THE EFFECT OF VARIOUS PRETREATMENTS ON THE NITRATION OF CELLULOSE

A Thesis

by

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CLAIMS TO ORIGINAL RESEARCH

1. The per cent of benzene retained by mercerized cellulose, solvent-exchanged through the series: water - methanol - benzene, and dried, was determined by a precise gravimetric method and found to be less than that reported by Staudinger and Döhle, being of the order of 1 per cent. This retained or 'included' benzene could be removed completely by prolonged extraction with water, but could not be removed by prolonged heating at 100° and less than 1 mm. pressure.

2. The per cent inclusion in cellulose of members of a homologous series of amines, ranging from ethylamine to triethylamine and from ethylamine to hexadecylamine was determined gravimetrically and checked by chemical analysis. The per cent of amine retained by mercerized cotton linters upon prolonged heating at 100° and less than 1 mm. pressure was found to increase with molecular weight of the amine. The lower molecular weight amines could be removed completely by exhaustive extraction with water, but the 12 per cent of hexadecylamine permanently included by a mercerized cellulose could not be removed by water and rendered the fiber impervious to penetration by water.

3. Mercerization of cellulose with 11 per cent sodium

hydroxide solution and removal of the alkali by repeated washing with ice water was adopted in the solvent 'inclusion' studies in order to obtain maximum retention of the solvent. The complete conversion of the 'water cellulose' formed by this procedure to the stable Hydrate allotrope by boiling the mercerized, washed cellulose for one-half hour yielded products which gave more reproducible results than had been obtained previously in the nitration studies.

4. Confirmation was made of results of a previous investigation which showed that when a dry, highly swollen cellulose was immersed in water and redried it formed a 'collapsed' product which yielded a technical nitrate with decreased nitrogen content.

5. The decrease in nitration reactivity of a collapsed cellulose was found to be magnified by a process of alternate wetting and drying or by reducing the time of nitration under otherwise constant conditions, and could be eliminated altogether by extension of the nitration time to 5 hours. The effect was found to be substantially independent of the composition of the nitrating acid for nitrogen levels ranging from 7 to 13 per cent.

6. The effect of heat upon the nitration characteristics of swollen and untreated cotton linters and wood pulp

was studied systematically for the first time. The nitration level was found to increase regularly upon heating the dried cellulose up to a temperature of 150° prior to nitration. The nitrogen level increased slightly with temperature for a given time of preheating, and with time of preheating at a given temperature.

7. The effect of the moisture content of untreated and collapsed cotton linters upon nitration reactivity was studied under a variety of conditions. The level of nitration was found to be a function of the moisture content of the starting materials to an extent which could not be accounted for by dilution of the nitrating acid.

8. Solutions of cellulose nitrates from collapsed linters were found to be optically imperfect, and an effort was made to determine the particle size of those components giving rise to imperfect solutions by a spectrophotometric method based on the principle of light scattering. The method failed, either because it was not applicable to the solute and solvents used, or because the particle size of the heterogeneously nitrated components was less than 500A units in diameter.

9. The nitrated products from several investigations were examined microscopically under ordinary and polarized light, both alone and after treatment with a number of different stains and solvents. Macro-heterogeneities were readily distinguishable under the microscope; the results for nitrates suspected of microheterogeneities, however, were inconclusive. The bulk of the microscopy work suggested that optical methods would fail to distinguish between nitrates prepared from swollen, collapsed or untreated linters or wood pulps

GENERAL INTRODUCTION

The present work is a continuation of an investigation initiated by Brown and Purves (1). They found that the nitrogen content of a cellulose nitrate from solvent-extracted cotton linters could be varied by pretreatments of the starting material, using strictly physical methods which could promote no change in chemical composition. A mercerized sample of cotton linters which had a high nitration reactivity could be converted to a topochemical modification with a lower nitration reactivity by the simple operation of drying from water rather than through the solvent exchange series: water - methanol - benzene.

It was the immediate purpose of the present work to examine in detail the dependency of the reactivity toward nitration on the pretreatment of cellulose, to increase or diminish the magnitude of the effect if possible, and to study the phenomenon in terms of a number of nitration variables. In a broader sense, therefore, the present work employed nitration as a means of studying the structure of cellulose in the range of magnitudes between the X-ray crystallites and the microscopically visible morphological building units.

The main body of the work involved the preparation of several hundred samples of cellulose nitrates from cotton linters or from wood pulp variously treated prior to nitration and under various conditions of nitration.

The nitrogen contents of the nitrated products were determined either by a standard micro Kjeldahl analytical method or by 'yield' calculations. In order to determine nitrogen contents by the latter method, the bone-dry weights of the starting materials had to be known, and in order to determine these weights with sufficient accuracy, it was found necessary to conduct a detailed but relatively independent investigation of the amount of solvent held by mercerized celluloses dried through solvent-exchange. Because the necessary equipment and materials were at hand at the time, and because techniques had already been developed in connection with the main nitration work, the inclusion study was extended to cover a number of amines. This study was not related directly to cellulose nitration, but was of direct interest to the long-range purpose of contributing to the knowledge of cellulose fine-structure.

An effort has been made in the Historical Introduction to collate a number of modern studies relating to cellulose fine structure. Only limited mention has been made of the literature dealing with the nitration of cellulose, because this field has been adequately reviewed by others.

In an attempt to organize the thesis to the best advantage, the voluminous experimental data were first

condensed into a section entitled 'Experimental Results', the principal features of which were then singled out and re-organized in the 'Discussion'. In order to include material of secondary importance without obscuring the principal discussion, liberal use has been made of foot-notes and appendices.

HISTORICAL INTRODUCTION

In the present work no effort will be made to cover the historical background of present-day concepts relating to the chemical and physical structure of cellulose. Atomic structure of the cellulose macromolecules, together with measurements and significance of numerous allotropic modifications which their aggregates exhibit, have been reviewed in detail in a number of excellent texts (2)(3)(4). These texts have been taken as the starting point in the present discussion, in which particular emphasis has been placed upon recent developments in the study of the fine structure of cellulose.

a. The Fine Structure of Cellulose:

It is now generally accepted that pure cellulose, such as constitutes over 98% of a cotton or ramie fiber, is a linear polymer built up of a large number of glucose anhydride units linked together through oxygen by primary valence bonds. The macromolecules are arranged within a cellulose fiber in a continuous network of crystalline and non-crystalline regions, the average length of a crystallite being not less than 600Å units (Table XVIII) and the amount of crystalline material in native cellulose being at least 70% (5). Statistically, one cellulose chain of average

length should traverse approximately (0.70)(25,000)[a] or 17,500A units of crystallites. The number of crystallites along the length of such a chain would be approximately 17,500/600 or 30, the number of amorphous regions likewise 30 and the average length of each amorphous region 7500/30 or 250A units. It has been assumed that the freedom of

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a. It is assumed that the chain length or average degree of polymerization (D. P.) of a macromolecule in native cotton or ramie fiber is at least 5000 and the length of each chain member is 5A units. Measurements of osmotic pressure and viscosity suggested that the average degree of polymerization of native cellulose was approximately 5000 (6). According to an ultra-centrifuge investigation By Gralen (7) the average chain-length of the macromolecules in a fiber was considerably higher. Even these values for a native cotton (Table I) were lower than those obtained recently by viscosity measurements of cuprammonium solutions with careful exclusion of air (8). The D. P. of cotton was found to increase from 5000 to 10000 upon decreasing the amount of

TABLE I

MOLECULAR WEIGHTS OF CELLULOSE IN CUPRAMMONIUM FROM SEDIMENTATION AND DIFFUSION STUDIES[b]

Cellulose	D.P.
Bleached American Cotton Linters	3000
Sulfite Cellulose	3100
Unbleached American Cotton Linters	9300
Georgia Cotton	10800
Nettle Fibers	11600
Ramie	12400
Flax Fibers	36000

oxygen present in the reaction medium, and extrapolation to zero per cent oxygen indicated a chain length of not less than 15000. It has been suggested (9) on a basis of electron microscope studies that the cellulose macromolecule might be as long as the fiber itself.

b. Gralen, N. (7).

rotation about a glycosidic bond is 5° or less, and that the length of a single glucose residue in the macromolecule is 5.15A units (2). The smallest complete circle the macromolecule could assume would therefore have a circumference of (5.15)(72) or 370A units. On this basis there is not sufficient distance between two consecutive crystallites for a macromolecule traversing them to form a complete loop.

