EFFECT OF DEGREE OF ACETYLATION ON MECHANICAL PROPERTIES OF CELLULOSE ACETATE FILMS

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V. INTRODUCTION

INTRODUCTION

Two important factors play a great role in affecting the mechanical properties of cellulose acetate films. They are polymolecularity and degree of substitution.

Polymolecularity indicates that cellulose acetate, as well as any other kind of polymer, consists of molecular chains of widely different lengths.

It was found by Thompson (89) that there was a definite relationship between mechanical properties of cellulose acetate films, and amounts of the various size molecules which were present.

Cellulose is composed of β - anhydroglucose units. Each of these units has three hydroxyl groups. These hydroxyl groups make it possible for cellulose chains to form hydrogen bonding. From this it may be concluded that the degree of alignment of the chains, that is, the degree of orientation, also influences mechanical properties, as the closer the packing the more the attractive forces are given full play. The forces holding the chains together are also sufficiently strong to resist deformation by a rise in temperature and consequently lead to a lack of thermoplasticity.

To increase thermoplasticity and improve the elastic properties, the chains must be separated in order to lower the forces of cohesion and consequently increase the intermolecular slip. This can be brought about by two methods; either by introducing substances which have greater attraction for the hydroxyl groups and thus are able to penetrate between and push aside the chains, or by replacing all or some of the hydroxyl groups with bulkier groups, such as acetate. The latter method also reduces the possibility of hydrogen bonding.

Because of the strong attraction between the molecular chains in cellulose and the close packing possible, very few solvents have been found, and none of these are at all permanent. This fact explains why cellulose itself is not available as a plastic, whereas its derivatives are.

The second method for bringing about the necessary separation of the chains is by replacing the hydroxyl groups by other groups. This can be done by the formation of ethers, such as ethyl cellulose, or of esters, such as cellulose acetate.

The extent or degree of substitution brings about variation in mechanical properties. This has been investigated by several authors on original samples of cellulose acetate disregarding the effect of molecular weight distributions which represents an uncontrolled variable.

It is the purpose of this investigation to find the effect of degree of acetylation, alone, on mechanical properties of cellulose acetate films. In order to accomplish this work four different samples of cellulose acetate with variable degree of acetylation were fractionated to an approximately constant degree of polymerization by fractional precipitation.

These samples, which varied from one another only by the degree of acetylation, were cast into films and various physical properties were determined for such films.

From the data thus obtained an attempt was made to determine the effect of degree of acetylation alone on mechanical properties of cellulose acetate films.

VI. LITERATURE REVIEW

LITERATURE REVIEW

The Structure of Cellulose

Cellulose is a naturally occuring high polymer. The elucidation of its chemical structure has occupied the attention of a large number of chemists for more than a hundred years (77), and a great deal is now known of its structure and mode of behavior. The generally accepted picture of a cellulose fiber is that it consists of a mass of long-chain molecules. The structure of the long chains themselves has been fairly definitely established as large numbers of β-anhydroglucose units, linked together as open chains in the manner shown in Fig.1.

It can be seen from fig. 1 that each glucose residue in the cellulose chain possesses three free hydroxyl groups, and, by the action of suitable reagents, these can be substituted to any degree.

The length of the molecular chain, which is, of course, directly proportional to the molecular weight, varies within each sample. Any given specimen of cellulose contains a large number of chains of widely varying length. The estimated chain length is therefore only an average value. These average values vary from sample to sample, according to the origin and treatment of the cellulose.

Other discussions concerning the structure of cellulose can be found in standard text books on cellulose (38, 61).

Acetylation of Cellulose

The earliest method for the preparation of cellulose acetate was given by Paul Schützenberger in 1865 (71). He heated cotton with acetic

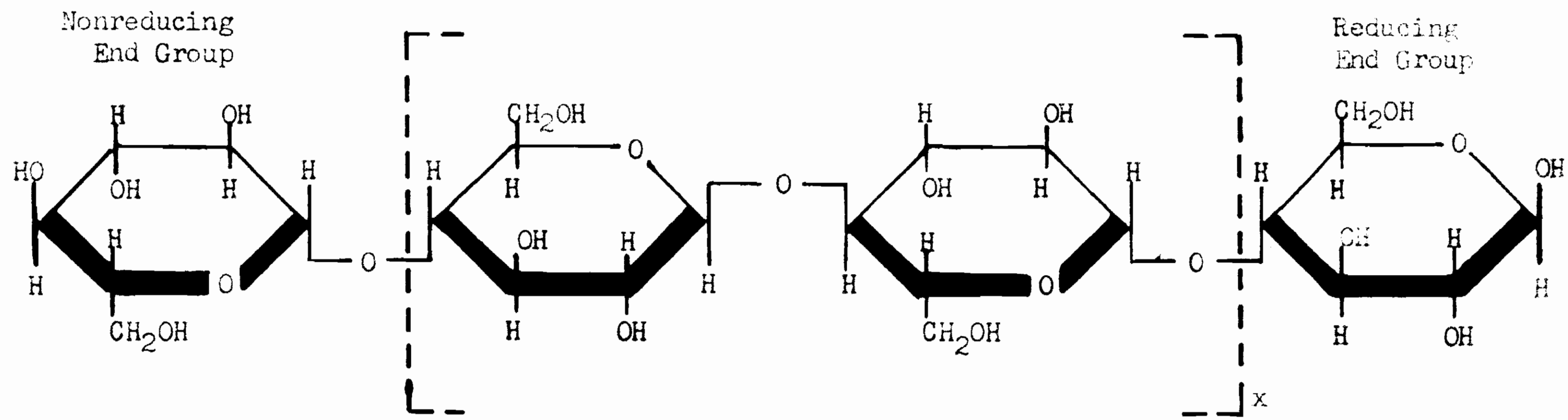

Figure 1.

Theoretical Configuration of the Cellulose Molecule

D.P. $= 2x + 2$

anhydride in a sealed tube at about 180 degrees C. until the cotton passed into solution. The cellulose acetate was then precipitated by the addition of water, separated, and dried.

Further investigations were carried out by a number of workers to improve this method of acetylation, but the next successful step was made in 1879 by Franchimont (29), when he added sulfuric acid to the reaction mixture which greatly improved the acetylation process.

Cross and Bevan (14) described the use of zinc chloride as a catalyst for acetylation.

Chemically, the acetylation of cellulose (17, 61, 77) follows a similar course to the conversion of any alcohol to the acetate ester. Practically, however, matters are complicated by the large size of the cellulose molecules, their high degree of association, and the necessity for avoiding any excessive breakdown of the cellulose molecule in the process.

The methods of acetylation fall into two categories. The first one is called the solution process by which cellulose acetate is dissolved as it is formed and remains in solution at the end of the reaction. The second method is called the non-solution process by which the fibrous structure of the cellulose remains unchanged, and the acetate is formed by surface attack on the swollen fibers. When the secondary, or acetone soluble acetate is required, the solution method is almost exclusively employed.

The physical condition of the cellulose fibers is of great importance in determining the speed and efficiency of acetylation. Correct adjustment of moisture content is, for instance, of great importance. Pretreatment of cellulose with suitable reagents greatly improves the acetylation process. The most usual method (38, 61, 77) is simply to treat the cellulose with glacial acetic acid at a slightly elevated temperature for a few hours, after which it is transferred to the acetylation mixture. The acetylation mixture consists of the solvent, the catalyst, and the acetylation agent itself. Normally, the latter is acetic anhydride while the catalyst is sulfuric acid and the solvent medium is acetic acid or methylene chloride.

The reaction is allowed to proceed under varying conditions of time, temperature and pressure to get the desirable range of viscosity and degree of acetylation.

Usually when acetylation is completed, the product is called primary cellulose acetate or cellulose triacetate. This is then hydrolyzed by acetic acid to the so called secondary cellulose acetate which is acetone soluble. The secondary cellulose acetate is precipitated in a large volume of water, washed thoroughly and dried.

The mechanism of the acetylation reaction, using sulfuric acid as a catalyst, has been discussed by a large number of investigators. For instance some investigators (30, 81, 87) claimed that sulfuric acid reacts with acetic anhydride forming acetylsulfuric acid which functions as the acetylation agent. Ost (59), however, believed that the function of sulfuric acid is to form cellulose sulfate ester at first and then the sulfate groups are replaced by acetyl groups.

The theory of Ost has been confirmed by several investigators notably in the most recent work by Malm and Tanghe (49).

The use of other catalysts in acetylation and their mechanisms are discussed thoroughly in several books on cellulose (17, 38, 61).

Solubility of Cellulose Acetate

Generally speeking cellulose acetate is divided into two classes. The first class is called primary cellulose acetate in which almost all the three hydroxyl groups of each glucose unit are acetylated. The second class is called secondary cellulose acetate which is the partially hydrolyzed form of the primary cellulose acetate.

The usual solvent for primary cellulose acetate is chloroform and for the secondary cellulose acetate is acetone (86), the latter having a degree of combined acetic acid between 50 - 58 % .

Further hydrolysis of cellulose acetate produces a grade which is completely soluble in water and has a degree of combined acetic acid below 30% (10). Continued hydrolysis below about 18% combined acetic acid results in regeneration of essentially deacetylated cellulose, which is insoluble in water and organic solvents.

The normal secondary grades of cellulose acetate of medium viscosity, such as are extensively used for plastics, are soluble only in acetone among the more common organic solvents (77). In addition, hot aqueous alcohol has a gelling effect, but does not give true and stable solution. Some esters, such as methyl acetate and ethyl lactate, are also good solvents, as are a number of odd solvents, including dioxane, pyridene and diacetone alcohol. The limited solubility is , of course, a great advantage for its use in plastics, as it confers a good measure of solvent resistance on the plastic artcle.

As a general rule , the efficiency or power of a solvent can be judged from the viscosity of the resulting solution, and the lower the viscosity the more active the solvent (21, 43).

Generally speaking, the solubility decreases with increase in degree of polymerization (23), and this effect is illustrated by its use for separating fractions of different degree of polymerization from a commercial sample.

Fractionation of Cellulose Acetate

Since a sample of cellulose consists of molecular chains of widely different lengths, and the same is true, of its derivatives, a thorough knowledge of the molecular - weight distributiŏn is of considerable importance in the study of degradation machanism; in the comparison of molecular weights obtained by different methods; and in the study of the mechanical properties of cellulose derivatives (61). For these and other reasons, a large number of attempts have been made to secure this information on various cellulose derivatives such as cellulose acetate. The methods employed have almost always been those of fractionation into fractions of narrower molecular weight distribution and the construction of the distribution curve from a knowledge of the weight and molecular weight of these fractions.

Fractionation of cellulose triacetate, in which all the three hydroxyl groups of a glucose unit have been acetylated, is very difficult and little information is available about it (22).

Most of the work published on fractionation refers to acetone-soluble acetates, and the most widely used method is that of fractional precipitation (38).

Generally speaking, the separation of a polymer mixture into fractions is based on the primary property of the individual polymer molecules, namely, the size of the molecule (15). Such properties as diffusion, sedimentation, solubility, and volatility are related to molecular weight, and as a result the fractionation of macromolecules may be accomplished in a number of ways. The methods of separating materials into fractions have been tabulated by Cragg and Hammerschlag and are given in Table 1 (13).

The fractionation of polymers is much more difficult and more complex than the fractionation of ordinary low molecular weight compounds (15). For example, in the fractionation of acetanilide or sucrose, a fraction is eventually obtained that consists of pure acetanilide or sucrose, in which each molecule is identical with each neighbor molecule. In high polymers, however, such a condition is never reached since further processing of these fractions shows that they are heterogeneous and contain polymers of different chain lengths.

Regardless of the method used in fractionation, the objective of the separation is to obtain fractions as narrow and as sharp as possible. To obtain this sharp distribution, it may be necessary to refractionate the isolated fraction, and to combine all fractions within the same molecular weight range. But it is claimed that no matter how many times the fraction is refractionated the best that can be attained is a fraction with an average degree of polymerization with $\pm$ 5% variation from the mean (15, 61, 70).

Since fractional precipitation is the most widely used method, it will

Table 1

Separation of Mixtures into Fractions

Method	Principle on which Separation is Based
I. Solubility Methods 1. Fractional Precipitation. a. By addition of Precipitant. b. By Cooling. 2. Fractional Solution a. Solvent of Varying Composition. b. Varying Temperature	Solubility decreases with increases in molecular weight.
3. Distribution between Two Immiscible Solvents.	Distribution Coefficient depends on molecular weight.
II. Rate-of-solution method (diffusion into a single solvent)	Smaller molecules diffuse faster.
III. Ultracentrifuge	Sedimentation velocity increases with molecular weight.
IV. Chromatographic adsorption.	Smaller molecules are preferentially adsorbed.
V. Ultrafiltration through graded membranes.	Sieving action.
VI. Molecular distillation	Larger molecules are less volatile.

be discussed in some detail.

A suitable combination of a solvent and a precipitant miscible with one another is selected, and the latter is added to a dilute solution of the polymer in the former until a slight turbidity develops at the temperature chosen for the fractionation (27). For the purpose of assuring establishment of equilibrium between the two phases which form, it is usually considered desirable to warm the solution to homogenity and then to allow precipitation to take place during gradual cooling to the temperature of the fractionation bath. The solution is stirred during precipitation. Thereafter the precipitated phase is allowed to settle. After it has formed a coherent layer, which may require from 2 to 24 hours, the supernatant phase is removed. Polymer in the precipitated phase, representing the first fraction, is recovered by drying or by coagulation in a large excess of precipitant. A judiciously chosen increment of precipitant is added to the supernatant portion from the first separation, and the operation is repeated to obtain the second fraction (27, 33, 50, 67, 75, 88, 89).

The precipitation process is more appropriately regarded as a separation of the system into two liquid phases. The one relatively rich in polymer is called, somewhat inaccurately, the precipitate and the other the supernatant phase (27). The precipitated phase actually contains much more solvent than polymer.

The successive fractions may be obtained by lowering the temperature in suitable increments rather than by varying the solvent composition isothermally. If a poor solvent is found from which the polymer precipitates in a convenient temperature range, it may be used alone without addition of another component.

Fractionation Efficiency and Polymer Distribution

The efficiency of the fractionation process determines the sharpness, or slopes, of the distribution curves, and inefficient fractionation distorts the distribution curve (15). The difference in the nature of the distribution curve between a good and poor fractionation is readily demonstrable by using a fractional-precipitation method. As a general rule, fractional precipitation by the addition of a precipitant to a concentrated solution of the polymer produces unsatisfactory results. Douglas and Stoops (19) have shown that the separation of a polymer into fractions is sharper when a dilute rather than a concentrated solution of polymer is used. Flory (27) explained that analysis showed a single fractional separation at high dilution may be as efficient as the laborious separation of the unwieldy array of overlapping fractions obtained by successive refractionations.

When sufficient sharp fractions have been isolated from a polymer, and the molecular weights of the fractions have been determined, the distribution of the fractions of the various molecular weights isolated from the original sample may be represented in a number of ways. For instance, by determining the percentage of each fraction and its degree of polymerization, it is possible to construct an integral distribution curve. This is done by plotting 100 - A, where A is the accumulative percent, starting with the fraction of highest degree of polymerization of the fraction.

The differential distribution curve can be obtained by differentiating the integral distribution curve if the equation for the integral distribution curve is known. Another method for determining the differential distribution curve can be done graphically by taking slopes of various points on the integral distribution curve and plotting them against the corresponding degrees of polymerization. Methods of determining the integral and differential distribution curves for cellulose acetate are discussed thoroughly in Thompson's Master's and Doctoral Theses (88, 89).

Molecular Weight Determination of Cellulose Acetate

Not only from the scientific aspect, but also in view of the various commercial uses of cellulose and cellulose derivatives, a knowledge of the molecular weight of a given sample is of great importance because of its influence on the behavior and usefulness of cellulose and its derivatives.

The methods used for the determination of molecular weight of cellulose acetate are numerous. The most important of which include; end group determination; osmotic pressure measurements; ultracentrifugation; light scattering; dielectric dispersion; and viscosity.

The end group method is based upon the assumptions that the chains in cellulose isolated from its various sources are open and that the end groups of the terminating units may undergo certain characteristic reactions (38). End group determinations make use of the fact that the two end groups are different from the groups in the repeating glucose units and represent certain percentages of the total chain. As the ratio of end groups to normal groups necessarily changes with the chain length, a small end group content of a given sample indicates a long average chain length and vice versa.

The osmotic pressure method is discussed thoroughly by Doty and Spurlin (61). In this method the technique of osmometry as applied to cellulose acetate is limited in the low molecular weight range by membrane permeability and in the high molecular weight range by the precision of measurement. As a consequence, the over-all precision of molecular weight determinations is highest for sharp fractions in the range of 20,000 - 100,000 where the probable error can be kept below $\pm$ 1%. The error in this range will increase, however, for unfractionated samples to an extent that depends on the molecular weight distribution and the selectivity of the membrane used.

