in test consisted of two parts of beeswax (m.p. 60.5 - 62°) and three parts of Rosin (m.p. 120 - 135°) by weight. The desiccant was C.P. calcium chloride.

(c) The wave length of the ultra-violet was greater than 2800 Å.

**NOTE:** At 37.5° (100° F.), the sample had a relative humidity of about 90 per cent on one face of the sheet and below 5 per cent on the other.

The assumption that the films became cross-linked through the polymerization of the allyl groups is not only consistent with chemical theory and the analytical data but affords qualitative explanations for the physical changes. Cross-linking would tend to prevent the chains from moving apart, thereby making solution and intramicellar swelling difficult or impossible. The interlocking of the chains would diminish their tendency to slip against each other under a tensile stress, thus resulting in a decrease in elongation. The increased rigidity of the system, owing to a large number of main valence bridges being formed between the cellulose chains, would also explain the increased brittleness or loss of flexibility of the polymerized films. The observation that the tensile strength of allyl starch films increased nine-fold on polymerizing (Table XX) is in accord with Dellenius (99) who has shown that the introduction of methylene bridges into low tenacity degraded viscose rayon greatly increased the tensile strength. These increases would be theoretically expected, but an explanation seems necessary in the case of the methyl allyl cellulose films, whose tensile strength was not markedly changed by polymerization.

The cellulose chains are loosely packed in the methyl allyl cellulose since the films are transparent and are not very dense. Also, the chains are known to have very limited flexibility and hence are not likely to move into any position that would enable the allyl groups they possess to polymerize more easily. The randomness and rigidity of the cellulose chains mean that even if strong primary valences are set up between some cellulose chains, as no doubt occurs in polymerization, there still may exist weak cross sections in the film owing to the local absence of cross linking. Now the tensile strength test measures the weakest part of the film, and so it is logical to assume that any sparsely polymerized section will break first resulting possibly in no "apparent" increase in tensile strength.

Another possible explanation for the lack in increase of tensile strength may be considered briefly. The tensile strengths of allyl plastics (100), as well as unpolymerized methyl allyl celluloses, are around 5,000 to 8,000 pounds per square inch. It is hard to see why a few allyl cross links in cellulose derivatives should confer strengths much greater than those of straight allyl plastics. Unlike cellulose films, unpolymerized starch films are very much weaker than allyl plastics (Table XX) and there is much room for improvement by allyl cross linking. The problem of predicting film properties from molecular structure is still in a highly empirical state. All the factors affecting tensile strength have not been brought to light, and so the above theorizing is tentative.

Samples 6 and 10, 12 and 13 (Table XX) decreased in tensile strength after being irradiated with ultra-violet light. This effect is possibly caused by a photochemical degradation of the cellulose derivatives. Much qualitative (101, 102), and recently quantitative data (103, 104, 105, 106), have been published to show that cellulose derivatives, such as cellulose nitrate and cellulose acetate, are affected by ultra-violet light in atmospheres of nitrogen, helium or oxygen. The degradation has been followed by measurement of increased copper numbers, decreased viscosities of dilute solutions and by other methods.

The moisture vapour permeability of methyl allyl cellulose films decreases markedly on polymerization (Table XXI). This decrease indicates that cross linking reduces the number of available spaces through which the water vapour molecules can pass, as a process that is supposed to "tighten up" the supermolecular structure of the film would be expected to do. The values given in Table XXI may not be absolute, but they definitely are comparable. Since allyl starch films were readily polymerized in the air, no permeability test on the unpolymerized film was attempted.

The "lower" substituted methyl allyl cellulose films either slightly polymerized or unpolymerized, failed to stop entirely the passage of nitroglycerine, as judged by the drastic test described in the Experimental portion. Since glycerol is immiscible with nitroglycerine and is often a good plasticizer for cellulose derivatives, it was thought that the impermeability of these films would be increased if they contained glycerol as a plasticizer. This addition, however, failed to stop the nitroglycerine.

## TABLE XXII

### Nitroglycerine Diffusion through Films

| No. | Treatment | Amount of Plasticizer (glycerine) % | Thickness (inches) | Change in Weight % | Reaction to Diphenylamine Reagent |
|---|---|---|---|---|---|
| 1 | Unpolymerized | 0 | 0.0054 | +3.5 | Faintly positive |
| 2 | Unpolymerized | 0 | 0.0056 | +0.4 | Positive |
| 3 | Unpolymerized | 8 | 0.0050 | +0.6 | Positive |
| 4 | Unpolymerized | 16 | 0.0056 | -0.6 | Positive |
| 5 | Unpolymerized | 28 | 0.0052 | -6.1 | Positive |
| 6 | Polymerized | 0 | 0.0056 | -0.4 | Negative |
| 7 | Polymerized | 8 | 0.0050 | -1.1 | Negative |
| 8 | Polymerized | 16 (a) | 0.0056 | -0.7 | Positive |
| 9 | Polymerized | 28 | 0.0056 | -3.8 | Negative |
| 10 | Polymerized | 0 (b) | 0.0060 | +10.0 | Negative |

(a) On retesting a hole appeared in the film, suggesting that there may have been a microscopic crack in the film which permitted the passage of nitroglycerine.

(b) Depression made by 30-pound Mullen tester.

The "higher" substituted unpolymerized methyl allyl cellulose films, both plasticized with glycerol and unplasticized, were also unsatisfactory, as judged from the positive result of the diphenylamine test for nitrate given by their under sides (Table XXII, Nos. 1 - 5). When similar films, both plasticized and unplasticized, were permitted to polymerize, the test was uniformly negative (Nos. 6 - 10) if experiment No. 8, which was probably faulty, is excluded from consideration.