Until recently the terms 'amorphous' and 'crystalline' as applied to cellulose have been somewhat loosely defined. In the present work, cellulose 'crystallinity' is considered to be as defined by Hermans (10): that fraction of cellulose which gives rise to a coherent x-ray diffraction pattern. If cellulose were an ideal structure, the crystalline and amorphous components would be described as follows:

1. The crystallites would be in a state of perfect three-dimensional order, all possessed of the same dimensions and all with the same degree of orientation. This state is approximated most closely by native ramie fiber[a].

2. The amorphous component of cellulose would consist of a perfectly isotropic aggregate of individual cellulose

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a. Because of the dissolution of the amorphous component of cellulose, possibly accompanied by a recrystallization of free chain ends, the products from the treatment of cellulose with hydrochloric acid - ferric chloride hydrolysis - oxidation reagent may be almost 100 per cent crystalline (p. 57).

chains of random length and orientation. This state is approximated in unstretched viscose, and presumably is attained by fibers which have been subjected to the action of a vibrating ball-mill[a].

Cellulose is usually less than ideal in its supermolecular structural pattern, and the crystalline and amorphous components may be represented as follows:

1. Crystalline Regions: at intervals throughout the cellulose structure the three-dimensional arrangement of the glucose anhydride units is repeated in such a manner as to build up localities sufficiently large to give coherent X-ray diffraction patterns. It is assumed that the crystallites are not all of the same length or of uniform cross-section, that the crystalline - amorphous interface is not sharp, and that a fraction of the crystallites may protrude in the form of fringes into the amorphous regions.

2. Amorphous Regions: the amorphous regions extend between

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a. The vibration ball-mill or 'schwingmühle' has been used in a number of cellulose investigations (11)(12)(13)(14). Interest in its utilization has been stimulated by the fact that it is possible to produce with it a completely amorphous cellulose, which, upon treatment with water, reverts in part to Hydrate cellulose (15)(16). Products from as little as 1 hour of grinding give only diffuse X-ray diffraction patterns, indicating a total absence of crystallinity. The schwingmühle offers the advantage of disintegrating a fiber by strictly mechanical means with no attendant chemical action and no thermal decomposition (17). For this reason it has been used in conjunction with the electron microscope to study cellulose fine structure.

the crystallites and act as a 'grundmasse' for them. The cellulose chains are more or less randomly kinked and in a state of more or less random orientation. In short, the amorphous component may comprise an infinite variety of structures ranging from a few parallel long-chain bundles or embryonic crystallites to very short-chain molecules with completely random orientation.

A macromolecular state intermediate between the amorphous and crystalline has been postulated by Baker, et al (19), and the concept has been applied by Nickerson and Haberle in a discussion of the reactivity of cellulose toward hydrolysis (20). The semicrystalline or mesomorphic state would represent a higher degree of order than that present in the truly amorphous regions, but would not be sufficiently highly ordered to contribute to coherent X-ray diffraction patterns. Hermans (21) has emphasized the difficulty involved in attempting to correlate per cent crystallinity with such fiber characteristics as water adsorption. In the limiting case, two macromolecules could conceivably be bonded in such a manner as to resist water penetration or adsorption, hence could not participate in sorption phenomena ordinarily associated with the amorphous regions. In brief, a variable and indeterminate fraction of cellulose classified on a basis of X-ray analysis as amorphous might possess the reaction characteristics of the crystalline component (p. 56).

In a review of his work Hermans (10) has outlined several methods for determining the degree of crystallinity in cellulose. The amount present in various regenerated samples was found to be constant within narrow limits; completely amorphous cellulose prepared in a vibrating ball-mill and moistened with water, rayon thread spun by the Lilienfeld process (in which orientation approached a maximum) or isotropic fibers (in which orientation was completely random) all gave the same per cent of crystalline component.

The absolute per cent of the crystalline component of native and regenerated cellulose has been calculated from X-ray diffraction patterns (5)(22)(23), but only a continual refinement of techniques has made it possible to obtain accurate values (10). Recent results obtained by the X-ray method are in fairly close agreement with the same values obtained by a number of other methods, as shown in Table II.

TABLE II

PER CENT OF CRYSTALLINE MATERIAL IN VARIOUS CELLULOSES[a]

Method of Determining Crystallinity	Type of Cellulose		
	Native Cotton	Pulps	Regenerated
X-ray Analysis	70 ± 2	....	39 ± 3
Sorption Isotherms	68	....	35
Density Determinations	60	50	25
Birefringence and Orientation	.....	....	≤ 40
Recrystallization of Amorphous Cellulose	.....	....	35% (6a)

a. Hermans, P. H. (10)

Heyn (24) has studied the small-angle scattering (that is, in the area immediately adjacent to the primary X-ray beam) of a number of different cellulose fibers treated in various ways with swelling agents. When jute fiber was soaked in 0.5 and 5% solutions of caustic soda there was a change in the area of small angle scattering which was reversed when the fiber was washed with water. When mercerizing alkali of 18% concentration was used, however, the area of scattering was irreversibly decreased, indicating a permanent increase in the distance between crystallites. Table III contains a number of selected values for small-angle scattering.

TABLE III

SCATTERING AND APPROXIMATE IDENTITY PERIODS FOR DIFFERENT FIBERS[a]

Fiber	Jute	Ramie	Cotton	Merc. Cotton	Viscose
Maximum Scattering Angle	1°35'	1°18'	36'	51'	1°9'
Average Period in A Units	55	68	146	95	73

Heyn suggested that the values shown for the average period might represent center - to - center distances between crystallites (or intermicellar regions), and that in the case of a cellulose with a high crystalline-amorphous ratio (ramie or cotton) the period value would be approximately equivalent to the crystallite diameter. It was concluded that fibers

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a. Heyn, A. N. J. (24).

such as hemp, flax and jute contained small crystallites and small inter-crystallite distances, ramie and cotton large crystallites and small inter-crystallite distances, and viscose small crystallites and large inter-crystallite distances.

This work is of particular significance in that it offers experimental evidence for the not unexpected conclusion that the crystallites vary in size as well as in amount, and provides a means for approximating the ratios of crystallite diameters for various cellulose modifications.

The fact that fibrous celluloses are penetrated readily by various liquids, and also by dye molecules of considerable size, would indicate that the cellulose fiber does not consist of a continuous phase, but rather of chain bundles or individual chains separated by interstices. Some evidence of the nature of the inter-cellulosic voids has been obtained by the deposition of crystallites of gold or silver metal within the open network. Large crystallites in the form of spindles, 2500A units in length and 400 A units in diameter, and lamellae of indefinite area and an average thickness of 70A units (25) have been detected. This method has been criticized (26) on the basis that the cellulose capillary system may have been drastically altered by the growth of the metal crystallites.

It has been calculated that the molecular volume of the largest molecule capable of penetrating the capillary system in a highly swollen, mercerized cotton linters is approximately 400 (27)[a].