The ultracentrifuge method was first developed by Svedberg (83, 84) who used this method in the study of proteins. The principle is based on the facts that particles suspended in a liquid distribute themselves so that their concentration diminishes with height due to gravitational influences, the size or weight of the particles, the temperature, etc., and the vertical distribution of the particles will be proportional to their weights. Under direct gravitational influence it is possible to show changes in concentration if the particles are of enormous size, that is, beyond the size of ordinary molecules. Molecular weights are usually determined in an ultracentrifuge by either of two methods: the sedimentation equilibrium method or the sedimentation rate method. The former method consists in subjecting the solution of the polymer to the high gravitational field and measuring the fall in concentration during the course of the centrifuging at definite time intervals. These changes in concentration are followed or recorded by optical changes in refractive index or light absorption and the average molecular weight can be calculated from a certain relationship between molecular weight and changes in concentration (15).

Lamm and Poulson (45) have perfected the use of the ultracentrifuge for the determination of molecular weights as based on sedimentation rate and diffusion. By measuring the rate of sedimentation per unit centrifugal field and the diffusion constant, the molecular weight can be calculated from the well-known Svedberg equation (85).

In the light scattering method of determining molecular weights of macromolecules, when a beam of light falls upon a liquid, a gas, or a solid, the electrical field of the light induces electronic oscillations in the material. The irradiated materials in turn serve as a secondary source of light and emit scattered radiation with a wave length equal to that of the incident light. If no fluorescence or absorption occurs when a parallel beam of light is passed through a transparent system such as a gas, a liquid, a solid, or a solution, all the decrease in light is due to scattering. By measuring, as a function of concentration, the absolute intensity of light scattered at various angles from a monochromatic, incident beam, it is possible to determine the weight-average molecular weight. The intensity of scattered light depends on the polarizability of the particles compared with that of the medium in which they are suspended; it depends also on the size of the particles and their concentration. If the solution is sufficiently dilute, the intensity of the scattered light is equal to the sum of contributions from the individual particles. The intensity of the light scattered in a given direction by a single particle will be proportional to the square of its size and independent of its shape if its polarizability is the same in different directions and its dimensions are small compared with the wavelength of the light. The total light scattered by a solution containing particles at a specified concentration by weight consequently is greater the larger the individual particles. Hence the size of the particles may be deduced from the intensity of the light scattered by a dilute solution or suspension, assuming, that the polarizabilities of the particles and of the medium are known. The irregularly coiled polymer particles in dilute polymer solutions fulfill the condition of polarizability, but if their molecular weights are very large, their mean dimensions in solution may not be much less than the wave length of the light. Corrections must then be made for the dissymmetry of the scattered light in order to calculate the molecular weight.

The modern work which dates from the paper in 1944 by Debye (16) has been reviewed by Oster (60) and Doty and Edsall (18).

A considerable part of the theory of dielectric dispersion method for determining molecular weights of high polymers is due to Debye (2) and extended by Scherer and Testerman (66) on cellulose nitrate. This method is still under investigation by Scherer and his co-workers in an attempt to determine not only the molecular weights of high polymers but also the distribution of chain lengths (35). The method generally consists of measuring the ability of a dipolar molecule to follow alternating charges between two electrodes. Small particles cease at higher frequency than large particles to follow the alternations.

The last and the most widely used method for determining the molecular weight of cellulose acetate is the viscosity method developed by Staudinger (7, 15, 27, 38, 61, 78, 80).

Solutions or melts of high polymers exhibit flow characteristics which are very different from those of ordinary liquids. Not only are the viscosities of the melts high, but the viscosities of their solutions are also large compared to that of the solvent, even when very dilute solutions are used.

Viscosity may be considered a phenomenon of internal friction which regulates the motion of adjacent portions of liquid, and its reciprocal is defined as fluidity (15).

The higher the molecular weight within a given series of linear polymer homologs, the greater the increase in viscosity produced by a given weight concentration of polymer. In other words, the intrinsic viscosity, which represents the capacity of a polymer to enhance the viscosity, increases with molecular weight. An absolute value for the molecular weight of a polymer cannot be derived from solution viscosity measurements. The dependence of the intrinsic viscosity on molecular weight must be established more or less empirically in each individual case by comparison with molecular weights determined by one of the absolute methods discussed above (27).

Staudinger (78) has developed the following equation for the relationship between the viscosity of cellulose or its derivatives in solution and its average molecular weight:

$$\frac{n_{sp}}{c} = K_m \times M$$

in which n_{sp} is the specific viscosity (i.e., the viscosity increase over that of the solvent); c is the concentration; M is the molecular weight; and K_m is a constant. Thus, if the value of the constant is known, the molecular weight of a given cellulosic material may be calculated simply from its specific viscosity.

To establish the value of the constant K_m, the molecular weight of the cellulosic material must be determined by one of the absolute methods. With the K_m thus established for one type of cellulose acetate it is possible to calculate the molecular weight of cellulose acetate by using the above equation (38) which can be written in the following manner

$$\frac{n_{sp}}{c} = \frac{n-n_o}{c\ n_o} = \frac{n_r-1}{c} = K_m \times M$$

where

n_{sp} = specific viscosity

n = viscosity of polymer solution

n_o = viscosity of pure solvent

n_r = relative viscosity

K_m = constant

M = molecular weight

c = concentration of solution in grams per liter

Many investigators proposed several modifications of Staudinger's equation (4, 5, 6, 37, 44) but it was found that the original equation of Staudinger was fairly satisfactory especially in dilute solutions of concentrations as low as one gram per liter, especially for low molecular weights (5, 38).

In almost all the viscosity measurements for cellulose acetate, acetone is used as the solvent. In a recent paper, however, (12) a method was described using cuprammonium hydroxide or cupriethylene diamine as the solvent which is sufficiently alkaline to de-esterify completely the cellulose acetate and the degree of polymerization determined is that of the pure cellulose formed.

This procedure is preferred since some intermediate products as well as the highly substituted cellulose acetate are difficultly soluble, and the factor for converting the viscosity of cellulose acetate solutions to degree of polymerization varies markedly with the degree of acetylation. Furthermore, mixed esters can be handled by the same technique, thereby avoiding the necessity for complicated formulas relating viscosity and degree of polymerization with degree of acetylation (61).

Factors Affecting Mechanical Properties of High Polymers

Several investigators discussed the mechanical properties of high polymers including cellulose acetate (3, 7, 9, 31, 52, 61, 77). Their discussions are more or less qualitative in their nature.

Factors which influence the mechanical properties of high polymers are numerous. They include such factors as molecular structure, degree of orientation, polymolecularity, degree of polymerization, degree of substitution, plasticization, atmospheric conditions and various other physical and chemical considerations. Only those factors which are of great importance will be discussed briefly.

It must be born in mind that these factors are interdependent on each other. Any change in any factor will produce a change in the effect of other factors, therefore in order to study the effect of one factor on the mechanical properties, other factors must be kept constant or eliminated.

It is an established fact that linear polymers with high degree of polymerization have better and higher physical properties than polymers with low degree of polymerization.

For cellulose derivatives a minimum value of degree of polymerization between 30 - 80 is required for mechanical testing. The mechanical properties, however, increase with increase in degree of polymerization until reaching a limit between 100 - 250 above which no appreciable change, if any, is found in the mechanical properties (9, 19, 64, 65, 73, 74, 76).

Native cellulose, particularly in the form of cotton and similar fibers, has an extraordinarily high tensile strength. The origin of this tensile strength is thought to lie in the powerful forces of cohesion between the molecular chains. Rupture of the fiber can obviously take place in two ways, either by fracture of the main valency links, that is, of the molecular chains themselves, or by the chains slipping past each other, causing thinning and ultimately breaking (77). The two processes have been shown pictorially by Meyer (55).

In practice, it is usually found that, up to a point, increase in chain length leads to an increase in tensile strength, and then there is a falling-off of this effect. Meyer (55) claimed that, at the point where this happens, the chains are so long that the forces of cohesion between them are greater than those required to break the main valency links, and, consequently, the latter process predominates. The origin of the forces between adjacent chains of cellulose is now known to be due to hydrogen bonding between the hydroxyl groups.

It should also be mentioned that the degree of alignment of the chains, that is, the degree of orientation, also influences tensile strength, as the closer the packing the more the attractive forces are given full play. The forces holding the chains together are also sufficiently strong to restrict deformation by rise in temperature and consequently lead to a lack of thermoplasticity. Using similar arguments to those employed when discussing tensile strength, it can be shown that other mechanical properties, including elongation, flexibility and impact strength, are also dependent on the amount of slipping which takes place between the molecular chains when stretched.

Substitution of the hydroxyl groups in cellulose reduces, by varying amounts, the attraction between cellulose chains simply by changing the character of the molecular grouping present (20). Thus, it is found that cellulose nitrate makes a somewhat stronger sheet than does cellulose acetate under comparable circumstances (69).

Most effective use of these forces of attraction can be made if the attractive centers are regularly spaced along the chain to permit active groups from adjacent chains to approach each other most closely. Hydrogen bonding and other polar forces drop off rapidly with increasing distance. Hence it is also important that molecular shape and flexibility be of such a nature as to allow the chains when fully extended and parallel to pack readily into a close lattice under the forces of lateral attraction (61). The presence of bulky substituent groups reduces the lateral adhesion and disrupts the regular geometrical close packing of the molecules. Thus, cellulose and cellulose triacetate can form highly ordered and rigid systems not possible with partly esterified cellulose acetate (92). Saponifying the incomplete cellulose acetate gives rise to a more highly crystalline cellulose with greatly enhanced strength (92, 72).

To increase thermoplasticity and improve the elastic properties, the chains must be separated in order to lower the forces of cohesion and consequently increase the intermolecular slip. This can be brought about by two methods; either by introducing substances which have greater attraction for the hydroxyl groups and thus penetrate between and push aside the chains, or by replacing all or some of the hydroxyl groups with bulkier groups, such as acetate, the latter method also reduces the possibility of hydrogen bonding while the former process is the same as plasticizing.

The second method for bringing about the necessary separation of the chains is by replacing the hydroxyl groups by other groups. This can be done by the formation of ethers, such as ethyl cellulose, or of esters, such as cellulose acetate. It would be expected that the larger the substituent group introduced, the greater the anticipated effects, that is, lowering of the softening points, increase in solubility and elongation, and so on.

The extent or degree of substitution also brings about variation of these properties. In general, elongation, flexibility and similar properties increase with increasing degree of substitution to a maximum, and then decrease somewhat. This decrease, as has been explained before, is thought to be because, with a completely substituted molecule, close packing of the chains is again possible, whereas, with partial substitution, the surfaces of the chains are more ragged with consequent increase in mobility and slip. Also the poorer packing resulting from uneven surfaces gives improved solubility characteristics. A similar effect can be brought about by substituting with two different sized groups, such as is the case of mixed esters, an example being cellulose acetate butyrate.

It should be noted that the separation of the molecular chains, although desirable because of its effect on such properties as softening point and flexibility, has an adverse effect on other important mechanical properties, such as tensile strength and rigidity, and the art of manufacture is to strike a balance between these many factors to give a product of maximum value (77). The distribution of the substituent groups also plays a great role in affecting the mechanical properties of cellulose acetate. For example, a molecule of cellulose acetate with an average of, say, two acetate groups per glucose unit, could have one end of the chain completely acetylated and the other end completely unsubstituted. This type of molecule would have different characteristics from an evenly acetylated type, owing to the opportunity for closer packing, etc., along the unsubstituted portion. Little work has been published on this topic, but it is obvious that properties such as solubility may be profoundly affected. The history of a cellulose derivative can never be completely known, and so the exact behavior of a given sample cannot be precisely predicted or explained (77).

Mention has already been made of the fact that a sample of cellulose consists of molecular chains of widely different lengths, and the same is true, of course, of its derivatives. The presence of a large number of short chains has been found to adversely affect the tensile strength and other mechanical properties, presumably due to the pulling out of the small chains under stress (76). It was found that the samples which are most uniform in molecularity have a greater folding strength than comparable samples of greater polymolecularity.

The real difficulty in the establishment of a satisfactory relationship between molecular weight and strength lies in the fact that the latter is influenced by many other factors difficult to control experimentally. The same difficulty is applied to the degree of heterogeneity. Many investigators have tried to correlate the degree of heterogeneity with mechanical properties but no precise conclusion has been attained yet due to the disagreements between the results of several investigators (61). Some investigators claimed that materials with high degree of heterogeneity possess better mechanical properties than others with low heterogeneity, such as fractions, (54, 58, 63), while others claimed that unblended materials are better than blended materials (19, 51, 68, 76).

Recent work, however, indicates that fractionated polymers have better mechanical properties than unfractionated polymers (73, 74). These results have been confirmed by Scherer and Rouse with cellulose nitrate (65) and by Scherer and McNeer with ethyl cellulose (64).

Further investigations on the effect of molecular weight distributions on mechanical properties showed that materials having up to 25% polymers with D.P. less than 100 have almost no harmful effect on the mechanical properties, (64, 65, 73, 74) although, White (91) in a patent claimed that a blend of 75% ethylcellulose of D.P. 1000 with 25% of partially ethylated glucose (ethyl cellulose of D.P. = 1) has good mechanical properties.

Thompson (89) found that the mechanical properties of cellulose acetate fractions when plotted against the average D.P. showed that at a D.P. of 60 or less the films were too brittle to form coherent films and were thus assigned a zero value for all mechanical properties. From a D.P. of 60 to a value in the range of 100 to 150 there was a rapid increase in mechanical properties, and above this there was little or no change in the mechanical properties. A plot of the mechanical properties of the blends against either their weight average D.P. or against their number average D.P. showed no apparent relation. A thorough discussion and explanation of the effects of molecular weight distribution of cellulose acetate on mechanical properties can be found in Thompson's doctoral dissertation (89).

Another important factor which affects the mechanical properties is the use of plasticizers which are always used commercially with cellulose acetate films. The reason for using plasticizers is that cellulose acetate films are too brittle to be useful and the ester is not sufficiently thermoplastic to be formed or manipulated by other techniques. In addition, its discoloration and decomposition points are near to its softening point. These disadvantages are completely overcome by the use of suitable plasticizers. The efficiency of the plasticizer is concerned with the amount of plasticizer needed to produce the required change in the desired physical property. Plasticizers produce changes in the physical properties by separating the chains of the polymer, thereby reducing the magnitude of the intermolecular forces (61, 77).

It has been mentioned before that cellulose acetate consists of long molecular chains of varying lengths, lying in part ordered and part disordered fashion. That is to say, some ordered regions occur where the long chains are aligned in a fairly regular fashion and show definite crystallinity. It was also pointed out that a high degree of attraction exists between neighboring molecular chains and it is this strength of cohesion which is thought to account for the remarkably high tensile strength and other mechanical properties of cellulose and cellulose acetate fibers and films.

It was also mentioned that extensibility, flexibility and other similar properties are thought to be due to the sliding over one another of the molecular chains when the plastic body is under stress.

The simplest and most effective way of separating the chains is by the introduction of plasticizers which are organic compounds of low volatility and have a very high power of attraction for the fringes of the cellulose acetate molecule. Consequently, these compounds have the power of overcoming the forces of attraction holding the polymer molecules together, and entering between the chains.

Plasticizers are often divided into two classes (77): solvent or gelatinizing types, and non solvent types, the latter sometimes being referred to simply as softeners. The solvent types are regarded as true solvents for the polymer and have the greatest power of solvation of the side groups of the long chain molecules. A practical method of testing the miscibility level of plasticizers and polymers are developed and extended by Jones (42).

Different plasticizers are found to produce a very different order of modification of the properties. For example, it is found that a cellulose acetate containing 28% of one particular plasticizer has the same flow temperature as one containing 35% of another; that is, with exactly the same grade of acetate being used in each case. Differences in the extensibility are often even more marked, and the same proportion of plasticizer can give varying figures in eleongation using different plasticizers (28, 32).

Reed (62) has recently published a very complete list of those factors which he considers to be of great importance concerning physical properties of polymers before selecting plasticizers for commercial use.

Temperature, has a marked effect on the mechanical properties of cellulose acetate. This is illustrated by Welch, Hayes, Carswel and Nason (90). At low temperatures the material has a high ultimate strength, but the elongation at break is small. The material is relatively brittle and hard. At higher temperatures the ultimate elongation increases and the material becomes tough, but the ultimate strength is reduced somewhat. With further increase in temperature the tensile strength is considerably reduced and the material becomes soft and weak. These researches found out that temperature changes on the ultimate elongation of cellulose acetate under tension showed that an increase is observed up to approximately 50°C., but at higher temperatures a decrease takes place. Tests by the same authors on the influence of temperature changes on the modulus of elasticity of cellulose acetate showed that over a certain range the modulus was directly proportional to the temperature.