The nitroglycerine diffusion tests therefore indicate that polymerized films are desirable as barriers, presumably because of a reduction in the number of available spaces through which the bulky nitroglycerine molecule may pass. The moisture vapour permeability (Table XXI) of allyl starch films indicates that if they could have been prepared in the same manner as the "higher" methyl allyl cellulose films, they too would have completely resisted nitroglycerine diffusion.

# SUMMARY

(1) The Historical Introduction contains a review of the pertinent literature on unsaturated esters of cellulose and ethers of starch and cellulose and the recent work concerning the mechanism of oxidation and polymerization of allyl derivatives of simple carbohydrates. Methods and mechanisms proposed for etherification were discussed with special reference to allyl starch and allyl cellulose, and to the estimation of the allyl group by halogenation of the double bond. Finally, the available literature on attempts to find coatings resistant to nitroglycerine diffusion was summarized.

(2) Technical methods were developed to prepare for the first time completely soluble methyl allyl celluloses of substitution, methyl 0.70, allyl 0.79; and methyl 0.59, allyl 0.95. A method for the preparation of a more highly allylated derivative, with substitution, methyl 0.59, and allyl 1.47, was also worked out. The solubilities and properties of these substances, together with the acetate and dibromide of the latter, were noted.

(3) Attention was given to methods of estimating the allyl groups. A modified standard bromide-bromate method, applied for the first time to unsaturated cellulose ethers,

gave reproducible results. The bromine consumed did not vary with the size of the sample, reaction time and temperature. Blank values were obtained with methylcellulose.

(4) A study was made of the changes in physical properties undergone by methyl allyl cellulose films cross linked by the polymerization of allyl groups. In general, polymerization of these films decreased their solubility, flexibility, elongation at break and moisture vapour permeability, while their tensile strength remained almost constant.

Films of the more highly allylated derivative, when polymerized, satisfied the standard sixteen day test for nitroglycerine barriers.

## CLAIMS FOR ORIGINAL RESEARCH

(1) Although allyl ethers of sugar derivatives and of starch with definite substitutions have been reported, those of cellulose have not been described except by Sakurada and in a few patents. Sakurada's allyl celluloses were only partially soluble and are possibly mixtures of unreacted cellulose and allyl ethers of various substitution. Patents generally give vague and incomplete directions for allylation.

The technical difficulties surrounding the allylation of the insoluble cellulose were overcome by the use of an alkali soluble low methylated cellulose. Detailed methods were worked out for preparing two methyl allyl celluloses of different substitution with only slight degradation, soluble in various common solvents.

(2) The first methyl allyl cellulose, obtained in 88 to 95 per cent yields, had 0.79 alloxyl and 0.70 methoxyl,or 0.95 alloxyl and 0.59 methoxyl,groups per glucose unit. It was completely soluble in morpholine and 90 per cent aqueous acetic acid.

(3) The second methyl allyl cellulose was obtained in 90 to 96 per cent yields, and contained 1.44 to 1.47 alloxyl and 0.59 methoxyl groups per glucose unit. It was completely

soluble in glacial acetic acid, chloroform, dioxane, methylene chloride, morpholine, pyridine and a benzene:ethyl alcohol (1:2) mixture.

(4) The preparation of a methyl allyl cellulose acetate in 90 to 93 per cent yields contained 1.47 alloxyl, 0.59 methoxyl and 0.93 acetyl groups per glucose unit. It was completely soluble in glacial acetic acid, acetone, benzene, chloroform, dioxane, methylene chloride, morpholine and pyridine.

(5) A rapid method for determining the degree of unsaturation of unsaturated cellulose ethers in a homogeneous, aqueous acetic acid solution at room temperature was devised. Although a modification of a standard bromide-bromate method, the application to unsaturated cellulose ethers containing short chained substituents, such as allyl, is new.

(6) The polymerization of methyl allyl cellulose films generally resulted in a decrease in elongation at break, in flexibility, in solubility and moisture vapour permeability, while their tensile strength remained approximately constant. In the case of allyl starch films, polymerization increased the tensile strength greatly. The polymerized films offered more resistance to the passage of nitroglycerine than unpolymerized films.

## SUGGESTIONS FOR FUTURE RESEARCH

(1) The preparation of a nitroglycerine barrier from a halogenated unsaturated cellulose ether by employing an etherifying agent that contains a long partly halogenated carbon chain with one double bond at the end, such as a 1-3-dichloro-7-heptene. From this thesis it is apparent that longer ether groups should improve the flexibility of the polymerized film and the halogens present should reduce the flammability of the film.

(2) The development of methods of coating cordite sticks with methyl allyl cellulose films and of conducting various weathering, aging and burning tests on the resulting coated stick.

(3) The investigation of the commercial possibilities of the methyl allyl cellulose acetate, soluble, in the unpolymerized state, in a wide range of common solvents.

(4) A study of the effects of cross-linking on the viscosity of methyl allyl cellulose acetate, the object being the further correlation of intrinsic viscosities with chemical structure.

(5) Attempts to increase the degree of allylation by using as starting materials either the "higher" substituted

methyl allyl cellulose swollen in benzene or the acetone soluble methyl allyl cellulose acetate. A nitrogen atmosphere and 50 per cent alkali would probably be desirable.

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