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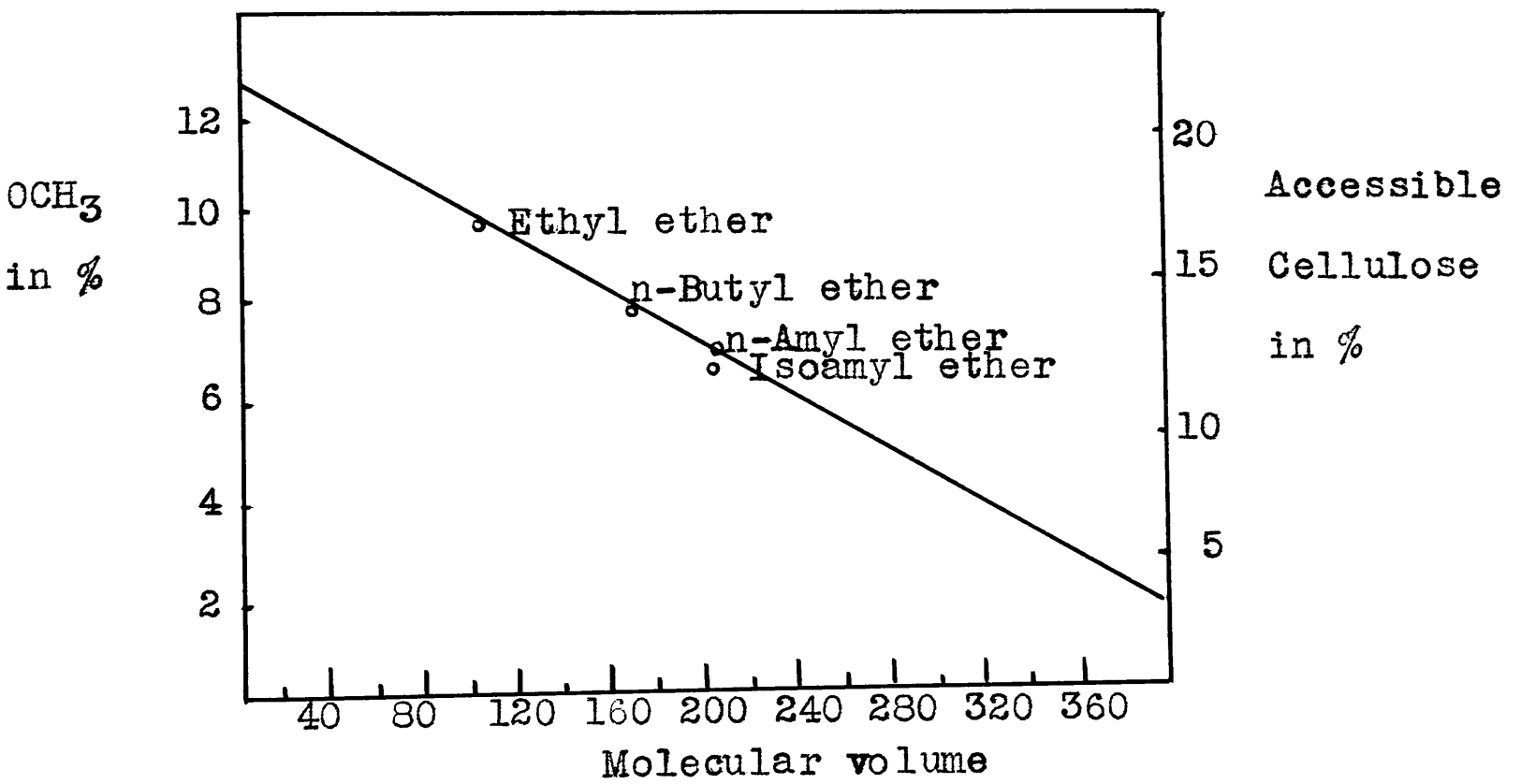
a. The maximum molecular volume was obtained by the following method. Thallous ethylate accessibility values (p. 61) were obtained for several cellulose modifications by the use of an homologous series of solvents for the thallous ethylate. In one series, where the solvents used were ethyl-, propy-, butyl- and amyl- ethers, a straight-line relationship was obtained (Figure I). Extrapolation to 0 molecular volume gave a theoretical measure of the per cent of hydroxyl groups accessible to thallous ethylate dissolved in a liquid of 0 molecular volume. Extrapolation to 0 methoxyl content gave the maximum molecular volume of a liquid capable of penetrating the cellulose structure.

FIGURE I

THE SUPERFICIAL METHYLATION OF A UNIFORM, SWOLLEN CELLULOSE BY THALLOUS ETHYLATE DISSOLVED IN VARIOUS LIQUIDS[b]

(triplicate estimations shown)



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b. Assaf, A. G., Haas, R. H., and Purves, C. B. (27).

The pore volume in ramie fiber has also been calculated from the difference in double refraction as determined (21) by two distinct methods[a]. The pore volume thus obtained (8 per cent) was considered to check fairly well the corrected value (10 per cent) for the porosity of ramie obtained by direct measurement (28).

In addition to discontinuities of molecular and X-ray dimensions, cellulose fibers have others of microscopic and submicroscopic size which may also effect the reactivity. The following brief outline is based upon a recent review of the morphological structure of cotton cellulose by Hock (29).

As an indication of the relative proportions of the micro and macro dimensions, it may be noted that the cotton linters fiber averages approximately 200,000A units

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a. The pore volume was determined by the difference in double refraction as calculated by the following methods:
   A. By the direct determination of fiber thickness and phase difference in polarized light, from the relationship $y\lambda/s$, where

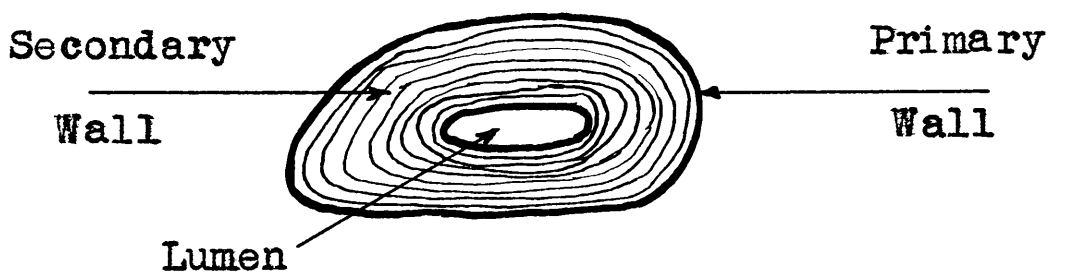
      y is the phase difference measured in wave lengths
      λ is the wave length of the light used.
      s is the distance of light travel, ie, fiber thickness.

   B. From the difference in refractive indices, $n_1 - n_o$, where
      n_1 is the refractive index of the fiber for light polarized parallel to the direction of the fiber axis.
      n_o is the refractive index of light polarized perpendicular to the direction of the fiber axis.

   The value obtained by Method B was 0.0708 and by Method A was 0.0657. The difference, 0.0051 or 8 per cent, was assumed to represent a measure of pore volume.

in diameter and many thousands of times this in length. The primary or outer wall, containing various non-cellulosic materials such as waxes and pectins, is approximately 5000A units thick and is just visible in the microscope. The secondary or inner wall of the fiber is made up of 15 to 20 double layers, each layer being from 1000A units to 4000A units thick. These layers surround concentrically the central lumen as shown in Figure II.

FIGURE II



CROSS-SECTION OF A COTTON LINTERS FIBER

The alternate layers may consist of cellulose only, in which case it is assumed that the slight difference in optical properties which makes it possible to distinguish between them visually is caused by slight differences in density. The alternating layers, however, may be at least in part non-cellulosic, in which case they are markedly different in appearance from the pure cellulose layers. Such non-cellulosic layers are quite variable, both as to size and location: they may extend from the primary wall to the central lumen, they may be concentrated in a few rings close to the lumen, or they may be absent altogether.

There is also considerable variation in the per cent of these so-called 'green-lint' fibers within the same cotton boll.

The cellulose layers of the secondary walls are made up of fine, threadlike strands which are oriented at an angle of approximately 45° with respect to the long axis of the fiber, and appear to be less than 1000A units in diameter. Between the inside of the primary wall and the outside of the secondary wall is located the fiber winding, in which the stands are rather coarse and the spirals are quite flat. The winding may have an S or a Z configuration, and its orientation may reverse several times along the length of an individual fiber. It has been suggested that the orientation of the fiber strands with respect to the fiber axis may be correlated with optical anisotropy, swelling, rate of hydrolysis, and form of X-ray diffraction patterns. The extinction bands noted when a cotton fiber is observed under crossed Nicols, and the areas of constriction between the ballooned sections in an alkali-swollen fiber both coincide with the points at which the strands reverse their direction of orientation.