Still another important factor affecting the mechanical properties of cellulose acetate is humidity which has a marked effect on tensile strength. This has been discussed thoroughly by the same authors above (90). They showed that as the moisture content increases, corresponding to increase in humidity, the tensile strength decreases; but as saturation point is reached, changes take place more slowly. The influence of humidity on cellulose acetate of high acetyl content is less than in the case of medium acetyl content, because of the superior water resistance of the former. Moisture acts in many ways as a plasticizer with cellulose acetate. However, when humidity is too high, a relative decrease in percentage elongation takes place, the effect being more pronounced in the case of highly plasticized cellulose acetate. The modulus of elasticity decreases rapidly, at first, with increase in humidity, but slows down as the saturation point is reached.

It worth mentioning here that the results obtained from mechanical tests are only strictly valid under the precise conditions of the test (77, 24).

The final property which is to be described is the so called creep.

The mode of fracture of cellulose acetate under tension has been described by Findley (26). He pointed out that fracture is usually a characteristic of brittle materials and, as a rule, starts as a tear from some slight surface imperfection which spreads until rupture takes place.

All materials when subjected to a constant tensile force tend to extend, and the gradual increase in length with time is referred to as creep.

The subject of creep has received considerable attention both from a theoretical and practical standpoint. An excellent discussion on the theoretical aspects has recently been published by Adams and Throdahl (1), while W.N. Findley (25) investigated the practical creep properties of cellulose acetate plastics.

Findley's work showed that cellulose acetate plastics undergo considerable deformation when subjected to relatively small loads for prolonged periods of time. Fracture may also take place if the load is maintained for a sufficient length of time, even though the stress is far below the ultimate strength as determined by short time tests.

VII. EXPERIMENTAL

EXPERIMENTAL

Chemicals Used

The acetone used was commercially pure grade obtained from Commercial Solvents Corporation, Newark, New Jersey.

The n - heptane was pure grade, 99 mole per cent minimum, obtained from Phillips Petroleum Company, Bartlesville, Oklahoma.

The cupriethylenediamine solution contained exactly one mol. of copper, obtained from Ecusta Paper Corporation, Pisgah Forest, North Carolina.

The cellulose acetates were obtained from Hercules Powder Company, Parlin, New Jersey.

		Per cent Combined Acetic Acid	
Type	Lot Number	Quoted	Found
PM_4	40441	52.0-52.8	52.0
PM_3	41037	52.5-53.5	52.8
LH_1	41038	54.0-55.0	54.4
PM_6	41039	55.5-56.2	55.6

INTRODUCTION

The four samples of cellulose acetates were chosen from the different types available at Hercules Powder Company (36). These four samples have approximately the same viscosity range but different degrees of combined acetic acid. They are all soluble in acetone. Other types of cellulose acetate, with higher or lower degree of combined acetic acid than the chosen four types are insoluble in acetone, and their fractionation, if possible, is extremely difficult.

Three of these fractions, namely, PM_3, LH_1, and FM_6 have been investigated by Myers (57). He determined their distribution curves using small scale fractionation. From these distribution curves and from subsequent investigations on the method of determining the degree of polymerization, using acetone as the solvent, a fraction with a D.P. of 300 was thought to be the fraction with the highest percentage in the original sample.

On this basis an attempt was made to fractionate the four samples of cellulose acetates to get as sharp a fraction as possible from each sample with a D.P. of 300.

It was also found that in order to get a sufficient amount of a sharp fraction to be used for mechanical testing, a starting material of at least 2000 gms was necessary.

Fractionation Procedure

The methods of fractionating the four types of cellulose acetates were extensions and slight modifications of that developed by Scherer and his co-workers (47, 57, 67, 88, 89).

Two methods of fractional precipitation were applied in this investigation. They are the step-wise fractionation and the selective fractionation.

Step-wise Fractionation

In this procedure four batches of a 4% solution of cellulose acetate was made in a twenty liter pyrex bottle by mixing together 500 gms of air dried cellulose acetate and 12000 gms of solvent (95% acetone and 5% distilled water). The bottle was then rotated in a rotating machine until complete solution was obtained. This required at least 12 hours. After dissolution was completed the bottle was transfered to a constant temperature room at 25° c for a period of about 12 hours after which a judiciously chosen amount of precipitant, n-heptane, was slowly added to the solution with continuous stirring to precipitate 50% of the original cellulose acetate. The bottle was rotated for about 1.5 hours and then placed in a 15° c air thermostat for 22 hours.

The supernatant solution, which contained 2% cellulose acetate after this operation, was decanted into another 20 liter pyrex bottle, brought to 25° c with infra red lamps and another measured increment of precipitant was added to precipitate about 10% of the original cellulose acetate and again placed in the 15° c thermostat for 22 hours. The operation was repeated to get four or five different fractions from the original supernatant solution.

The 50% original fraction was dissolved in sufficient solvent to make 2% solution to which a measured amount of precipitant was added to precipitate about 10% fraction by the same procedure described above.

This fraction contained, in most cases, very high D.P. material and several kinds of impurities including gums, resins and dust. This fraction was stored for future use if needed.

The supernatant solution was fractionated in the same manner as the original supernatant into four or five fractions.

The same procedure was followed for the three other batches of the same type of cellulose acetate. The degrees of polymerization of these fractions were then determined and those fractions which had a D.P. not too far from 300 were combined together and dissolved in a 20 liter pyrex bottle to make a 2% solution. To the solution was added enough precipitant to precipitate about 10 - 15% fraction and separated out. Another 10 - 15% fraction was separated from the supernatant layer and the process was repeated until 6 - 8 fractions were obtained. The degrees of polymerization of these fractions were determined. The fractions which had D.P.s close to 300 were again combined and refractionated by the same procedure described above.

The process was repeated until a very sharp fraction of a D.P. 300 was reached. Refractionation of this fraction gave no appreciable change in D.P. which meant that the fraction had reached the highest possible sharpness by this method.

It was found that this method of fractionation was a very efficient one but unfortunately it was very tedious and very lengthy.

Selective Fractionation

In this method, four batches of a 4% solution of cellulose acetate are made in the same manner as that described for the step-wise fractionation and the temperature is brought to 25°c.

A measured amount of precipitant or non-solvent (n-heptane) is added to precipitate 50% of the original cellulose acetate. The bottle is then rotated for at least 1.5 hours, brought to 25°c and then placed in the 15°c air thermostat for 22 hours. The supernatant solution is separated and stored for future use if it is needed, although, it is usually discarded in most cases because it is found that it contains fractions of very low D.P.

The 50% fraction is dissolved in sufficient amount of solvent to make 2% solution to which a measured amount of precipitant is added to precipitate about 10% fraction. This is the purification fraction which is stored for future use.

To the supernatant liquid is added enough precipitant to precipitate 75% of the remaining fraction, rotated for 1.5 hours and placed in the 15°c thermostat for 22 hours. The degree of polymerization of this fraction is determined and found to be, in most cases, between 150 - 200 using acetone as the solvent. The fraction is then dissolved in enough solvent to make 2% solution and 75% of it is precipitated by the procedure described above. The degree of polymerization of this fraction is again determined. The same procedure is repeated until reaching a fraction having approximately a D.P. of 300.

The same procedure is followed in fractionating the other three batches of the same type of cellulose acetate.

By the time all the four batches reach a D.P. of 300, (sometimes before that), the amounts of cellulose acetate in the four bottles can be combined in one bottle and refractionated until the last fraction reached a D.P. of 300.

This last fraction is then dissolved to make a 2% solution. Non-solvent is added to precipitate between 5 - 10% fraction. The D.P. of this fraction is determined. If it has a value over 300 it is discarded. At this stage, the cellulose acetate in the supernatant layer has an average D.P. less than 300. To the supernatant liquid is added enough non-solvent to precipitate 75% fraction. This is repeated until a fraction with an average D.P. of 300 is again reached. This fraction is again dissolved and between 5 - 10% of it is precipitated. If the average D.P. of this fraction is again over 300 the same method of fractionation is repeated on the supernatant solution to get a sharp fraction which has an average D.P. of 300 and gives no appreciable change in degree of polymerization no matter how many times it is refractionated.

Experience showed that this procedure is also an accurate method and consumes, relatively, much less time than the step-wise fractionation.

It is to be noted that the fractions, in all cases, were most easily obtained from the gel state by redissolving them in acetone and after being rotated for several hours to insure complete dissolution and uniformity, then, poured into flat pyrex dishes and left for several hours, sometimes overnight, until a very viscous solution is left in the dishes. Distilled water is then added to the viscous solutions and the cellulose acetate fractions are precipitated in the fiber form. The cellulose acetate fibers are then dried in an oven at 50°C overnight. They are then stored at room temperature in brown glass jars away from sunlight until used.

By following the above two procedures of fractionation it was possible to get sharp fractions with an average degree of polymerization of 300 for each of the types of cellulose acetates, PM_3, LH_1, FM_6 using acetone as the solvent. The highest attainable sharp fraction for cellulose acetate type PM_4 had an average D.P. of approximately 240. Another sharp fraction of PM_4 was prepared which had a D.P. of 215. This was prepared to show later if such a change in D.P. could cause any appreciable change in mechanical properties. From the discussion on mechanical properties it will be seen that if the D.P. of a sharp fraction reaches 200 or more of the same type of cellulose acetate there is little or no change in mechanical properties which means that if there is any change in mechanical properties of the four different types of cellulose acetates it must be due to differences in the degree of combined acetic acid only since the effect of molecular weight distributions as well as the effect of D. P. are eliminated.

Location of the Precipitation Point of the Various Fractions

The location of the precipitation points was done by small scale fractionation of four grams of each of the four types of cellulose acetated by the step-wise method using 4% and 2% solutions of each type of cellulose acetates. The n-heptane was added drop by drop from a burette with continuous shaking of the solution until two milliliters in excess of the amount needed to give a turbidity to the solution.

To the supernatant liquid from each fraction, n-heptane was added until turbidity was obtained.

The process was repeated until seven fractions were obtained. The fractions were dried and weighed. A graph was plotted using milliliters of n-heptane along the abscissa and cumulative per cent fraction along the ordinate.

From the curves obtained, it was possible to determine the amount of precipitant necessary to precipitate a desired per cent fraction.

The data for the precipitation curves are tabulated in tables 2 - 9, while curves are shown in figures 2 - 9.

Determination of Degree of Polymerization

The method applied in determining the average degree of polymerization of the various samples of cellulose acetate was the viscosity method of Staudinger (78), which was described by several authors in the literature (67, 75).

Both acetone and cupriethylenediamine were used as solvents for the various samples.

The following procedure used acetone as the solvent:

0.05 gram of air dry cellulose acetate was dried in an oven at 105°C for two hours, cooled in a desiccator and weighed accurately to the nearest 0.1 milligram. The sample was then transferred into an Erlenmeyer flask (size 125 ml.) with a glass stopper. The exact weight of the sample was obtained by difference. Fifty milliliters of acetone were then pipetted into the Erlenmeyer flask and the flask was stoppered immediately and allowed to stand for at least 24 hours with occasional shaking to insure complete solution. The solution was then filtered through a coarse sintered glass filter into a large test tube (2.5 cm diameter 20 cm

Table 2

Precipitation Data For 4% PM_4 Type Cellulose Acetate

Type of Cellulose Acetate:	PM_4 (51.9% Combined Acetic Acid).
Concentration of Solution:	4%.
Solvent:	95% Acetone and 5% Distilled Water.
Precipitant:	n-heptane.
Inital amount of n-heptane added to obtain turbid solution:	11.5 ml.

Fraction Number	Milliliters n-heptane Added	% Fraction in Original Sample	Accumulative %
1	1.5	7.5	7.5
2	1.0	11.8	19.3
3	1.5	25.0	44.3
4	1.5	20.5	64.8
5	1.5	11.5	76.3
6	2.0	10.0	86.3
7	3.0	8.5	94.8

Table 3

Precipitation Data For 2% PM_4 Type Cellulose Acetate

Type of Cellulose Acetate: PM_4 (51.9% Combined Acetic Acid).

Concentration of Solution: 2%

Solvent: 95% Acetone and 5% Distilled Water.

Precipitant: n-heptane.

Inital Amount of n-heptane added to obtain Turbid Solution: 23.5 ml.

Fraction Number	Milliliters n-heptane Added	% Fraction in Original Sample	Accumulative %
1	3.0	5.3	5.3
2	2.0	8.5	13.8
3	2.5	12.8	26.6
4	2.5	14.5	41.1
5	2.8	9.5	50.6
6	3.2	15.0	65.6
7	4.5	13.4	79.0

Table 4

Precipitation Data For 4% PM_3 Type Cellulose Acetate

Type of Cellulose Acetate: PM_3 (52.8% Combined Acetic Acid).

Concentration of Solution: 4%

Solvent: 95% Acetone and 5% Distilled Water.

Precipitant: n-heptane.

Inital Amount of n-heptane added to obtain Turbid Solution: 15.5 ml.

Fraction Number	Milliliters n-heptane Added	% Fraction in Original Sample	Accumulative %
1	1.5	8.8	8.8
2	1.0	17.5	26.3
3	1.0	21.1	47.4
4	1.2	19.0	66.4
5	1.5	12.2	78.6
6	2.0	9.7	88.3
7	3.0	7.1	95.4

Table 5

Precipitation Data For 2% PM_3 Type Cellulose Acetate

Type of Cellulose Acetate: PM_3 (52.8% Combined Acetic Acid).

Concentration of Solution: 2%

Solvent: 95% Acetone and 5% Distilled Water.

Precipitant: n-heptane.

Inital Amount of n-heptane added to obtain Turbid Solution: 33 ml.

Fraction Number	Milliliters n-heptane Added	% Fraction in Original Sample	Accumulative %
1	3.0	11.3	11.3
2	2.0	12.0	23.3
3	2.0	14.3	37.6
4	2.2	14.2	51.8
5	2.6	12.1	63.9
6	3.2	12.4	76.3
7	4.5	10.2	86.5

Table 6

Precipitation Data For 4% LH_1 Type Cellulose Acetate

Type of Cellulose Acetate: LH_1 (54.4% Combined Acetic Acid).

Concentration of Solution: 4%

Solvent: 95% Acetone and 5% Distilled Water.

Precipitant: n-heptane.

Inital Amount of n-heptane added to obtain Turbid Solution: 18.5 ml.

Fraction Number	Milliliters n-heptane Added	% Fraction in Original Sample	Accumulative %
1	1.5	24.7	24.7
2	1.0	23.0	47.7
3	1.2	16.0	63.7
4	1.3	12.1	75.8
5	1.6	8.0	83.8
6	2.1	5.3	89.1
7	4.0	5.1	94.2

Table 7

Precipitation Data For 2% LH_1 Type Cellulose Acetate

Type of Cellulose Acetate:	LH_1 (54.4% Combined Acetic Acid).
Concentration of Solution:	2%
Solvent:	95% Acetone and 5% Distilled Water.
Precipitant:	n-heptane.
Inital Amount of n-heptane added to obtain Turbid Solution:	39 ml.

Fraction Number	Milliliters n-heptane Added	% Fraction in Original Sample	Accumulative %
1	3.0	20.5	20.5
2	2.0	16.5	37.0
3	2.5	19.2	56.2
4	2.5	12.3	68.5
5	3.0	9.9	78.4
6	3.6	7.8	86.2
7	5.0	5.5	91.7

Table 8

Precipitation Data For 4% FM_6 Type Cellulose Acetate

Type of Cellulose Acetate:	FM_6 (55.6% Combined Acetic Acid).
Concentration of Solution:	4%
Solvent:	95% Acetone and 5% Distilled Water.
Precipitant:	n-heptane.
Inital Amount of n-heptane added to obtain Turbid Solution:	20.5 ml.

Fraction Number	Milliliters n-heptane Added	% Fraction in Original Sample	Accumulative %
1	1.5	28.5	28.5
2	1.0	24.5	53.0
3	1.3	15.9	68.9
4	1.4	11.0	79.9
5	1.7	6.1	86.0
6	2.3	4.5	90.5
7	4.5	3.5	94.0

Table 9

Precipitation Data For 2% FM_6 Type Cellulose Acetate

Type of Cellulose Acetate:	FM_6 (55.6% Combined Acetic Acid).
Concentration of Solution:	2%
Solvent:	95% Acetone and 5% Distilled Water.
Precipitant:	n-heptane.
Inital Amount of n-heptane added to obtain Turbid Solution:	43 ml.

Fraction Number	Milliliters n-heptane Added	% Fraction in Original Sample	Accumulative %
1	3.0	19.7	19.7
2	2.0	18.7	38.4
3	2.5	20.6	59.0
4	2.5	12.8	71.8
5	3.0	9.1	80.9
6	3.6	7.0	87.9
7	5.0	6.4	94.3

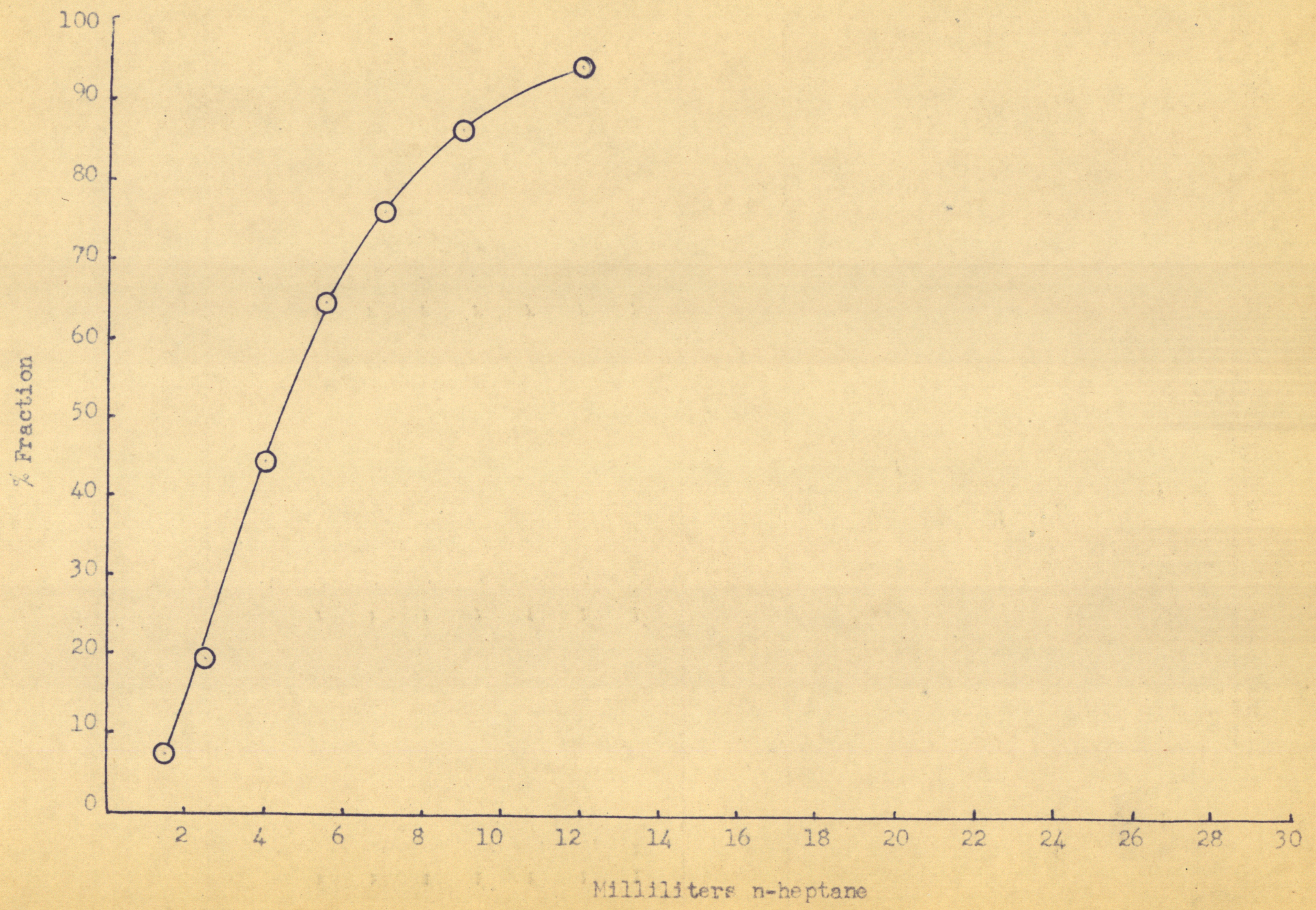

FIGURE 2

Precipitation Curve for 4% PM_4 Type Cellulose Acetate

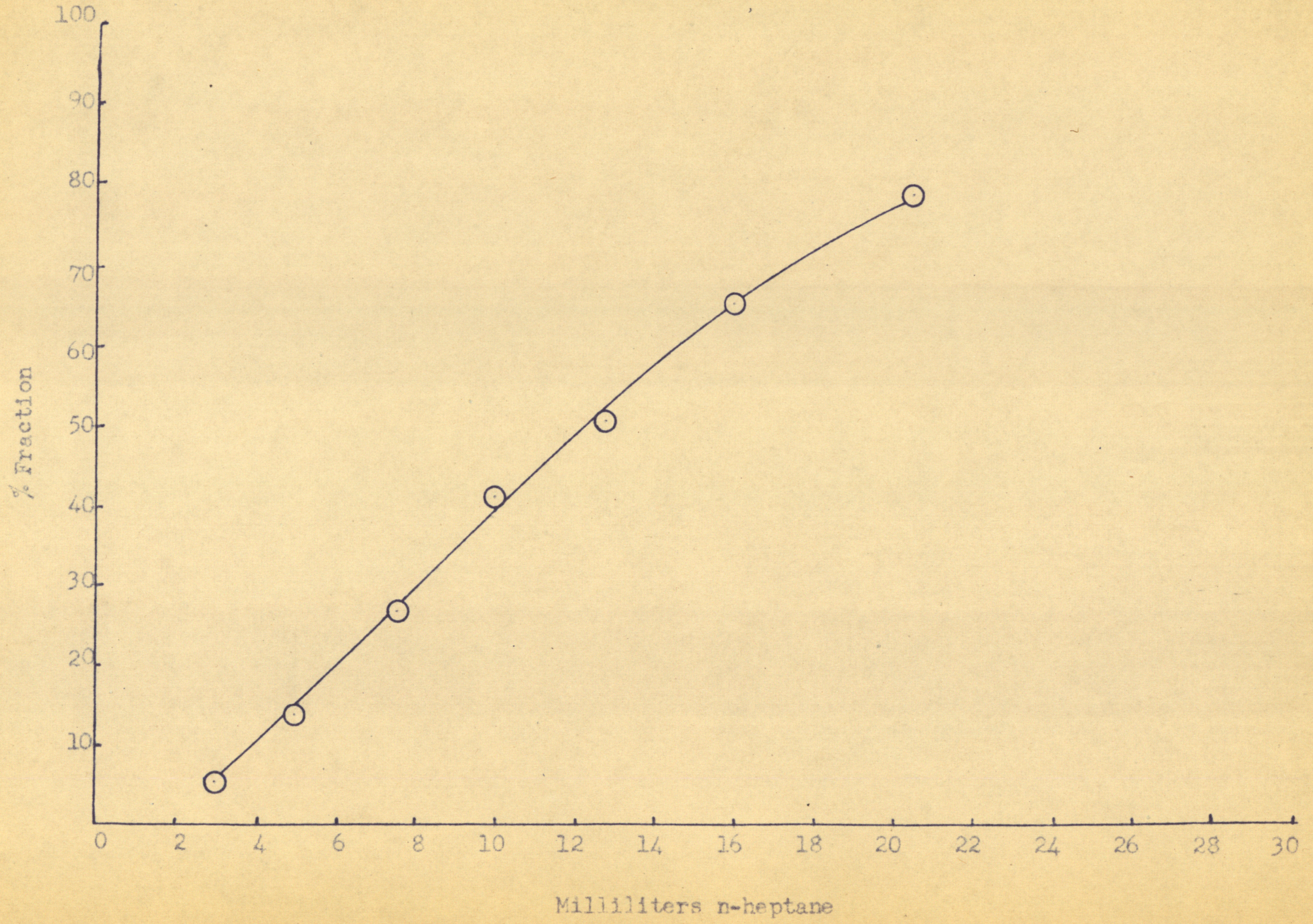

FIGURE 3

Precipitation Curve for 2% PM_4 Type Cellulose Acetate

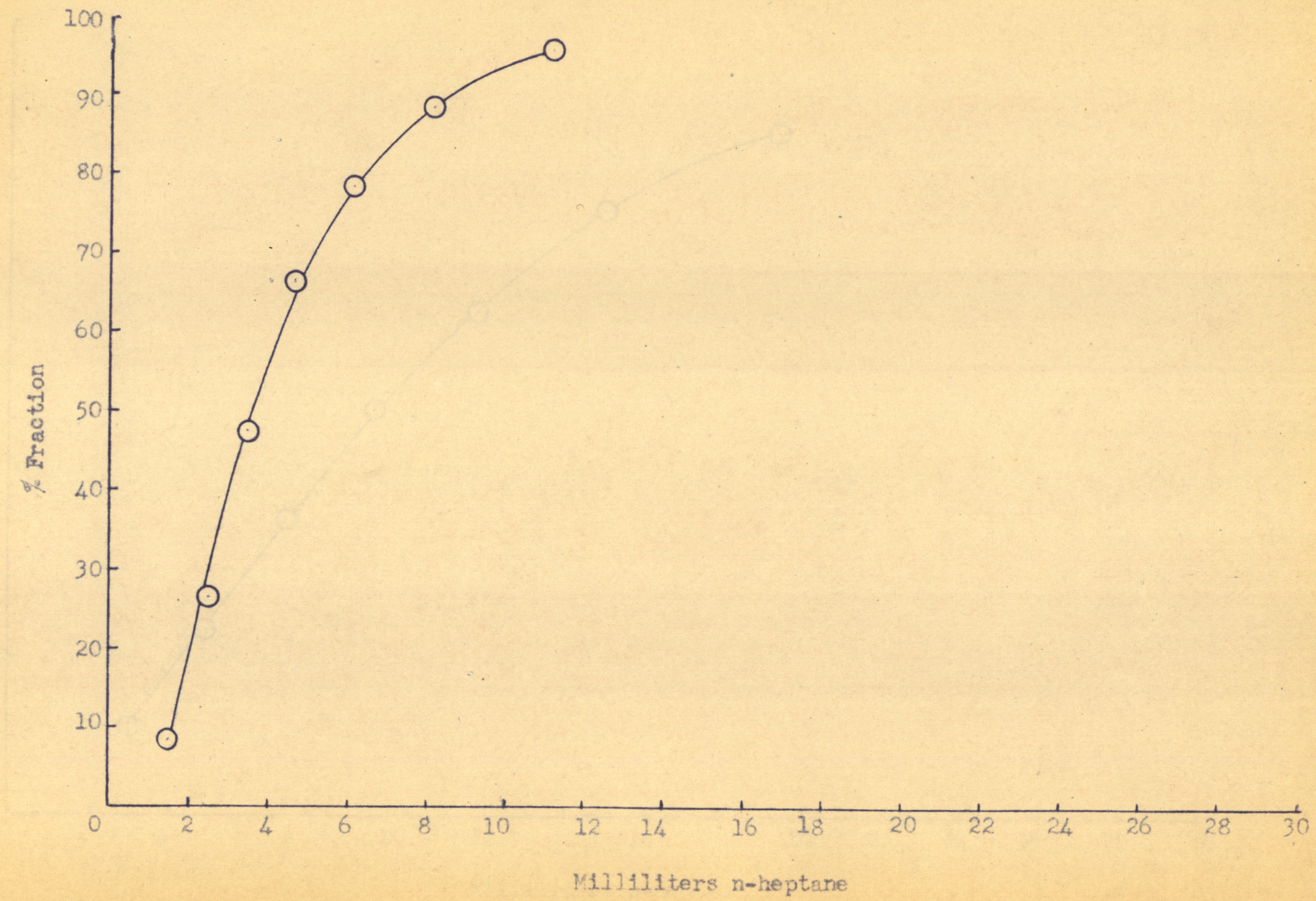

FIGURE 4

Precipitation Curve for 4% PM_3 Type Cellulose Acetate

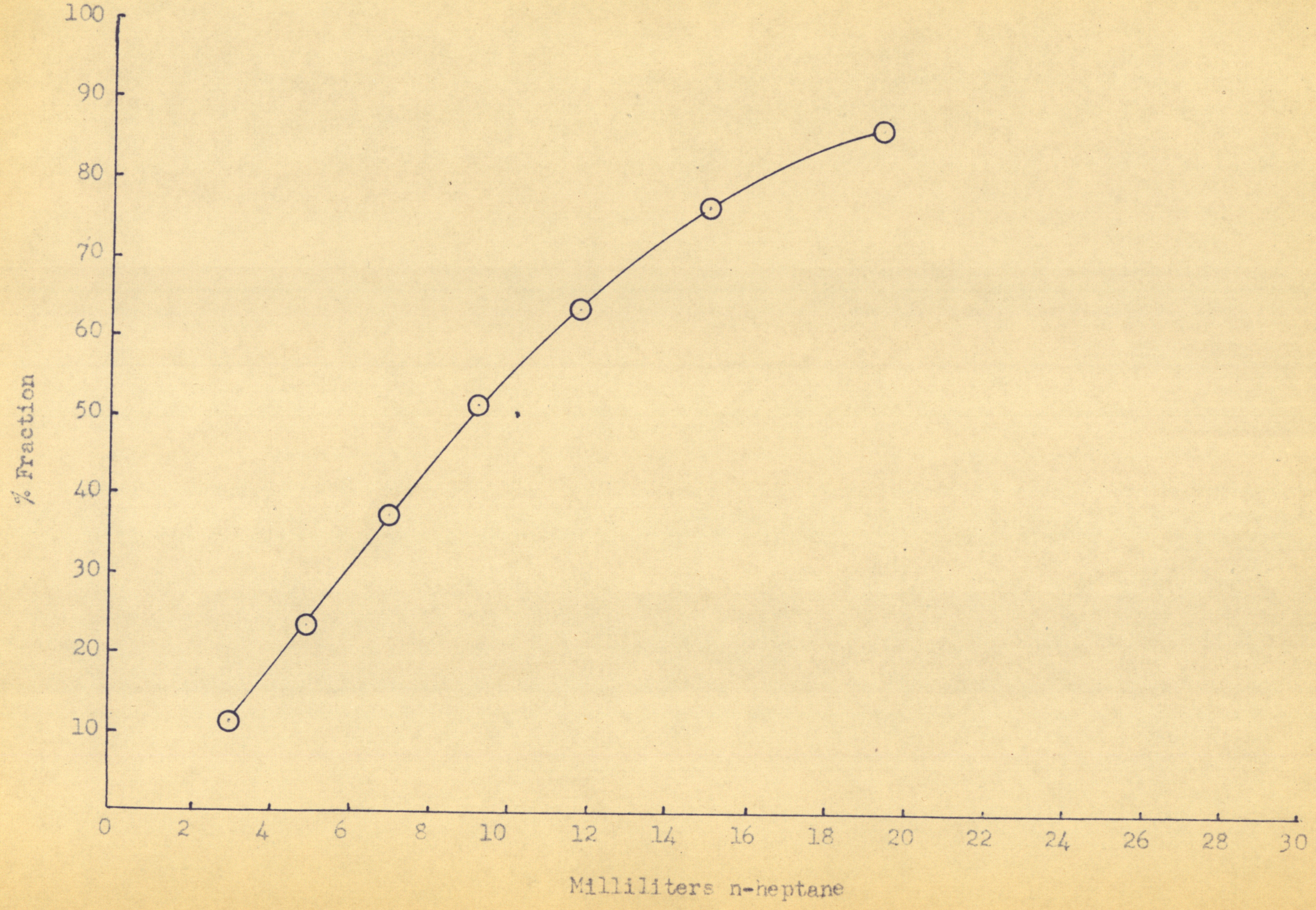

FIGURE 5

Precipitation Curve for 2% PM_3 Type Cellulose Acetate

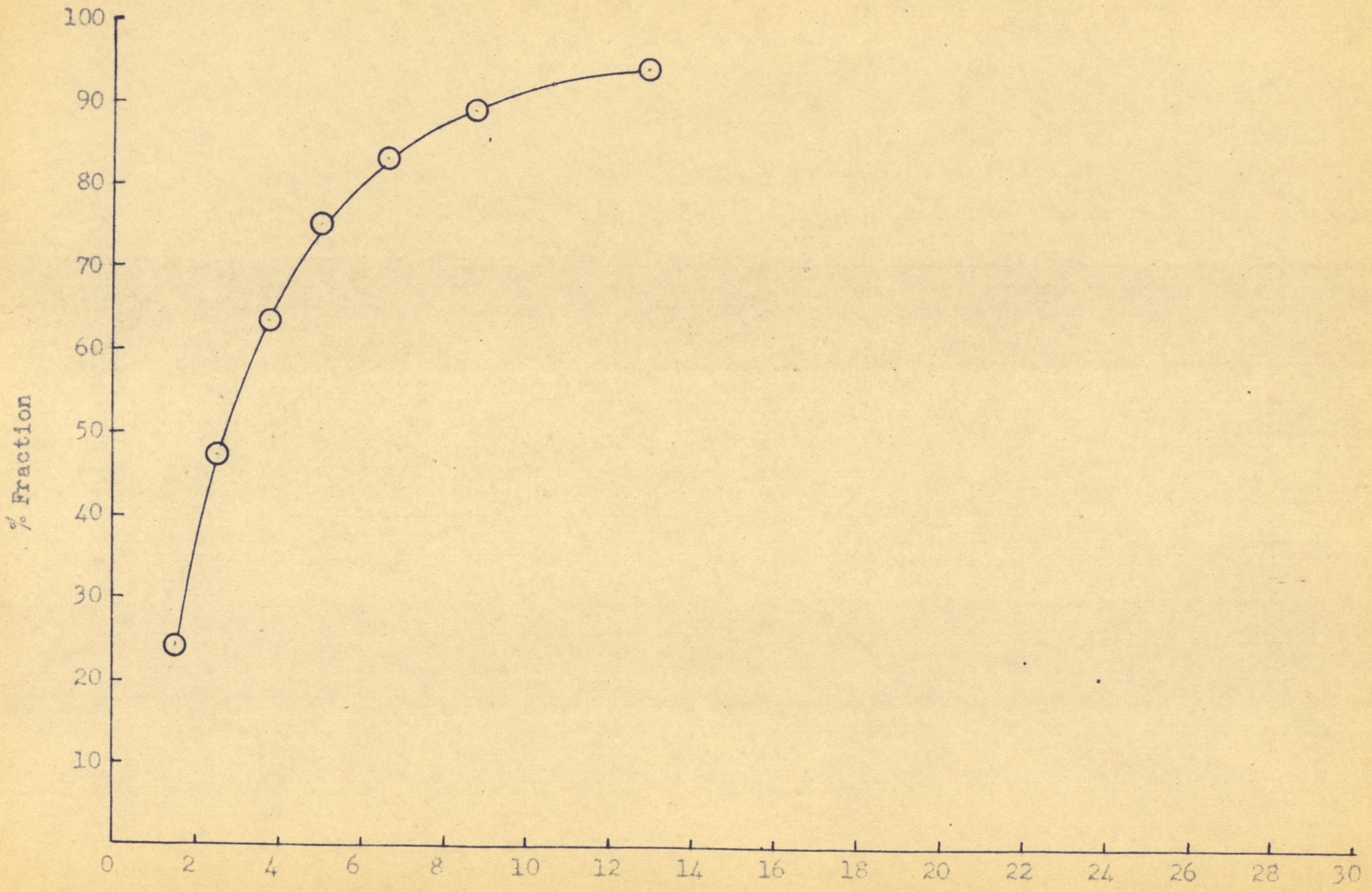

FIGURE 6

Precipitation Curve for 4% LH_1 Type Cellulose Acetate

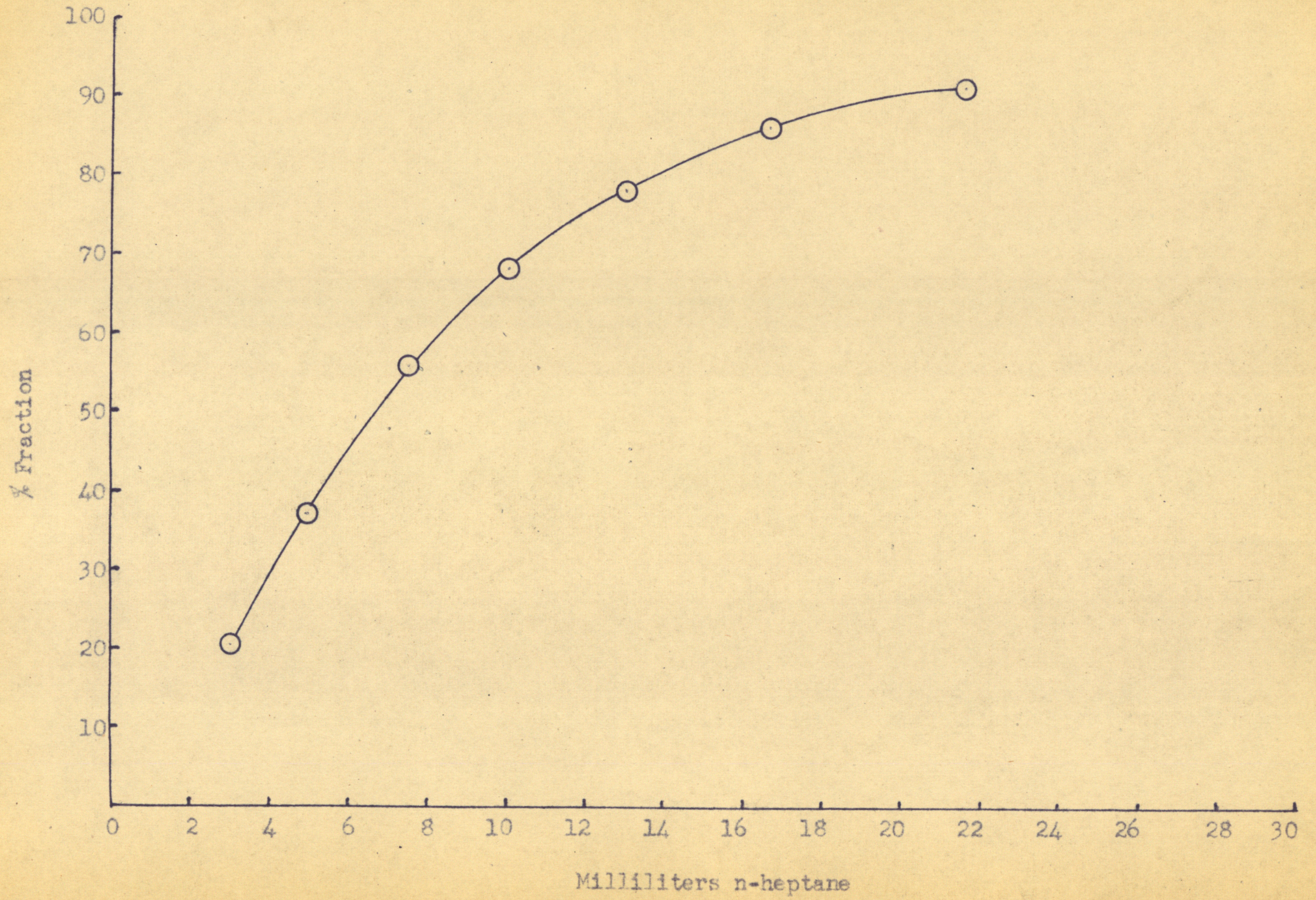

FIGURE 7

Precipitation Curve for 2% LH_1 Type Cellulose Acetate

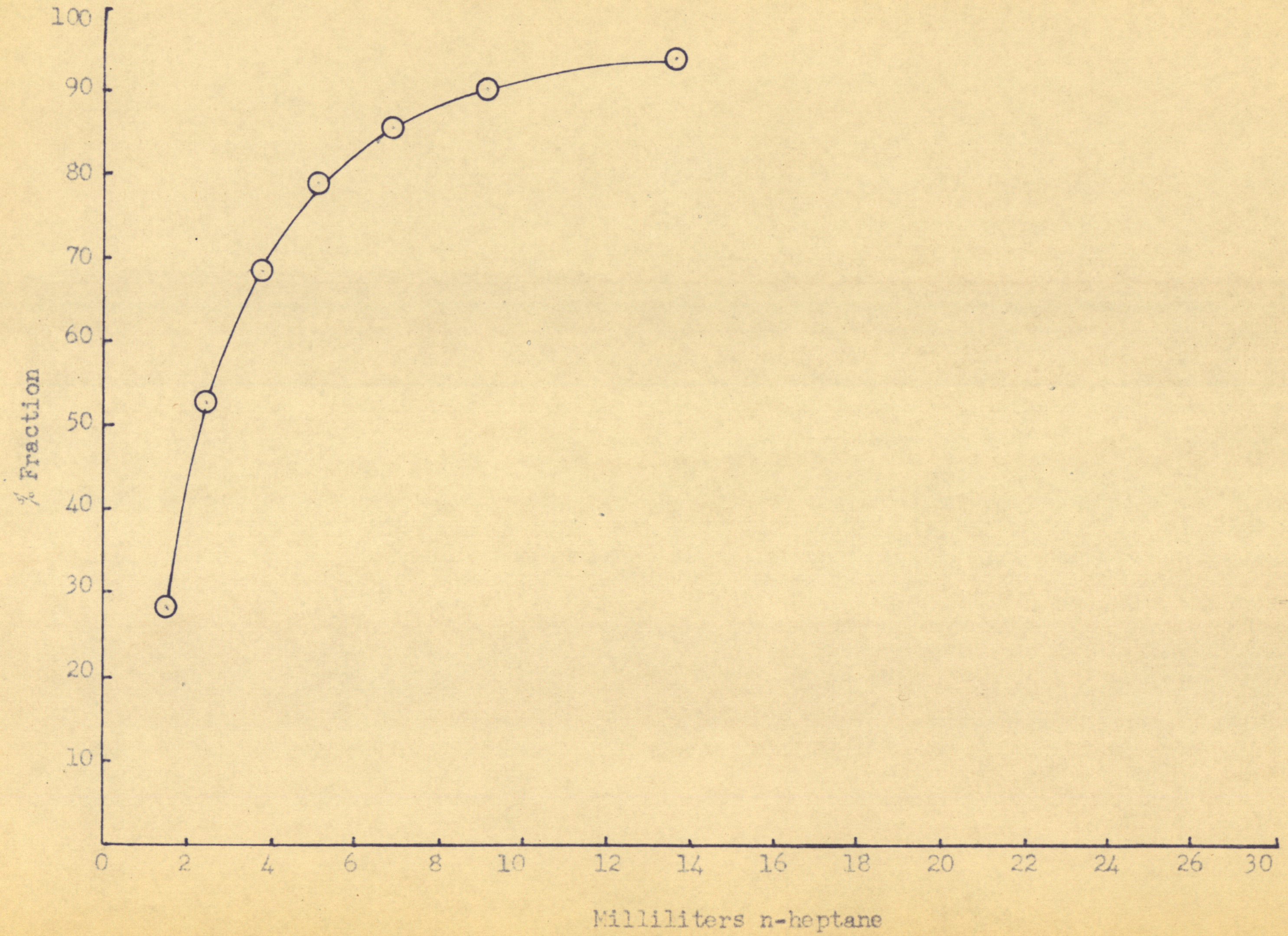

FIGURE 8

Precipitation Curve for 4% FM_6 Type Cellulose Acetate

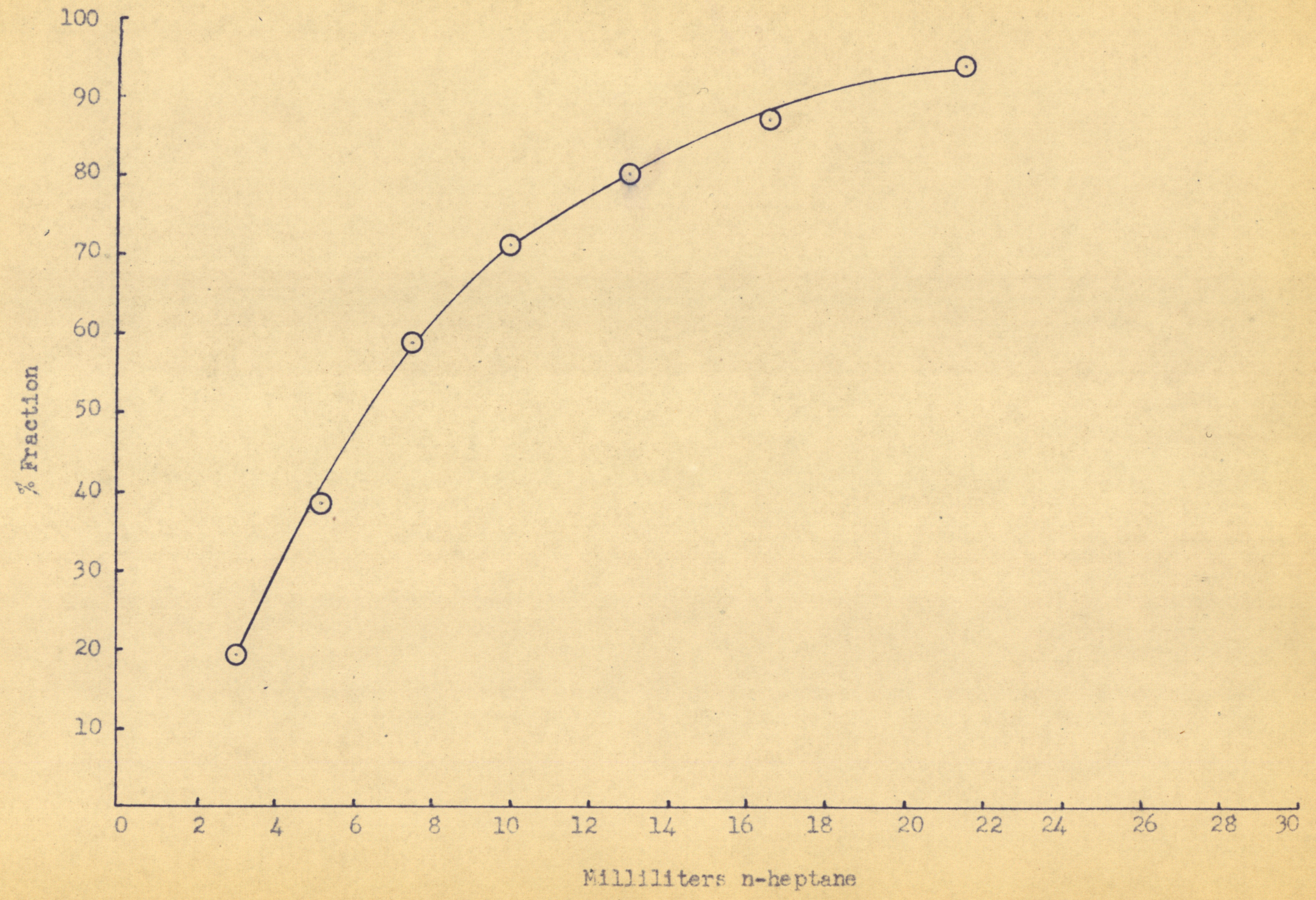

FIGURE 9

Precipitation Curve for 2% FM_6 Type Cellulose Acetate length), which was immediately stoppered with a neoprene rubber stopper previously extracted with acetone. The test tube was placed in a constant temperature water bath maintained at 20°c (± 0.05°c). The viscosity of the solution was determined at this temperature, on a five milliliter sample of solution, in an Ostwald Fensk viscosimeter which was standardized with pure acetone.

It is to be noticed that the above procedure was done in duplicate on each sample of cellulose acetate using two different viscosimeters of size 50.

The degree of polymerization was calculated from the following equation

$$\overline{D.P.} = \frac{t - t_o}{t_o\, KC}$$

where

t = time of efflux of solution

t_o = time of efflux of solvent

K = constant