Thus far, unequivocal evidence has been produced for no more than three definite units in the structural organization of cotton linters: the cellulose macromolecules, the crystallites with a diameter of the order of 100A units, and the spiral windings of the cellulose fiber with a diameter

exceeding 1000A units. An exceedingly large body of work in the field of cellulose research has involved efforts to locate, measure, or prove the existence of intermediate structural units, variously termed fibrilles, fibrillites, particles, threads or micellar strands[a]. This concept of intermediate structural units is not in accord with the results of detailed investigations carried out by Frey-Wyssling (25), who believes that there is an unbroken continuum in structure from the crystallite to the fiber itself. The proposals of Frey-Wyssling and his associates concerning the microstructure of cellulose have been developed in detail by Mühlethaller (30) in a contribution relating to the structure of various types of colloidal gels, including cellulose, and on various

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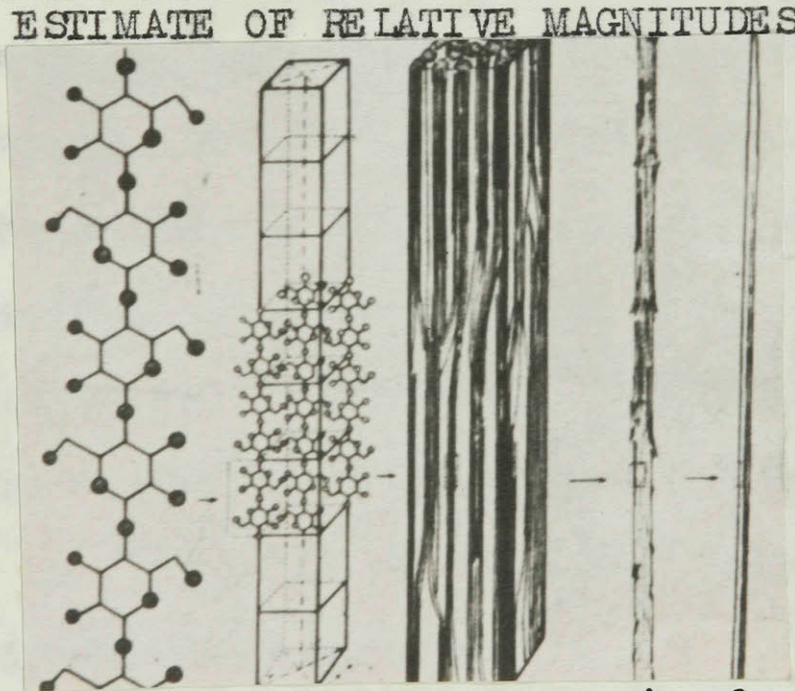
a. In recent years the micro- and macro-structure of cellulose fibers have been extensively studied by a number of investigators, including Dolmetsch and co-workers (31)(32)(33), Franz and co-workers, (34)(35)(36)(37), Wergin, and Frey-Wyssling. Of the various systems which have been proposed for the morphological structure of cellulose, possibly the most elaborate and detailed has been advanced by Dolmetsch (31). On a basis of optical and electron microscope studies it was proposed by Wergin (38)(39) that the cellulose fiber was built up of small units of definite size, into which cellulose might be subdivided by suitable means. The secondary wall of the cotton fiber was pictured as being composed principally of cellulose in a lattice structure (40). Upon decomposition of the cellulose structure, by swelling or by ultrasonic disintegration, the secondary wall broke down into fibrillae approximately 2 microns in width. Under the electron microscope, elementary fibrillae or fibrille bundles, 80 to 150A units thick, could be identified. These elementary fibrillae were considered to be 15,000A units long and to be characterized by a periodicity of approximately 2500A units. They were arranged in regular layer lattices, separated by a water-soluble, non-cellulosic component.

cellulose types, including bacterial, cotton, flax and hemp.

Cellulose is pictured as being built up from a special type of crystalline lattice, or 'Kettengitter', or bundle of chain molecules, formed into micellar strings of definite thickness but indefinite length. A schematic representation of the continuous development of cellulose structure from macromolecules to visible fibers, envisaged by Frey-Wyssling (41) is shown in Figure III.

FIGURE III

SCHEME FOR THE FINE STRUCTURE OF CELLULOSE, WITH AN ESTIMATE OF RELATIVE MAGNITUDES[a]



a. Cellulose Chain: 15 million to 1.
b. Chain Lattice: 5 million to 1.
c. Micellar Bundle: 0.5 million to 1.
d. Fibrille Fiber Fragment: 5000 to 1
e. End of a Flax Fiber: 500 to 1.

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a. Frey-Wyssling, A. (41).

Light- and electron-photomicrographs were obtained for ramie, hemp, cotton and bacterial cellulose disintegrated by means of ultrasonic waves. At magnifications of 20,000, the finest fibrilles observable were from 50 to 100A units in diameter, dimensions corresponding in magnitude to those of the cellulose crystallites as determined by X-ray analysis. There was no evidence of the existence of submicroscopic or microscopic fibrilles, and there was no method of determining whether the smallest micellar strings represented true morphological building units or whether they could be further broken down to the limit of individual molecular chains. The general conclusion drawn from this series of light- and electron-microscopic studies suggested that regardless of the source of the cellulose there was a continuous gradation, unbroken by visible discontinuities, from macroscopic to sub-electronmicroscopic dimensions. Variations in the properties of the bulk fiber were considered to be the result of differences in the order of the cellulose macromolecules rather than to differences in kind.

It was suggested by Wuhrmann, et al (42) from an examination of electron photomicrographs, that there was no clearly defined end to the fibrilles within the fiber, and that the crystallite diameter determined by X-ray analysis should be considered as an average value from a flat distribution curve including all possible values from an individual chain to chain bundles with diameters considerably in excess of 100A units.

b. The Concept of Cellulose Accessibility and Reactivity:

A precise knowledge of the molecular and macromolecular structure of the various modifications of cellulose is essential to an understanding of its reaction characteristics, and is also an aid in the development of 'use' tests which can predict the behaviour of a given cellulose under a given set of conditions. Two principal methods of approach have been utilized in studying the reaction characteristics of cellulose; one, an essentially fundamental approach, might be represented by the thallous-ethylate method (p.61). The other method involves the development of practical 'use' or 'suitability' tests to be used in conjunction with commercial processing. Much of the work by Jayme and his associates (p. 21) would be included in the latter category.

The terms 'amorphous', 'accessible' and 'reactive' have been used widely with reference to the physical and chemical behaviour of cellulose. In order to avoid ambiguity it is understood that in the succeeding discussion these terms are defined as follows:

'Amorphous' cellulose is that component which does not contribute to a coherent X-ray diffraction pattern.

'Accessible' is that fraction of the cellulose, restricted to the amorphous component and the crystallite surfaces, together with some small fraction of the crystallites in the case of hydrate cellulose, which is acted upon

by a given reagent[a].

'Reactive' cellulose is that fraction which enters into a given reaction, ie, esterification, oxidation or hydrolysis, usually in a permutoid reaction[b].

It should be emphasized that the amount of cellulose accessible to a given reagent or acted upon in a given reaction may be related only indirectly to the amount of non-crystalline material present. Early in the development of cellulose it was thought that the physical and chemical properties of cellulose might depend to a large extent upon the crystalline-amorphous ratio. In some cases

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a. A reagent such as water which fails to penetrate the crystallites of a native cellulose may enter readily between chain segments in the more loosely packed amorphous areas. This penetration is ordinarily accompanied by limited swelling. The action of such a non-permutoid reagent may be represented as the cleavage of hydrogen bonds at random points within those regions surrounding the crystallites. The chain segments freed by the coordinate-bond cleavage spring apart and thereby render fresh localities 'accessible' or available to the action of the reagent.