C = concentration of cellulose acetate expressed in grams / liter

The value of the constant K for each type of cellulose acetate was obtained from Myers Master's theses (57). Myers used a ratio whereby the constants based on Kraemer's work (44) could be converted to the constants based on Staudinger's work (41), and found, that for types PM_4 and PM_3 cellulose acetate the constant K in the above equation had a value of 9.4×10^{-4} while for types LH_1, and PM_6 cellulose acetate the value of the constant K was 9.2×10^{-4}.

Cupriethylenediamine Method of Determining the Degree of Polymerization

It is very unfortunate that there is no practical method for measuring the molecular weight of cellulose and cellulose acetate in terms of absolute degree of polymerization units. Until a universally acceptable method becomes available for doing this, it is necessary to qualify the use of a degree of polymerization expression by describing clearly how the degree of polymerization result is arrived at from measured viscosity data.

The method which is about to be described involves the use of cuprammonium hydroxide or cupriethylenediamine which are sufficiently alkaline to de-esterify completely certain cellulose esters. When a cellulose ester such as cellulose acetate, therefore, is dissolved in cupriethylenediamine, the resulting specific viscosity of the sample is due to chains of regenerated cellulose. In other words, a solvent such as cupriethylenediamine is suitable for the measurement of the viscosity or weight-average molecular weight of both cellulose and cellulose acetate (12).

Various investigators (8, 12, 34, 39, 40, 41, 79) already have considered de-esterifying cellulose esters for the purpose of measuring the molecular weights of the resulting regenerated cellulose in a cellulose solvent such as cuprammonium hydroxide.

Malm and his associates (48) found that in the case of a series of aliphatic acid esters of cellulose, the intrinsic viscosities of these esters varied with the acetyl group and the solvent used. However, after these esters were completely de-esterified, the degrees of polymerization of the regenerated celluloses were found to be substantially the same.

Kraemer (44) has shown from ultracentrifuge experiments that the intrinsic viscosity is related to the degree of polymerization, and he gives these relationships for cellulose in cuprammonium solutions as follows:

$$\frac{D.P.}{[n]} = 260$$

where

$$[n] = \text{intrinsic viscosity}$$

Since cuprammonium hydroxide and cupriethylenediamine solutions are known to disperse cellulose to the same degree, the above equation can be used when the solvent is cupriethylenediamine (82).

In the case of 0.5% cuprammonium solutions of cellulose having basic degree of polymerization less than 300, it has been shown that

$$\frac{n_{sp}}{c} = [n]$$

and the equation for determining the degree of polymerization can be written as follows:

$$\overline{D.P.} = 260\,\frac{n_{sp}}{c}$$

where

$\overline{D.P.}$ = basic degree of polymerization

n_{sp} = specific viscosity

c = concentration in grams / 100 ml.

260 = constant for pure cellulose

The cupriethylenediamine solution obtained from Ecusta Paper Corporation contained one molar solution of copper and had to be diluted with distilled water to obtain exactly 0.5M of copper. The solution was analyzed for copper and ethylenediamine to insure exact molarity. The solution was then stored under nitrogen until used.

The following procedure was carried out for the determination of degree of polymerization (12).

Experience showed that cellulose acetate in the form of powder is easily de-esterified and dissolved in cupriethylenediamine. Cellulose acetate sample, in film or fiber form, was dissolved in acetone and enough distilled water was added to the solution to obtain turbid solution. The turbid solution was then transfered to a flat dish and placed in an oven at 50°c for overnight to dry. The cellulose acetate thus obtained was in the form of powder.

Approximately 0.25 grams cellulose acetate powder was placed in an oven at 105°c for two hours. The sample was then cooled in a desiccator and weighed accurately by difference to the nearest 0.1 milligram. The sample was then transfered into a large test tube (2.5 cm diameter 20 cm length) and 25 ml. of cupriethylenediamine solution was pipetted into the test tube. The mixture was then stirred for one hour by a glass stirrer rotating at approximately 400 r.p.m. The solution thus obtained was stable for four hours in the presence of atmospheric oxygen. The solution was then filtered through a coarse sintered glass filter into another large test tube which was stoppered with a rubber stopper and placed in a constant temprature water bath maintained at 20°c (± 0.05°c). The viscosity of the solution was determined at this temperature, on a five milliliter sample of solution, in an Ostwald Fensk viscosimeter size 100 which was standardized with pure cupriethylendiamine.

It should also be mentioned that the above procedure was done in duplicate on each sample of cellulose acetate using two different viscosimeters of size 100.

The concentration of the regenerated cellulose can be calculated from the weight of cellulose acetate used and its per cent of combined acetic acid.

From the data obtained and the equation mentioned before, the degree of polymerization can be calculated.

It was found that the degree of polymerization of the various samples of cellulose acetate determined by the cupriethylenediamine method had values approximately four times as much as the D.P. determined by the acetone viscosity method. On the other hand a sharp fraction of cellulose acetate type PM, was sent to Picatinny Arsenal, Dover, New Jersey (11) for the determination of the degree of polymerization by light scattering method and the value was found to be approximately equivalent to the value obtained by the cupriethylenediamine method, i.e., the light scattering D.P. was almost four times as much as the D.P. determined by the acetone viscosity method.

Table 10 illustrates the different values of the degree of polymerization obtained by several methods,

Determination of Degree of Combined Acetic Acid

The method applied was an extension and slight modification of that developed by Murray, Staud and Gray (56).

The method which is about to be described is usually used for the acetone soluble cellulose acetate.

Table 10

Comparison of the Different Methods of Determining the Degree of Polymerization of the Various Samples of Cellulose Acetate

Type of Cellulose Acetate	Degree of Combined Acetic Acid	Acetone D.P.	Cupriethylenediamine D.P.	Methyl cellosolve D.P.	Light Scattering D.P.
PM_4 (original)	52.0	126	560	-	-
PM_3 (original)	52.8	163	650	-	-
PH_1 (original)	52.8	-	732	178(89)	-
LH_1 (original)	54.4	203	806	-	-
FM_6 (original)	55.6	187	737	-	-
PM_3 (sharp fraction)	52.0	300	1380	-	1240

Approximately 0.5 grams of air dry cellulose acetate was dried in an oven at 105°C for two hours, cooled in a desiccator and weighed accurately by difference to the nearest 0.1 milligram. The sample was then transfered into a 500 milliliter wide-mouth Erlenmeyer flask. 50 milliliters of acetone was pipetted into the flask containing the sample of cellulose acetate and the flask was stoppered and allowed to stand for 24 hours with occasional shaking until complete dissolution. 50 milliliters of standardized 0.5N NaOH was added to the solution and the flask was loosely stoppered and placed in an oven at 50°C for one hour with occasional shaking. The solution was then back titrated with standardized 0.5N HCl solution using phenolphthalein as the indicator. The milliliters of NaOH solution consumed for the saponification of the cellulose acetate sample was used for the calculation of the degree of acetic acid in the sample.

The above procedure was performed in duplicate for each sample of cellulose acetate and a blank was run using the same procedure on pure acetone.

The equation used for calculating the degree or % of combined acetic acid for the cellulose acetate samples is:

$$\%\ CH_3COOH = \frac{(CC_b \times N_b) - (CC_a \times N_a)}{\text{wt. of Sample}} \times 0.06 \times 100$$

where

CC_b = milliliters of NaOH solution

N_b = normality of NaOH solution

CC_a = milliliters of HCl solution

N_a = normality of HCl solution

0.06 = milliequivalent weight of acetic acid

The degrees of combined acetic acid for the four sharp fractions are shown in Table 11.

Method of Casting and Conditioning Films

The fractions were dissolved in pure acetone to make highly viscous solutions which can be poured without great difficulty. The solutions were made in one liter Erlenmeyer flasks and shaken in a shaking machine for about ten hours. PM_4 type cellulose acetate required at least 24 hours shaking before complete dissolution. The solutions were then allowed to stand at room temperature for 24 hours for removal of air bubbles and to allow any solid impurities to settle down

The films were made by pouring a portion of the viscous solution on a carefully leveled glass plate which had been thoroughly cleaned and dried. A film spreader was then immediatly drawn across the glass plate at an even rate. This operation was performed in an air thermostat at 15°c to minimize the rate of evaporation of acetone and obtain a very smooth, uniform and transparent film. The glass plate containing the film was left standing for about one hour after which it was removed from the 15°c constant room and placed on a leveled stand at room temperature for about one additional hour to dry completely.

One edge of the film was carefully loosened with a spatula blade using a small amount of distilled water. The film was then pulled up carefully and came out in one piece.

Using the same method, several films were obtained for each fraction. The films thus obtained were hung from the edges with spring type clothes

Table 11

Degree of Polymerization and Degree of Combined Acetic Acid of the Sharp Fractions

Sharp Fraction Cellulose Acetate Type	Acetone D.P.	% Combined Acetic Acid
PM_4	215	50.8
PM_4	240	50.8
PM_3	300	52.0
LH_1	300	54.2
FM_6	300	55.8

pins in a room maintained at 77 ± 1° F and 50 ± 2% relative humidity for at least three days before running mechanical tests on them.

The film spreader used was obtained from Yerkes Research Laboratory of E.I. duPont de Nemours and Company in Buffalo, New York. It consisted of stainless steel rod and stainless steel side plates. By turning the rod the distance between it and the bottom of the side plates could be varied. This had to be adjusted differently for each fraction of cellulose acetate so that the final thickness of the dry films of all the fractions had a value of 0.002 inches as shown in Table 12. The degrees of polymerization and the degrees of substitution were also inserted in table 12 for comparison.

<u>Mechanical Testing of the Films</u>

<u>Atmospheric Conditions</u>. Mechanical testing of the films were made in a conditioned room as specified in the <u>Tentative Method of Conditioning Paper and Paper Products for Testing</u> (A.S.T.M. Designation: D685) of the American Society for Testing Materials.

The specifications require that the temperature should be 77 ± 1.8°F and the relative humidity 50 ± 2%.

The temperature and relative humidity were recorded by the Brown Recorder, Model 6882 - 601, manufactured by Brown Instrument Company, Philadelphia, Pennsylvania. The values were 77 ± 1°F and 50 ± 1% respectively which were well within the A.S.T.M. specifications.

<u>Thickness of Films</u>. The thickness of the conditioned films were measured with a dead weight micrometer. Only those parts of the films which measured 0.002 inches in thickness were used for testing.

Table 12

Data for Casting Films of Cellulose Acetate Fractions

Film	D.P.	Degree of Combined Acetic Acid	Concentration of Solution	Thickness of the Dry Films
PM_4	215	50.8	7.0 %	0.002 inches
PM_4	240	50.8	6.5 %	0.002 inches
PM_3	300	52.0	8.0 %	0.002 inches
LH_1	300	54.2	8.5 %	0.002 inches
FM_6	300	55.8	9.0 %	0.002 inches

<u>Tensile Strength and Elongation.</u> The tensile strength and the elongation of the films were determined by the Schopper Type Tensile Strength and Elongation Tester, manufactured by Testing Machines, Inc., New York, New York. The films were cut very carefully to obtain specimens with 0.5 inch in width and at least 5 inches in length. Results on specimens which broke at some obvious flaw or which broke in the grips were discarded. The tests were made according to the <u>Tentative Method of Test for Tensile Properties of Thin Plastic Films</u> (A.S.T.M. Designation : D882) of the American Society for Testing Materials, except that gage marks were not used and the elongation was obtained directly from the scale readings of the tester.

The results of the tensile strength and elongation tests on the fractions are given in tables 13 and 14 and the graphs correlating the tensile strength and elongation to the degree of acetylation are shown in figures 10 and 11 respectively.

<u>Bursting Strength.</u> The bursting strength of the films was determined on the Mullen Tester, manufactured by B.F. Perkins and Son, Inc., Holyoke, Massachusetts. The gage measuring the pressure in pounds per square inch was graduated from 0 to 200. The films were cut carefully to give test specimens 2.5 x 2.5 inches. The tests were made according to the <u>Standard Method of Test for Bursting Strength of Paper</u> (A.S.T.M. Designation : D774) of the American Society for Testing Materials.

The results of the bursting strength tests on the fractions are given in table 15 and the graph correlating the bursting strength to the degree of acetylation is shown in figure 12.

<u>Folding Endurance</u>. The folding endurance of the films was determined on the Schopper Type Folding Endurance Tester, manufactured by Testing Machines, Inc., New York, New York. The machine was equipped with a counter which counted the number of double folds before rupture. The films were carefully cut to give test specimens 0.6 inch in width and 4 inches in length. The tests were made according to the specifications of <u>Standard Methods of Test for Folding Endurance of Paper</u> (A.S.T.M. Designation : D643 of the American Society for Testing Materials.

The results of the folding endurance tests on the fractions are given in table 16 and the graph correlating the folding endurance to the degree of acetylation is shown in figure 13.

Table 13

Tensile Strengths of the Cellulose Acetate Fractions

Fraction	Acetone D.P.	Degree of Combined Acetic Acid	Avg. T.S. (lbs/in^2)	Max. T.S. (lbs/in^2)	Min. T.S. (lbs/in^2)	Avg. Deviation (lbs/in^2)	No. of Samples
PM_4	215	50.8	8,900	10,700	6,200	900	12
PM_4	240	50.8	9,000	11,000	7,600	590	10
PM_3	300	52.0	8,800	11,600	6,400	900	25
LH_1	300	54.2	8,900	11,700	6,900	600	26
FM_6	300	55.8	9,400	10,900	7,200	800	23

Table 14

% Elongation of the Cellulose Acetate Fractions

Fraction	Acetone D.P.	Degree of combined Acetic Acid	Avg. Elong. %	Max. Elong. %	Min. Elong. %	Avg. Deviation %	No. of Samples
PM_4	215	50.8	38	46	27	4.0	12
PM_4	240	50.8	38	47	34	2.5	10
PM_3	300	52.0	39	46	30	4.0	25
LH_1	300	54.2	39	50	32	5.5	26
FM_6	300	55.8	40	49	33	6.0	23

Table 15

Burst Strengths of the Cellulose Acetate Fractions

Fraction	Acetone D.P.	Degree of Combined Acetic Acid	Avg. B.S. (lbs/in²)	Max. B.S. (lbs/in²)	Min. B.S. (lbs/in²)	Avg. Deviation (lbs/in²)	No. of Samples
PM_4	215	50.8	82	100	70	6	15
PM_4	240	50.8	81	91	70	7	16
PM_3	300	52.0	83	98	60	6	27
LH_1	300	54.2	84	98	75	7	28
FM_6	300	55.8	84	99	71	7	23

Table 16

Fold Endurance of the Cellulose Acetate Fractions

Fraction	Acetone D.P.	Degree of Combined Acetic Acid	Avg. F.E.	Max. F.E.	Min. F.E.	Avg. Deviation	No. of Samples
			(Number of Schopper Double Folds)				
PM_4	215	50.8	56	130	30	12	12
PM_4	240	50.8	57	88	30	15	17
PM_3	300	52.0	58	118	37	16	15
LH_1	300	54.2	58	134	35	15	16
FM_6	300	55.8	59	99	32	14	27