In a calculation of the theoretical maximum accessibility of various cellulose modifications (p. 68) it is assumed that a fraction of the hydroxyl groups within the hydrate lattice may be classified as 'accessible'.

b. It is not possible to define 'reactivity' with any degree of exactitude, since a reactivity test must be specific for the reagents and conditions used. In general, that portion of a cellulose which behaves satisfactorily in a given technical operation such as xanthation or acetylation is termed 'reactive'. That portion which fails to dissolve, or which yields imperfect solutions, is termed 'unreactive'.

the inverse relationship between accessibility and per cent crystallinity may be a fairly precise one, but the amount of accessible cellulose probably never coincides with the amount of amorphous cellulose, and a fiber may be treated in a manner which will effect no observed change in the crystalline-amorphous ratio, but which will result in a maximum range of accessibility values. There are two reasons for this lack of correlation: the activity of the crystallite surfaces and the dependence of reactivity and accessibility upon the state of the amorphous fraction as well as upon its amount. In other words, the correlation may depend upon the degree and kind of molecular order within the amorphous regions. The chain-length distribution of the cellulose macromolecules and their spacial configurations, as well as the nature and intensity of the bonding forces between them, are functions of a large number of variables, all of which may not be known, and many of which are not clearly understood. The chemical and physical properties of a given cellulose may be altered by:

a. The chemicals and conditions used in extraction and purification.
b. Treatment with swelling agents, the most important of which are water and alkali solutions.
c. Mechanical treatment such as would take place in a ball-mill or under the action of ultrasonic waves.

d. The action of atmospheric oxygen, with or without the presence of moisture.

e. Thermal treatment of a cellulose, with or without the presence of oxygen and moisture.

f. The method of drying, whether by different schedules at atmospheric pressure, under vacuum, or through solvent exchange.

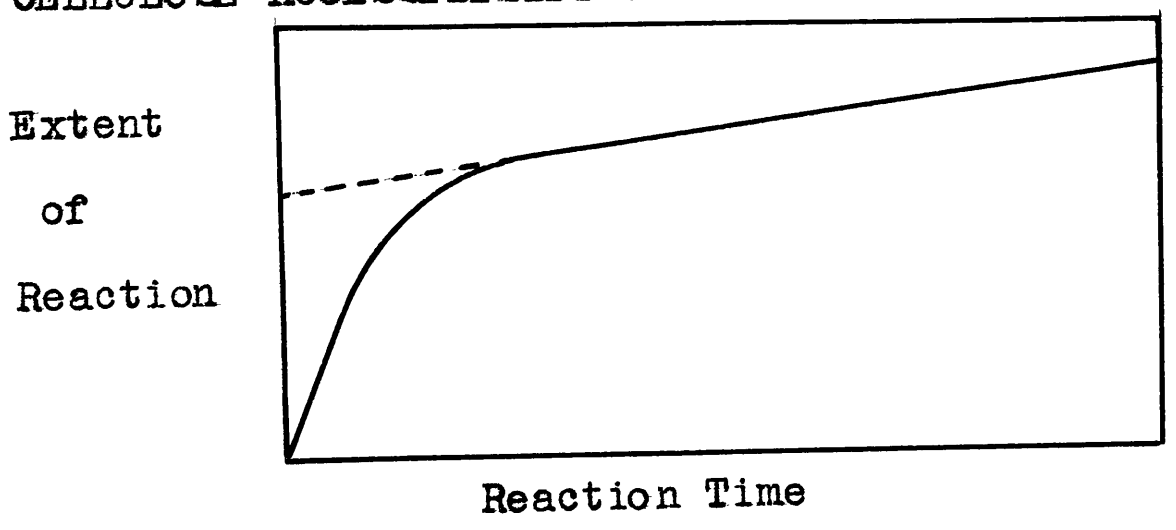
g. Beating.

Measurements of accessibility and reactivity will vary as a result of the changes induced by processing, and also according to the type and amount of impurities present in the starting material in the form of admixed contaminants or of chemically bound, morphological components. Finally, the chemical and physical characteristics of cellulose may vary markedly between different types, within the same type from different sources, and, upon occasion, between samples from the same source and with presumably identical histories. In a recent contribution Staudinger and co-workers (43) have discussed in detail differences in the physical and chemical properties of native and regenerated cellulose, and have demonstrated most conclusively the complex nature of native fiber microstructure. They conclude that 'cellulose' is merely a collective term referring to a variety of polymers constructed from glucose monomers linked together by -glucosidic bonds, and they suggest that each type of plant may build up its own characteristic cellulose.

The development of the many accessibility and suitability tests which have been devised in recent years has been necessitated primarily by the fact that analytical data derived from tests ordinarily employed to characterize cellulose (alpha-cellulose, copper number, viscosity, etc.) have frequently proven inadequate to predict the behaviour of a given cellulose in a given technical process or of derivatives obtained from it (44 to 50). Many of the methods depend upon the interpretation of reaction-rate plots obtained by the treatment of cellulose with a large excess of reagent. An ideal reaction-rate curve of this type is shown in Figure IV.

FIGURE IV

IDEAL REACTION-RATE CURVE IN THE MEASUREMENT OF CELLULOSE ACCESSIBILITY OR REACTIVITY[a]



a. The ordinate in Figure IV might be expressed in terms of:
   1. The fraction of hydroxyl groups involved in deuterium exchange (p. 51).
   2. The per cent water adsorbed by a dry cellulose (p. 64)
   3. The quantity of carbon dioxide given off upon treatment with hydrochloric acid - ferric chloride reagent (p. 55)
   4. The inverse of degree of polymerization upon hydrochlori acid - ferric chloride oxidation-hydrolysis.
   5. The moles of chromium trioxide consumed upon immersion of the cellulose in an acetic anhydride - acetic acid - chromium trioxide mixture (p. 39).

The initial rapid reaction is attributed to the accessible or highly reactive component of the material being studied, and the later, more nearly linear portion of the rate plot is credited to the inaccessible or unreactive component. Extrapolation of the linear section to zero reaction time gives a value which is interpreted as representing a measure of accessibility.

In the following discussion, those studies of accessibility are included which are considered an aid in explaining the results obtained in the experimental investigation of nitration.

c. The Accessibility of Cellulose Toward Water:

The most important reagent in the field of cellulose chemistry is water, not only because water plays an intimate rôle in all plant growth, but also because it is a powerful swelling agent for cellulose and because most industrial processing of cellulose is carried out in the presence of water. This statement is particularly true of the conversion of cellulosic materials to paper, where pulping, grinding, purifying, bleaching, beating, sheet formation and drying are carried out in or from water dispersions of the fiber.

c-1. Measurement of the Water-binding Power of Pulps:

Recently Jayme and a number of co-workers have conducted a series of investigation relating to the

water-binding power of cellulose, and have developed two physical methods for its measurement. Jayme, together with Froundjian (51) and Heininger (44) immersed cellulose in anhydrous dioxane and allowed the mixture to stand until equilibrium has been established between the sample, its water content and the dioxane. The dielectric constant of water is 80, that of dioxane is 2, and that of a 1 per cent solution of water in dioxane is 12; a measure of the dielectric constant therefore permitted a rapid and accurate measurement of the amount of water incapable of removal from the cellulose by the dioxane. Because of mechanical difficulties inherent in this method, and because the dioxane had a deswelling action upon the immersed cellulose, it was replaced by a centrifuging method (44). The material under examination was centrifuged under standard conditions, weighed, dried and reweighed and the swellability, water-retention value, or Q-value[a] was calculated from the relationship:

$$Q = \frac{(\text{Wt. of Centrifuged Material} - \text{Bone-dry Sample Wt.})(100)}{(\text{Bone-dry Sample Wt.})} \qquad \text{.....(I)}$$

During the centrifuging an equilibrium was

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a. Because of its bearing on subsequent discussion, it should be emphasized that the Q-value is actually the weight of water associated with 100 grams of bone-dry cellulose, or in other words, the per cent moisture in the sample.

established between centrifugal force drawing water out of the fiber and a number of forces (primary, secondary hydrogen bonds, residual valence forces, capillary attraction forces) holding water within the fiber. The method was used to study the relationship between water-binding capacity (hereafter referred to as Q-value) and a number of technically important processing variables.

c-2. Q-value and Time of Immersion of a Dried Pulp in Water:

An unbleached sulfite pulp which had been dried (conditions of drying not given) was immersed in water for a number of days and the Q-value determined. The results shown in Table IV indicate that the resistance of a dried pulp to

TABLE IV

THE RELATIONSHIP BETWEEN Q-VALUE AND TIME OF IMMERSION IN WATER OF A DRIED PULP[a]

Time of Swelling	Q-value (%)
2 hrs, 10 min.	128
4 days	146
6 "	153
11 "	155
14 "	162
18 "	167
22 "	169
25 "	169

the penetration of water was first rapidly and then slowly overcome upon immersion in water. The immersion had the effect of rendering the structure more porous and swollen, as more and more alcohol - to - alcohol hydrogen bonds in the sample were broken, and more coordinatively-bonded water

a. Jayme, G. (44).

and capillary-held water was retained within the cellulose fiber against the opposing centrifugal force.

c-3. Q-value and Conditions of Drying:

In another experiment, an unbleached sulfite pulp was dried under various conditions, immersed in water for periods of 10 minutes and 60 minutes, and the Q-values determined.

TABLE V

INFLUENCE OF DRYING ON THE Q-VALUE OF AN UNBLEACHED SULFITE PULP[a]

Conditions of Drying	Cellulose [b]	Swelling for 10 Minutes		Swelling for 60 Minutes	
		Q-value	I.V.[c]	Q-value	I.V.[c]
	%		%		%		%
Never Dried	30.2	159	....	159	....
Air-dried	91.6	107	32.6	113	29.3
At 70°, 6 hrs.	98.6	99	37.9	104	34.9

The fact that the Q-value decreased with increasing intensity of drying could be attributed to the smaller amount of water in the cellulose after drying. It is doubtful if the question of hydrogen bonding is of importance in this case, since at the highest temperature of drying (70°) hydrogen bonds would probably be unaffected. It is reasonable that the higher the moisture content of the starting material

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a. Jayme, G. (44)
b. Bone-dry content of moist cellulose.
c. Irreversible vitrification (or 'hornification' as the term is used by Jayme), defined as the per cent decrease in Q-value, is essentially a loss in water-bonding power. As demonstrated clearly in Table IV, it is not irreversible.

(and hence the more extended the capillary system) the more rapidly would water penetrate the fiber. This assumption is substantiated by the results obtained by the dioxane method as shown in Table VI. In this case irreversible vitrification increased with increasing temperature of drying up to 80°, but increased very little more up to 101°. No data are available, but by analogy with results obtained in acetylation and nitration studies, more intense prolonged heating might decrease the vitrification.

TABLE VI

MEASUREMENT OF IRREVERSIBLE VITRIFICATION RESULTING FROM THE DRYING OF PULPS[a]

Conditions of Drying	% Moisture After Drying	Time in Water Prior to Testing	Q-value %	I. V.[b] %
Air-dry, 1 month	10 ca	1 week	17.5	0
Air-dry, 20°	10.0	2 hours	14.8	15.4
	10.0	5 hours	14.8	15.4
80°, 24 hours	0.8	18 minutes	13.0	25.7
	0.8	153 "	13.0	25.7
101°, 2 1/2 hours	0.2	18 minutes	12.7	27.4
	0.2	125 "	12.9	26.2

Jayme offers the following explanation for the phenomena of irreversible 'hornification' or 'vitrification'. In a pulp the crystalline regions are considered to be surrounded by thin layers of hemicellulose, cross-linked to the cellulose. This portion of the fiber is connected to

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a. Jayme, G. (46)

b. Irreversible vitrification: per cent decrease in Q-value.

the fiber capillary system by means of sub-capillary pores. When the fiber is dried, forces of cohesion and adhesion result in the formation of a polysaccharide layer which leads to an increase in crystallinity, a contraction of the porous regions, a partial disappearance of the capillary system, and a contraction of the bulk fiber. As water is removed from the fiber interior, adjacent cellulose chains become bonded. Some of the new linkages cannot be broken upon re-immersion of the fiber in water, and in these areas the cell wall becomes strongly cross-bonded, or 'irreversibly vitrified'. As a result, less water is able to enter the fiber structure.

c-4. Q-value and Degree of Beating:

The Q-values of an unbleached sulfite pulp increased markedly by beating for various times (Table VII). In the case of a pure cellulose, in which results would be uncomplicated by the presence of non-cellulosic components with different degrees of hygroscopicity, the Q-value should be dependent primarily upon the number and size of capillaries, and secondarily upon the amount of chemically bound water.

Because the amount of chemically bound water is small and the amount of capillary-held water is high, the second value probably masks the first in the Q-value measurement.

TABLE VII

CHANGE IN THE Q-VALUE OF AN UNBLEACHED SULFITE PULP DURING BEATING[a]

Beating Time (min)	Q-value (%)
0	187
10	223
15	238
22	255
32	269
40	287

c-5. Changes in Fine Structure and Original Q-value:

A series of samples were prepared by bleaching an unbleached sulfite pulp with sodium chlorite. The Q-values (Table VIII, Column I) were measured on the moist products,

TABLE VIII

CHANGE IN THE SWELLING VALUE BY DRYING IN RELATION TO THE ORIGINAL SWELLING VALUE[b,c]

Initial	Air - drying[d]			Drying at 70°[e]		
Q-value[c]	Dry Wt.	Q-value	I. V.[f]	Dry Wt.	Q-value	I.V.[f]
%	%	%	%	%	%	%
I	II	III	IV	V	VI	VIII
152	90.4	127	16	98.3	108	29
156	90.6	129	17	97.2	111	29
158	88.6	129	19	97.6	114	28
163	88.9	132	19	97.4	116	29
174	88.9	135	22	98.2	117	33
186	90.4	134	28	97.2	118	37
187	90.1	134	28	97.3	117	37

a. Jayme, G. (44)
b. Jayme, G. (45)
c. After the bleaching, samples kept moist at 20° and Q-value measured on the following day.
d. Dried in air to asymptotic drying equilibrium, then immersed in water for 2 hours, 20° and Q-value measured.
e. Dried for 6 hours at 70°, immersed in water at 20° for 2 hours and the Q-value measured.
f. Irreversible Vitrification: per cent decrease in Q-value.

Column II gives the per centages of air-dried cellulose the samples contained and Column III the Q-values for the air-dry products. Column IV gives the per centage decrease caused by the drying, and corresponds, according to Jayme, to the amount of 'irreversible vitrification'. Columns V, VI and VII summarize the more drastic changes caused by drying at 70°. The results substantiate what appears to be a principle of wide applicability, namely, that the more reactive a cellulose when immersed in water, the more unreactive it is likely to become when dried directly from water. As will be illustrated later in some detail, the principle extends to acetyl contents upon acetylation or nitrogen contents upon nitration.

c-6. Q-value and Time of Immersion in Boiling Water:

An unbleached sulfite pulp which had never been dried was boiled in water for various periods, cooled, left standing in water for various times and the Q-values determined.

TABLE IX

CHANGE IN THE Q-VALUE OF AN UNBLEACHED, UNBEATEN SULFITE PULP UPON TREATMENT WITH BOILING WATER [a]

Time of Boiling in Minutes	Sample Cooled to 20° and Q-value Determined in:		
	1 min.	1 hour	24 hours
	%	%	%
Untreated	187	...	...
5	171	...	174
30	168	171	172
60	166	167	170

The boiling treatment resulted in a drop in Q-values (Table IX). The longer the heat treatment the greater the

a. Jayme, G. (45).

drop in Q-value, and the longer the immersion time after boiling the greater the recovery of the Q-value. One obvious explanation of these results would be the assumption that the thermal agitation during the boiling period brings about a slight rearrangement of cellulose chains, resulting in the formation of finer capillaries, hence a lower Q-value. The so-called 'irreversible vitrification' was found to be slightly variable with time[a], as it was in the case of dried

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a. A comparison of the losses in 'irreversible vitrification' in Tables IV and IX would suggest that those in Table IX would be fully or almost fully recovered upon immersion of the sample in cold water for a sufficient length of time.