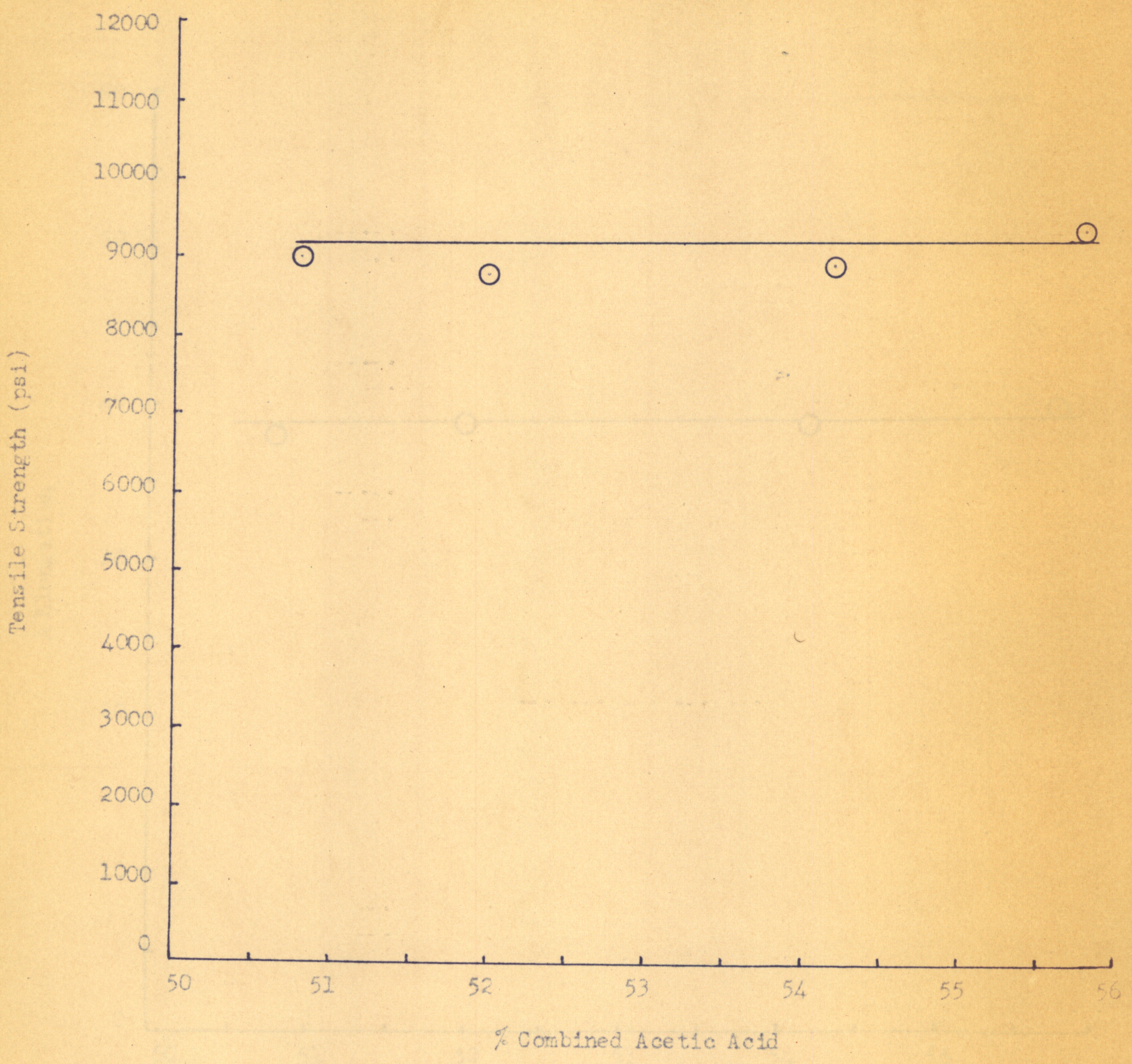

FIGURE 10

Effect of Degree of Acetylation on Tensile Strength

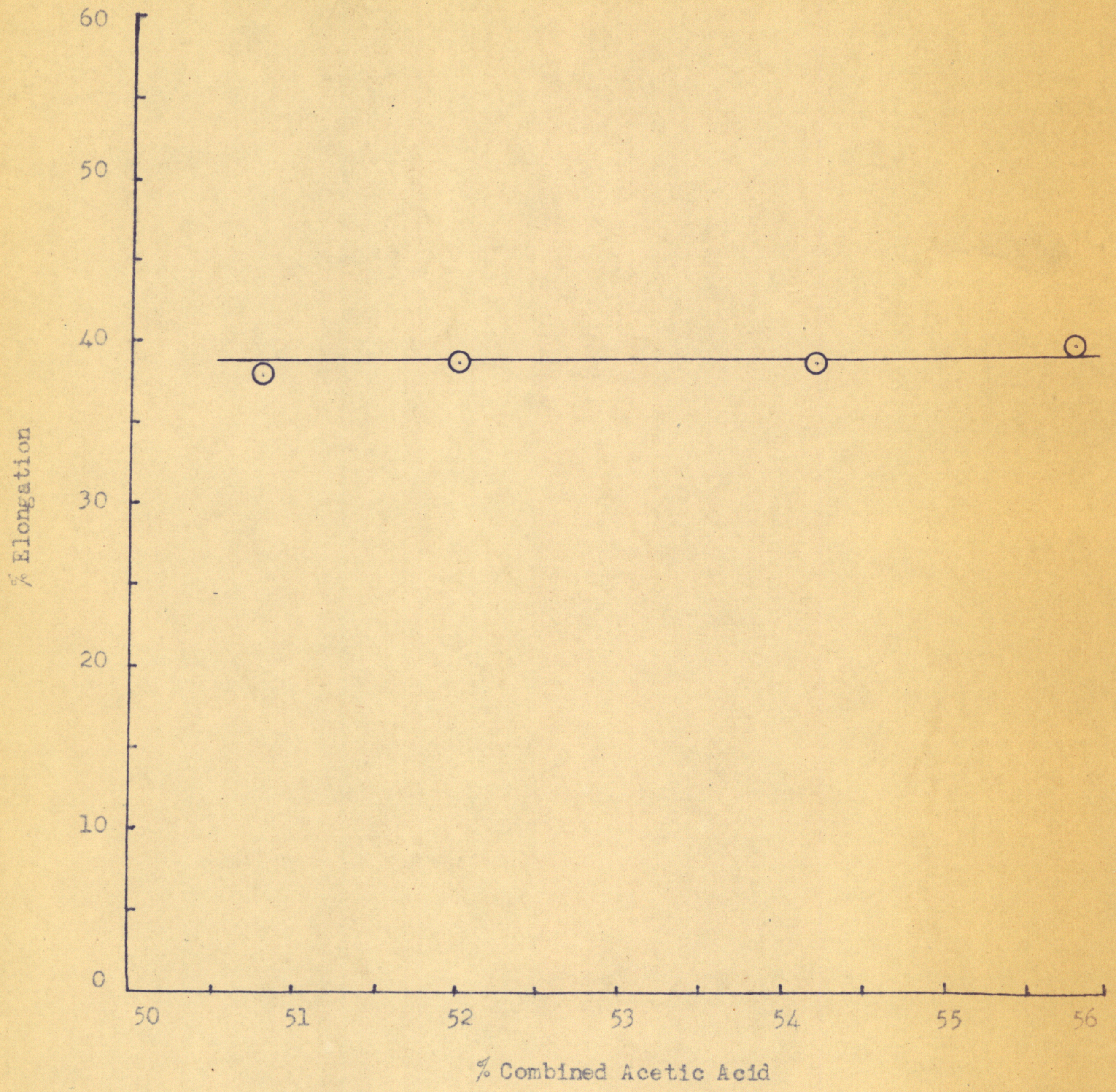

FIGURE 11

Effect of Degree of Acetylation on Elongation

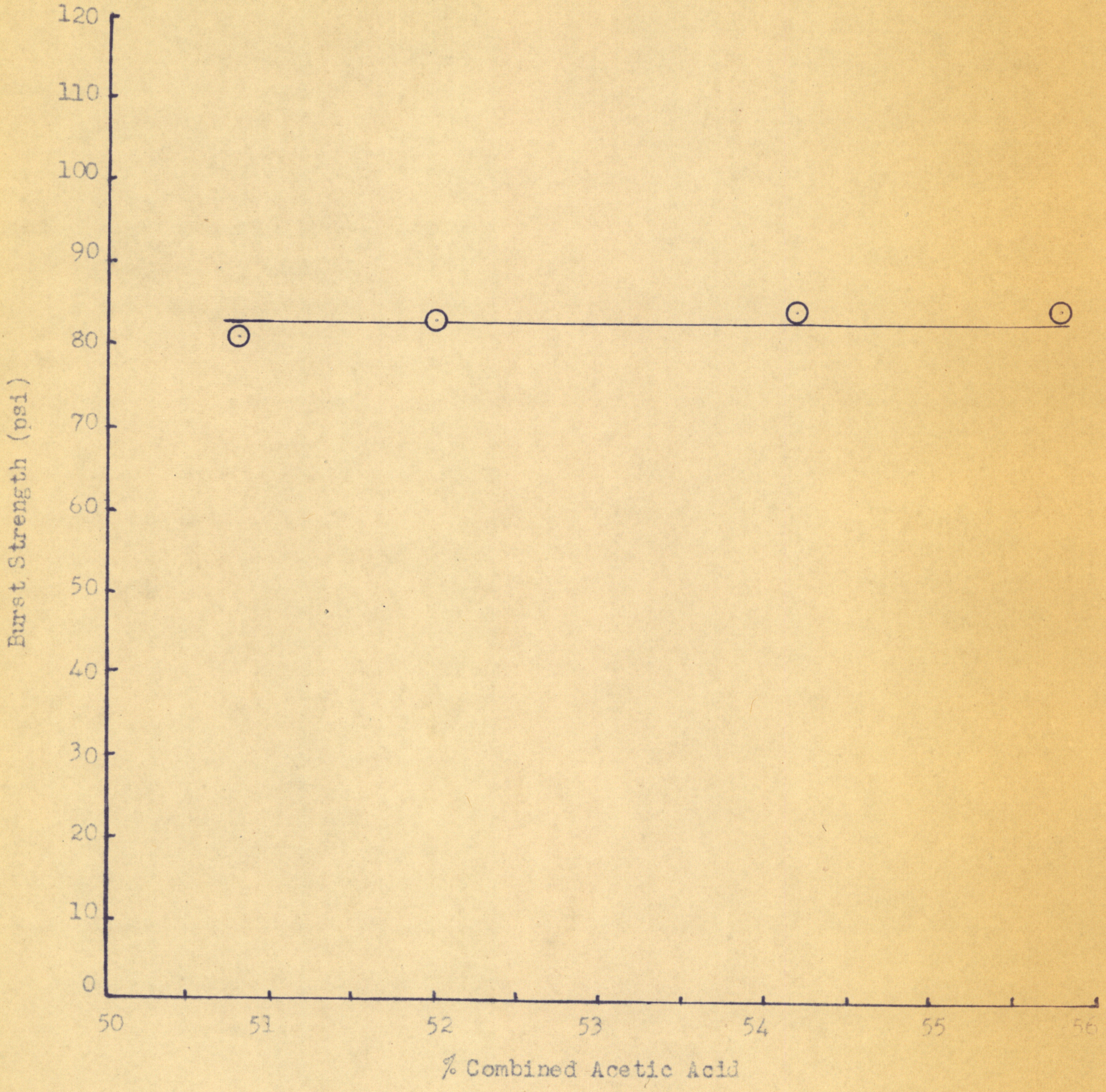

FIGURE 12

Effect of Degree of Acetylation on Burst Strength

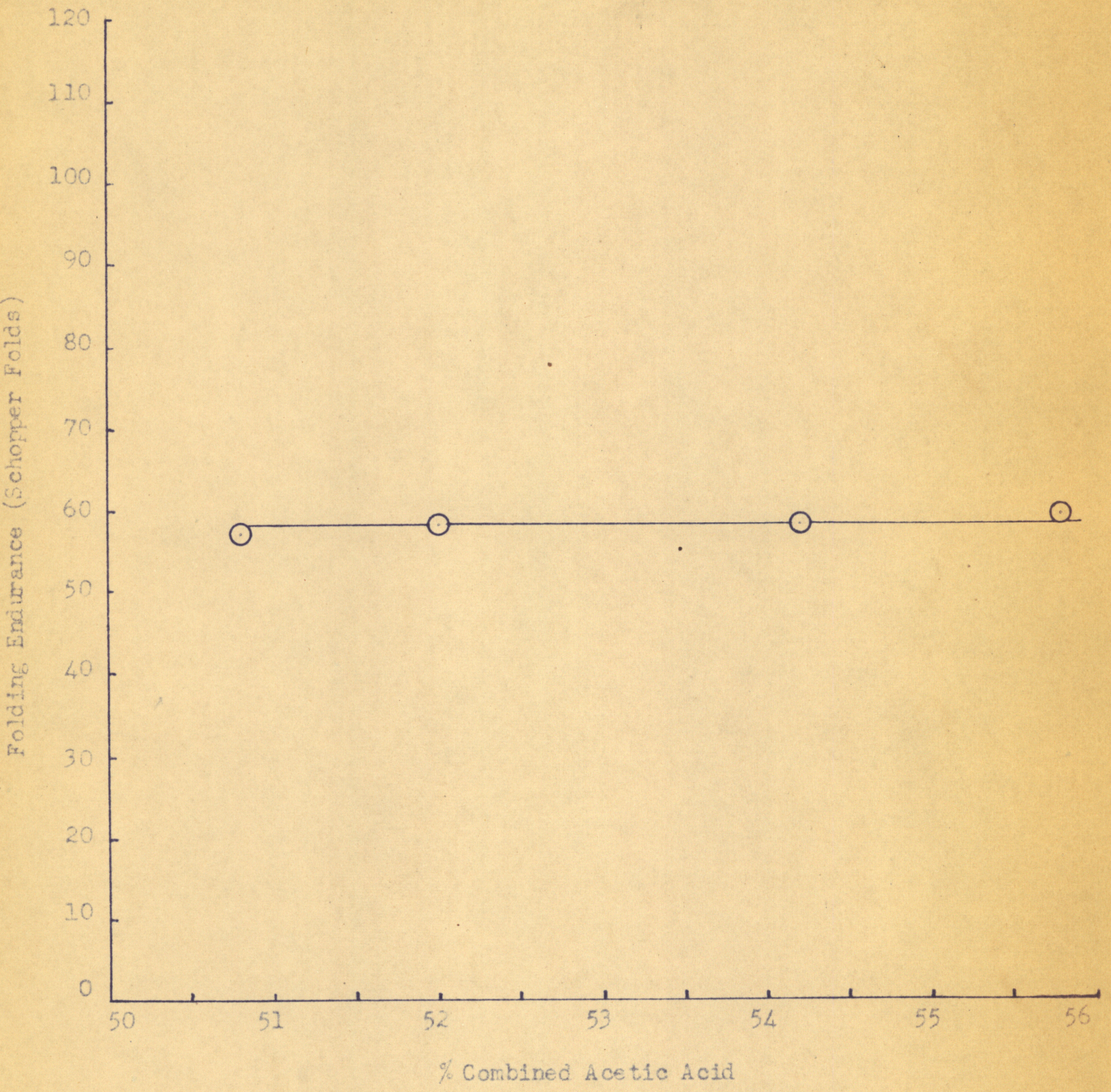

FIGURE 13

Effect of Degree of Acetylation on Fold Endurance

VIII. DISCUSION OF RESULTS

Discussion of Results

Before discussing the results obtained in this investigation it seems of importance to indicate certain factors closely related to them.

Mention has already been made in the review of the literature that factors influencing the mechanical properties are numerous, such as, molecular structure, degree of orientation, polymolecularity, degree of polymerization, degree of substitution and various other chemical and physical factors.

These factors are interdependant on each other and a change in any factor will bring about a change in the effect of other factors. Therefore, in order to study the effect of one factor on the mechanical properties of cellulose acetate films, other factors must be kept approximately constant or eliminated.

In this investigation an attempt was made to eliminate all the important factors affecting the mechanical properties of the cellulose acetate films with the exception of the degree of substitution. Hence any change in mechanical properties should be due to the degree of substitution alone.

The theoretical consideration of the effect of degree of substitution on mechanical and other physical properties of cellulose acetate has been considered by various authors (7, 36, 38, 53, 55, 61, 77). All of these authors seem to agree that the degree of substitution has a marked effect on the physical properties. This effect is brought about by substitution of the hydroxyl groups of cellulose by bulky substituent groups, thereby, reducing the attraction between the cellulose chains, so that hydrogen bonding as well as other polar forces drop off. On the other hand, the presence of bulky substituent groups reduces the lateral adhesion and disrupts the regular geometrical close packing of the molecules. The larger the substituent groups, the greater the disruption of the regular geometrical close packing. Thus it is reported in the literature (69) that cellulose nitrate makes a somewhat stronger sheet than does cellulose acetate under comparable circumstances. This is due to the fact that the acetate groups are larger than the nitrate groups and less polar and hence the chains in cellulose acetate are more separated and held by weaker forces than the chains in cellulose nitrate.

Malm and his co-workers (48) prepared cellulose triesters using various organic acids which differ from each other by the number of carbon atoms. These investigators found that, in general, the larger the substituent group, the lower the melting point of the triester. These results confirmed the theoretical interpretation of the effect of the size of substituent groups on the melting point of cellulose triesters.

The degree of substitution also brings about variation of the physical properties (77). In general, it is expected that elongation, flexibility and similar properties should increase with increasing degree of substitution, while tensile strength and other similar properties should decrease with increase in the degree of substitution.

A careful consideration of tables 13 - 16 pages 77-80 reveals that the changes in degrees of acetylation caused almost no appreciable changes in the mechanical properties of the various cellulose acetate films. This seemed to disagree with the theoretical interpretation. An attempt will be made later to give some explanations for such unexpected results.

It is of interest to notice that although the sharp fraction of PM_4 type cellulose acetate has a D.P. of 240, its mechanical properties are almost the same as the sharp fractions of the other types of cellulose acetates PM_3, LH_1, and FM_6 which have D.P.'s of 300 each.

Another sharp fraction of PM_4 type cellulose acetate of lower D.P. had to be prepared to find out if such a change in D.P. would cause any serious change in the mechanical properties. The second sharp fraction of PM_4 type cellulose acetate had a D.P. of 215. Its mechanical properties were almost the same as those of the fraction having a D.P. of 240. This result was in agreement with several investigators (27, 53, 55, 61, 64, 65, 74, 77, 89) who found that if the D.P. of cellulose or cellulose derivative reached 200 or above, no appreciable change in mechanical properties was noticed.

This was done since the highest D.P. available in PM_4 type cellulose acetate was found to be 240, and no fraction of a D.P. 300 could be obtained from this type of cellulose acetate. On the other hand it was found that the fractionation of PM_4 type cellulose acetate was very difficult compared with the fractionation of the other three types of cellulose acetate. The reason could be attributed to the low degree of substitution which made it difficulty soluble in acetone.

Hercules Powder Co. (36) determined the mechanical properties of original cellulose acetate samples having the same range of degree of acetylation as the samples used in this investigation. They obtained variable results for each sample tested, but no correlation could be made between the degree of acetylation and mechanical properties of the cellulose acetate films.

These variable results could be attributed to the differences in molecular weight distributions between the various samples. The molecular weight distribution curves of the various samples of cellulose acetates obtained from Hercules Powder Co. were studied by Myers (57) who found that the various samples of cellulose acetates had widely different molecular weight distribution curves. Thompson (89) found that there was a marked influence of the molecular weight distributions on the mechanical properties of cellulose acetate films.

Therefore, as a consequence of Thompson's and Myer's investigations the effect of degree of acetylation on mechanical properties of cellulose acetate films can not be determined on original samples.

Mineral impurities, which are found in original materials, greatly affect the physical properties of cellulose acetates. An example which can be found in the literature (46, 61) is the marked difference between solubility curves of original samples and fractionated or purified cellulose acetates. This result has been confirmed and thoroughly discussed in Lee's Master's Thesis (46). From these and other discussions already mentioned in the review of the literature it can be concluded that original samples of cellulose acetates can not be used to study the effect of one variable unless all the other variables are eliminated or kept constant for samples of cellulose acetates under investigation.

It has been mentioned before that the results of this investigation do not support the theoretical interpretation of the effect of degree of acetylation on mechanical properties of cellulose acetate films within the range of the degree of combined acetic acid and the degree of polymerization of the sharp fractions used.

Several interpretations can be made in an attempt to explain this anamoly.

One possible explanation could be based on Meyer's assumptions. Meyer, in his book "Natural and Synthetic High Polymers" (55) pages 387 - 393 explained the extraordinarily high tensile strength of cellulose fibers and well-oriented acetate rayons. He deduced his arguments from the primary valence chain structure of native fibers which had been previously considered by Mark (53). Meyer assumed that in a fiber composed of primary valence chains of indefinite length, each extending over the whole length of the fiber, all the chains must be broken in the same region. From the projection of the unit cell, the cross-sectional area of a chain amounts to about 32 Å., that is, a fiber 1 sq. mm. in cross section will consist of about 3×10^{12} primary valence chains lying parallel to each other. Hence Meyer concluded from Mark's calculations that the work necessary to rupture such a fiber is equal to the chemical work required to separate the organic primary valence linkage. Using certain calculations Mark found that the highest cellulose polymer strength is only about one tenth the force required to break simultaneously all the chains in any cross section of cellulosic fiber. This conclusion forced Meyer to assume that in practice the tension was not shared equally between the primary valence chains as he and Mark had originally assumed. Therefore, Meyer concluded, if this assumption was true, then the most heavily loaded chains should rupture first and the rest will follow in succession. The less the orientation, the less the number of chains simultaneously placed under tension, and the less the tensile strength.

In well-oriented artificial fibers, the internal cohesion is so considerable that, in practice, rupture occurs only by chain fracture.

Meyer explained that slipping of the chains along each other would occur when the energy required was less than that for the rupture of a primary valence linkage, and he assumed that if the energy required to start slipping, by releasing the linkage between hydroxyl groups of glucose units in neighboring chains amounted to 1000 to 2000 cal., then if 70 glucose units of one chain were associated with 70 glucose units of a neighboring chain, 70 to 140 kg. cal. would be required to effect a separation, which was greater than the energy necessary to break a chain at a glucosidal linkage. From this Meyer assumed that, in preparations where the chain length was of the order of several hundred glucose units, fracture was always by rupture of the chains, rather than by slipping. Preparations of high chain length would, therefore, exhibit a tensile strength independent of the number of links in the chain.

Based on Meyer's assumptions it seems possible that rupture of the chains occurs in all cellulose acetate films under examination. This will reveal that no matter what the degree of substitution is, the mechanical properties will have to be the same since the degrees of polymerization of all the fractions tested are several hundreds of glucose units. If Meyer's assumptions are correct it will be safe to say that the results of this investigation seem to be in agreement with his theoretical interpretations. If this argument is true, it might be possible that a cellulosic polymer with a D.P. of 200 or more will give the same mechanical properties no matter how high the D.P. is since the breakage is always occuring by rupture of the chains.

If Meyer's assumptions are not correct another explanation will have to be made for the experimental results obtained in this investigation.

Another plausible explanation may be based on Mark's assumptions on the rupture of cellulosic fibers and films. Mark discussed thoroughly his ideas in the old edition of Ott's book "Cellulose and Cellulose Derivatives" (53) pages 997 - 1004.

Mark made two assumptions in order to arrive at a calculation of the tensile strength of cellulose and its derivatives. The first assumption was that rupture was due only to a break of the chains themselves, while the second assumption was that rupture was solely due to slipping of the chains along each other. He used the first assumption as a first approximation to the order of magnitude of the tensile strength in the following manner. Assuming that a fiber consisting of infinitely long cellulose chains is subjected to a stress at its ends parallel to the direction of the chains, if all the chains are parallel their individual cross section is 33×10^{-16} cm^2 and hence the number of chains passing perpendicularly through the unit cross section of 1 cm^2 is 3×10^{14}. If the chains are not completely oriented, the number of chains per cm^2 will be smaller. The force necessary to break one cellulose chain must next be calculated. The most labile points in the chain will obviously be the - C - O - C - bridges which connect the glucose rings. The energy of the C - O bond is about 90 kg. cal. per mole. From this and the interatomic distances Mark has been able to calculate the theoretical tensile strength due to the breakage of chains only. It is found to be almost ten times greater than the values measured with well oriented and highly crystallized natural and artificial fibers and Mark concludes that the breakage should be due to a different mechanism.

This leads to the second assumption which is concerned with slippage of the chains along each other by the rupture of van der Waal's forces.

Mark assumes a sample of completely parallel cellulose chains with finite length, overlapping each other irregularly. A weak point will be found in such a system where overlapping does not exist i. e. a point where the cross section of the fiber or film contains only chain ends.

Mark concluded after making certain calculations that the energy required to break these van der Waal's forces at the chain ends was in fair agreement with the tenacity of poorly oriented viscose or acetate rayon's fillaments and hence the rupture was probably due to the breaking of van der Waal's forces and perhaps other secondary valence forces.

With increasing overlapping of the chains, the ragged cross-sectional area over which only secondary valence forces need to be broken will be larger also. In other words, if the co-valent bonds are so strong that they do not rupture, van der Waal's forces must be opened over a much larger area because the chains are overlapping each other in an irregular way. Instead of breaking 3×10^{14} van der Waal's forces along a smooth cross section in one and the same instant, those parts of the chains which overlap must tear loose and slip along each other. In order for two chains to slip along each other, it is only necessary that the chains become uncoupled.

After certain calculations Mark found that the theoretical force necessary to overcome the secondary forces and produce slipping was about

50 to 100% higher than the tenacities of highly oriented viscose rayon fibers.

Based on Mark's assumptions the breakage of the films must occur by slipping of the chains along each other. Therefore, in cellulose acetates, the higher the degree of combined acetic acid, the easier would be the slippage of the chains because the strength of secondary valence forces between the chains will be lowered. However, the results obtained in this investigation showed no effect of the degree of acetylation on the mechanical properties of the films.

A possible explanation would be that since all the fractions are sharp and have approximately the same D.P. therefore, the probability of finding cross sections of the films in which only chain ends exist should be very small or even negligible. In addition, the probability of finding points at which the chains are overlapping each other irregularly might not only be very small but also the same in the four sharp fractions investigated and hence the force necessary to slip the chains along each other may be approximately the same for all the four sharp fractions. The same argument has been used by Mark in an attempt to explain why in cellulosic materials when a D.P. of 200 or above is reached there will be little or no change in mechanical properties primarily because the chains are so large that the probability of finding weak points at which the chains are irregularly overlapping each other is lowered and hence no appreciable change in mechanical properties is found as the D.P. goes over 200.

A third possible interpretation of the results obtained in this investigation would be that the range of the degree of substitution studied was small or not enough to give definite changes in mechanical properties. This meant that a much wider range was needed to find precisely its effect on mechanical properties of the cellulose acetate films. But the great difficulty in such an interpretation is that cellulose acetates having degrees of acetylation lower or higher than the samples used are insoluble in most organic solvents and their fractionation, if possible at all, is exceedingly difficult as pointed out in the review of the literature.

An interesting point concerning the degree of substitution is that the physical properties of cellulose acetates having few percentages combined acetic acid more than the highest one used in this investigation are significantly different (36, 38).

On this basis, it is possible, that since such little change in degree of substitution produces a marked change in physical properties the degree of acetylation range used in this investigation might not be too small to effect the mechanical properties. This point will not be clear unless further investigations are carried out which will be recommended later.

A fourth explanation which might throw some light on the problem is that the degrees of polymerization chosen for the fractions were too high. These D.P.'s were chosen because it was thought that they represent the highest percentage in the original samples, and even in this case, a very large amount of starting material was needed to give just enough sharp fractions to be used for mechanical testing. The D.P.s seemed to be so high that their effect on mechanical properties overlapped the effect of degree of acetylation and hence the effect of the degree of acetylation alone could not be detected.

This explanation could be in agreement with the assumptions of both Meyer and Mark.

Based on Meyer's assumptions the D.P.s were so high that the forces of cohesion between the chains were great. Hence the fracture of the films was caused by rupture of the chains carrying the highest load, then the most heavily loaded chains would rupture and so on until all the chains in a cross section were ruptured. This could be true for all the fractions used since all of them had approximately the same D.P., and hence the effect of the degree of acetylation could not be readily detected no matter how large the degree of substitution range might have been in the different samples.

Based on Mark's assumptions, the probability of finding weak points at which the chains were irregularly overlapping each other to enhance slipping was very small and hence the force used to overcome the van der Waal's and secondary valence forces holding the chains would be so great that the effect of the degree of acetylation on it could not be detected.

If the D.P.s of the fractions under examination were much less than 300, for instance, 80 or 100, then, as a consequence of Meyer's and Mark's assumptions the slippage of the chains over each other during film rupture would be greatly enhanced and little force would be needed to do so, and any change in mechanical properties, could be attributed to the increase or decrease of the degree of acetylation. This low range of D.P. might also help in reducing the effect of the D.P. itself on the mechanical properties i.e. the effect of the D.P. might not overlap the effect of the degree of acetylation and hence the degree of acetylation would have a better chance to show its effect on the mechanical properties of the various films.

These are mere assumptions which can not be valid unless supported by further investigations which will be mentioned in a later section on recommendations for future work.

A fifth and final possible interpretation of the unexpected results obtained in this investigation would be that the machines used for testing the mechanical properties were not sensitive enough to determine the effect of degree of acetylation on mechanical properties of the cellulose acetate films.

In the discussion above, the values mentioned for the degree of polymerization of the sharp fractions were those determined in acetone solutions.

A careful consideration of table 10 page 69 reveals that the degrees of polymerization of the various samples of cellulose acetates determined by the acetone method or methyl cellosolve, using constants obtained from the literature, are only about one fourth the degrees of polymerization determined by the cupriethylenediamine method.

The reason for the use of cupriethylenediamine was to check the validity of the constants obtained from the literature for the determination of the D.P. in acetone or methyl cellosolve. The cuprithylenediamine method was found to be reproducible and as accurate as the acetone method except that great care had to be taken in keeping the solution under nitrogen to prevent atmospheric oxygen from coming in contact with it when it was stored since it could be easily oxidized by air and the solvent power of the solution would drop markedly if any change occured in its exact composition. The results of the D.P.s obtained by cupriethylenediamine were found to be very high and unexpected. A sharp fraction was sent to Picatinny Arsenal for the determination of the D.P. by the light scattering method (11). The result was in good agreement with the cupriethylenediamine method.

As a matter of fact the cupriethylenediamine method measured the D.P. of the pure cellulose formed after complete de-esterification of cellulose acetate. The constant used in this method was obtained from the literature for pure cellulose in cuprammonium hydroxide or cupriethylenediamine.

It is very unfortunate, however, that there is no practical method for measuring the molecular weight of cellulose and cellulose acetate in terms of absolute degree of polymerization units. A universally accepted method is needed for such determination to overcome the difficulty of finding the proper constant for a certain polymer in a certain solvent.

If the D.P.s of the samples of cellulose acetates under investigation were as high as the values found by cupriethylenediamine and light scattering, the interpretations made for the unexpected results of the mechanical properties would probably be valid.

IX. CONCLUSIONS

Conclusions

1. It was found that the degrees of acetylation of the various sharp fractions of cellulose acetates under investigation had no measurable effect on the mechanical properties of their films.

2. Several possible explanations for the lack of variation in mechanical properties with the degree of acetylation are the following:

(a) It is possible that the degrees of polymerization of the various fractions are so high that the forces of cohesion between the chains are great. Hence, during mechanical testing, rupture of the chains occurs in all cases and the mechanical properties of all the fractions would be the same and independant of the degree of acetylation.

(b) It is also possible that if fracture of the films is caused by slipping of the chains along each other, then the force necessary to overcome the secondary valence forces holding the chains together is so great that the effect of the degree of acetylation on it could not be detached by the methods of measurement available.

(c) It is possible that the effect of the high degree of polymerization of the fractions on mechanical properties is high enough to overshadow the effect of the degree of substitution.

(d) It is also possible that the range of the degree of acetylation in the fractions under investigation is not large enough to give appreciable changes in the mechanical properties of the various fractions.

(e) It is possible that the sensitivities of the machines used for mechanical testing are not high enough to detect changes in the mechanical properties of the various fractions due to variations in the degrees of acetylation.

3. Of the explanations offered in "2" the most possible appears to be (a) and it is therefore concluded that at a D.P. of 300 the forces required to rupture a film has reached the value required to rupture a C - O - C bond and is independant of the secondary valence forces and so not affected by variation in the degree of acetylation.

4. It was found that the degrees of polymerization of various samples of cellulose acetates determined by the cupiethylenediamine viscosity method were almost four times greater than the degrees of polymerization of the same samples determined by the acetone viscosity method using constants obtained from the literature. It was also found that the D.P. of a sharp fraction determined by light scattering method was in good agreement with the D.P. of the same sharp fraction determined by the cupiethylenediamine viscosity method. It is concluded that a considerable variation exists in the D.P. as determined by various methods but that for purposes of comparison of the properties any one method is satisfactory until the reason for such difference be found.

X. RECOMMENDATIONS

Recommendations

1. Since the most plausible explanation for the unexpected results obtained in this investigation is attributed to the high degree of polymerization of the fractions, it is recommended that mechanical properties be determined on sharp fractions of much lower D.P., such as, 80 or 100 in an attempt to determine the effect of degree of acetylation alone on mechanical properties.

2. It is recommended that a thorough and precise investigation be made on the molecular weights of the sharp fractions obtained in this investigation in an attempt to evaluate the correct constants for the determination of the degree of polymerization of cellulose acetates by the viscosity method using various organic solvents. The investigation should include some absolute methods such as light scattering method or ultracentrifuge method or both, and comparison of the results with the viscosity methods using cupriethylenediamine, acetone and other common solvents.

3. It is recommended that physical properties other than mechanical be determined on the sharp fractions obtained in this investigation. Such properties as, melting points and rate and degree of solubility in various solvents might help in an attempt to correlate the effect of degree of substitution on these and other physical properties.

4. It is finally recommended that an attempt be made to fractionate cellulose triacetate into sharp fractions which, after testing mechanical and physical properties, might throw some light on the problem of abnormal properties of original cellulose triacetates compared with the partially hydrolyzed or acetone soluble original cellulose acetates.

XI. SUMMARY

Summary

Four samples of cellulose acetates having degrees of combined acetic acid between 50.8 - 55.8% were fractionated to obtain sharp fractions of approximately the same degree of polymerization.

About 2000 grams starting material of each sample of cellulose acetate were needed to obtain approximately 50 grams of sharp fraction for testing the mechanical properties of their films.

Fractionation of the cellulose acetate was from an acetone-water mixture, by addition of n-heptane to precipitate a certain fraction. After a series of refractionations, a sharp fraction of each of the four cellulose acetates was obtained. These fractions had different degrees of acetylation but approximately the same degrees of polymerization. These fractions were then dissolved in acetone and cast into films which were conditioned for three days and their mechanical properties were determined in an attempt to determine the effect of degree of acetylation on the mechanical properties.

It was found that the degrees of acetylation of the various sharp fractions of cellulose acetates had no appreciable effect on the mechanical properties of their films.

It was concluded that the degrees of polymerization of the various fractions were so high that the effect of the degree of acetylation on the mechanical properties could not be detected.

The degrees of polymerization of the various samples were determined by the viscosity method using acetone and cupriethylenediamine as the solvents. It was found that the degrees of polymerization of the various

samples of cellulose acetates determined by the cupriethylenediamine viscosity method were almost four times greater than the degrees of polymerization of the same samples determined by the acetone viscosity method using constants obtained from the literature.

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XIV. VITA

Vita

Adnan Husayn Awni, was born in December 1, 1924, in Baghdad, Iraq. He graduated from Adhamia Secondary School in June 1945. He was awarded a Government fellowship to study chemistry at the American University of Beirut, Beirut, Lebanon. He received his B.A. degree in June 1950, with a major in chemistry. From 1950 to 1952 he worked at the Industrial Research Institute at Baghdad, Iraq. In August 14, 1952 he came to the United States of America under a Government grant to study for one year. He entered Georgia Institute of Technology in September 1952 and received his M.S. degree in Chemistry in January 1954, in absentia. In January 1954 he entered Virginia Polytechnic Institute for further graduate study in chemistry. He has served as a research assistant, and as a teaching assistant while studying for his doctorate degree.

Adnan Awni