From Table IV:

Original Q-value	169
After Drying	128
Loss in Q-value	41
Q-value after 4 days immersion in water	146
After 2 hours immersion in water	128
Recovery in 4 days	18
Recovery in 1 day, 18/4	5 ca

Thus per cent Q-value recovery in 1 day, (5)(100)/(41) 12%

From Table IX, for a 60-minute boiling period:

Original Q-value	187
After boiling for 60 minutes	166
Loss in Q-value	21
Q-value after 24 hours immersion in cold water	170
Immediately after boiling treatment	166
Recovery in 24 hours	4

Thus per cent Q-value recovery in 1 day, (4)(100)/(21) 19%

The two values, 12% and 19%, are of the same order of magnitude, and the higher value in the second case would be even more favorable to full recovery upon immersion in water for a sufficient length of time. The recovery, of course, may fall off asymptotically, so that the original Q-value is never regained.

pulps.

c-7. Q-values of Regenerated Cellulose:

The centrifuge method has been used by Hubert, Matthes and Weisbrod (52) to study a number of variables involved in the preparation of viscose fiber. A freshly regenerated fiber, in spite of its high wet strength, must have an exceedingly porous structure, probably consisting of an interconnecting network of interstices capable of retaining large quantities of water against centrifugal force[a].

In one series of experiments, rayons with original Q-values ranging from 84 to 117 were moistened with distilled water and then dried at various rates of drying, and the procedure was repeated 13 times. The Q-values obtained by each successive drying are plotted against the number of drying procedures in Figure V. Each successive drying resulted in a Q-value decreasing asymtotically to a limit value, dependent upon the drying conditions. The higher the relative humidity of drying (ie, the slower the drying) the lower this limiting Q-value. These results may be

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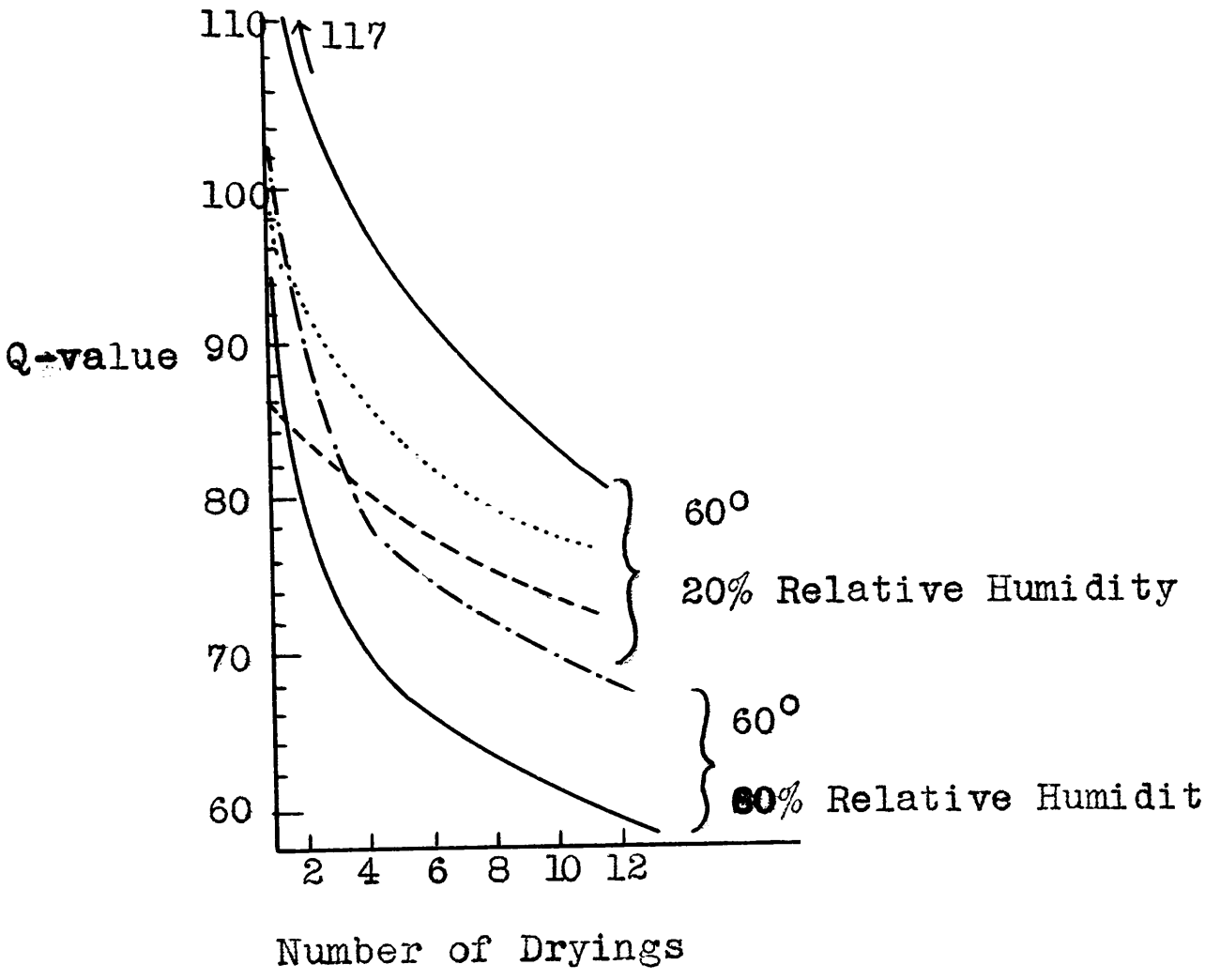
a. A normal commercial rayon was found to have a Q-value of 150, corresponding to 30 volume per cent of cellulose, and a freshly regenerated cuprammonium fiber contained only 20 to 25 volume per cent cellulose. Q-values as high as 340 were found for freshly regenerated viscose, compared with values ranging up to 200 for an unbeaten, up to 290 for a beaten, sulfite pulp (Table VII).

FIGURE V

Q-VALUES OF 5 DIFFERENT FIBERS UPON REPEATED DRYING[a]



explained as representing a typical retarded syneresis[b] phenomenon. A certain amount of water within the fiber structure is required for syneresis, and during drying this water is removed faster than the syneresis can procede, and

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a. Hupert, E., Matthes, A., and Weisbrod, K. (52).

b. Syneresis: the constriction or contraction or shrinkage of a gel structure during drying.

the slower the water removal, the more time the macromolecules will have to rearrange into a more stable configuration. A given fiber gel structure will attain to an increased degree of dry rigidity each time it is dried and re-moistened.

c-8. Q-value and Effect of 'Steaming'[a]:

A characteristic property of high polymers which have been regenerated from solution (or which by some other

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a. In his determination of the densities of various cellulose modifications by the hydrostatic method, Hermans (21) found that the values were surprisingly dependent upon the prehistory of the sample. When air-dried rayon fibers were submerged in air-free water, the density increased from 1.6003 to 1.6180 in 16 hours. When the same fibers were exposed to a current of air-free water-vapor at 45 to 50° at reduced pressure the density rose to 1.6167, and upon immersion of the 'steamed' fibers in water, the density further increased to 1.6187 in 16 hours. Alternate boiling of the fibers and allowing them to stand in cold water for 16 hours gave the results shown in Table X.

TABLE X

EFFECT OF STEAMING UPON THE DENSITY OF A RAYON FIBER[b]

Treatment of the Fiber	Density in Water
	1.6105
Boiling and Cooling.	1.6137
Standing in air-free water for 16 hours	1.6116
Reboiling and Cooling.	1.6139
Standing for 16 hours.	

The density increase upon steaming the fibers is a further indication of a progressive syneresis effect operative within the gel structure. Thermal agitation in the presence of water leads to a closer packing of the chains (hence a higher density) and a decrease in water-binding power (ie, a lower Q-value).

b. Hermans, P. H. (21)

mechanism have passed through a high degree of swelling) and can absorb water from air, is the reduction in their capacity to swell and to absorb dyes that is caused by steaming, ie, the process of subjecting a predried gel to a moist, swelling atmosphere, say at 80° and 90 per cent relative humidity.

TABLE XI

Q-VALUE IN RELATION TO RELATIVE HUMIDITY AND TIME OF DRYING[a]

Time to Attain Q-value.	Relative Humidity %	Q-value %
Several days.	75 to 90	70
24 hours.	80°, satd. steam	60 to 65
1 to 2 hours.	100°	50 to 55

The Q-values of 50-55 (Table XI) were the lowest found, and were termed the limit swelling value; all other Q-values were regarded as arbitrary values representing unstable states in a continuous but restricted syneresis. The restriction might be caused by a dry-state rigidity, and if this rigidity was eliminated by the present of a large amount of water absorbed on the cellulose chains, and the process was accelerated by high temperatures, then the final limiting Q-value would be attained rapidly by the syneresis effect. It was indeed found that the limiting Q-value, which could be approached asymptotically by alternate wetting and drying, could be reached in a single stage by soaking a dry fiber in liquid ammonia and allowing the liquid ammonia to evaporate.

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a. Hubert, E., Matthes, A., and Weisbrod, K. (52).

c-9. Q-value and Pressure:

In one experiment, freshly coagulated, undried viscose fibers were subjected to varying pressures in a hydraulic press. The results obtained are shown in Table XII and Figure VI.

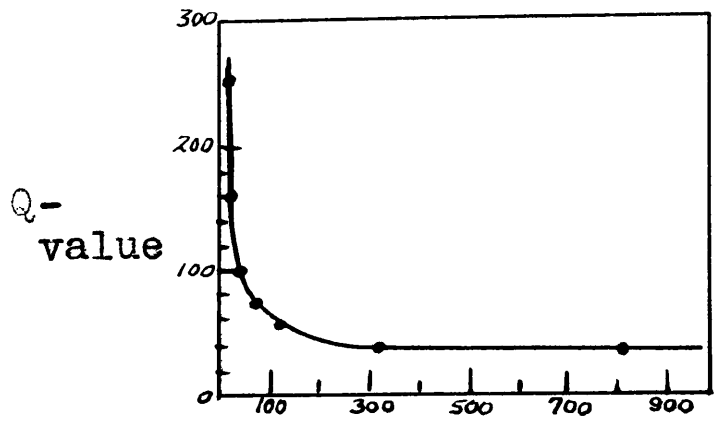
TABLE XII

RELATIONSHIP BETWEEN PRESSURE AND WATER CONTENT OF A VISCOSE FIBER[a]

Pressure in Kg/cm^2.	Q-value %
6.3	252
12.5	164
31.3	96
62.5	71
125	52
313	38

FIGURE VI

PRESSURE - SWELLING CURVE FOR HYDRATE CELLULOSE[a]



The swelling pressure was related mathematically to the amount of water held by the relationship:

$$-\log(Q - 20) = A + B.\log P \quad \ldots\ldots\ldots \quad (II)$$

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a. Matthes, A. (53)

where Q was the swelling value in per cent, P was the pressure in Kg/cm^2, and A and B were constants.

The value 20 in Equation II represents the amount of water that could not be removed at any pressure, and this value probably represents the upper limit of chemically bound water for a regenerated cellulose. The large contribution of the non-adsorbed water (ie, capillary water) to the total Q-value indicates that variation in swelling values between various hydrate cellulose fibers is due primarilly to differences in pore volume.

Matthes (53) considers that water within the cellulose structure is made up of 'free' (wandering or dissolving) water at liberty to move freely within the gel phase, and 'bound' non-dissolving or adsorption water. From an extrapolation of Urquhart's data (54) for the isotherm of a cellulose hydrate from 95 per cent relative humidity to 100 per cent relative humidity, Matthes has calculated the adsorption and the desorption saturation points to be 35.3 and 39.6 per cent, respectively. Thus the hysteresis curve is not considered to be closed. The swelling value, which can be reduced to approximately 50 (p. 33) and the desorption saturation value are considered to differ because the former is too high, primarily because syneresis is not complete, and the gel has not reached final equilibrium conditions.

The three saturation points are thus represented to be experimentaly valid, and may be interpreted as follows:

1. The true saturation is represented by the desorption point, which represents true equilibrium conditions and which is the most difficult to determine. The desorption plot represents the most accurate picture of conditions within the cellulose hydrate fiber.
2. The adsorption saturation points represents a value less than the true saturation point.
3. The swelling value represents a value higher than the true saturation point.

Upon formation of a regenerated cellulose, the macromolecules become bonded together at an increasingly large number of junction points along their length. As the fiber is dried, the process of network shrinkage and chain-bonding continues as long as the chain remains mobile. Below a moisture content of ca 25 per cent, this process becomes increasingly inhibited, and further removal of water leaves interstices between macromolecules across which the inter-macromolecular forces become operative. Thermal agitation in the presence of water as a result of steaming or boiling causes the formation of an increased number of permanent points of cohesion, and an increasing number of areas become inaccessible to water penetration. As a result, sorptive power and density decrease, and increase, respectively.

Matthes concludes that the number of bonding centers differs in the wet and dry hydrate fiber, and agrees with Hermans (21) that during the drying the hydroxyl groups of the cellulose form contact points which are not immediately

broken during sorption. It is further assumed that such contact points will be weakened only when the capillaries are partially or completely filled: then only will the Q-value correspond to the increase in gel volume.

c-10. The Hydrates of Cellulose:

Much of Hermans' interpretation of cellulose phenomena and its dependency upon prehistory is based upon the postulated existence of at least two distinctive hydrates (21). That Hydrate Cellulose undergoes intramicellar swelling in the presence of water was demonstrated by an X-ray measurement on mercerized ramie fiber, as may be seen from the results shown in Table XIII. On the basis of this and other evidence

TABLE XIII

SHIFT OF THE DISTANCE BETWEEN THE 101 PLANES[a] IN CELLULOSE II IN RELATION TO MOISTURE CONTENT IN MERCERIZED CELLULOSE[b]

Relative Humidity of Air. %	Moisture Content. %	Distance Between 101 Planes (A units)
0	0	7.32
7.5	2.8	7.46
35	6.6	7.52
65	11.4	7.73
85	17.0	7.73

Hermans concludes that when a bone-dry Hydrate Cellulose is moistened, it forms a hydrate with the probable composition $C_6H_{10}O_5$ 1/3 H_2O, containing 3.7 per cent of water. This

a. Later X-ray diffraction measurements on mercerized cellulose by Legrande (55) gave smaller changes than those noted above.

b. Hermans, P. H. (21)

hydrate has been designated as 'Cellulose Hydrate I'. A second hydrate, with a probable composition of $C_6H_{10}O_5$ 1 1/3 H_2O and containing 14.8% water and designated as 'Cellulose Hydrate II', is formed when Hydrate Cellulose, (alkali cellulose or regenerated cellulose, designated as Cellulose II) is converted to Water Cellulose at a low temperature.

The crystallite lattices in both the Hydrate I and the Hydrate II modifications differ from that of Cellulose II only in the distance separating the 101 planes between the hydrophylic or hydroxyl-containing faces. Hydrate II is a metastable form, readily transformed into the stable Hydrate I modification, rapidly in hot water or over a period of several days at room temperature. In contradistinction to Hydrate Cellulose, the native modification shows no lattice change in the presence of water, and the native cellulose crystallite is assumed to be inpervious to water. Upon immersion of a bone-dry Hydrate Cellulose in water, the free energy of hydration is sufficient to expand the lattice to the Hydrate I form, but insufficient to overcome intramolecular bonding to the extent necessary for the formation of Hydrate II. If the cell lattice is widened by treatment with alkali of mercerization strength, the cohesive forces between adjacent chains within the crystallite lattice become so weakened that it is less than the free energy of hydration of Hydrate II, which accordingly forms.

The movement of macromolecules as a result of even slight thermal agitation, however, causes the adhesive forces to become operative wherever adjacent chains approach within a given distance of each other; water molecules are squeezed out of the lattice[a] and Hydrate I forms. Cellulose chains within the amorphous component or on the crystallite surfaces will, however, continue to exist as Hydrate II as well as Hydrate I. The initial moisture regain by a bone-dry cellulose will lead to Hydrate I, first within the amorphous regions, where no energy will be required in expanding the crystallite lattice. A considerable amount of Hydrate II must be also formed in the amorphous regions (See Table XIII) before the formation of Hydrate I is complete in the crystalline regions, since more than 11 per cent of water is adsorbed before expansion to the Hydrate II lattice is complete, and 3.7 per cent water would represent formation of Hydrate I throughout the mass of the cellulose. Parallel determinations of the sorption ratios of native and mercerized linters at desorption showed that

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a. The effect of these allotropic modifications upon the accessibility of cellulose was strikingly illustrated by Jorgenson (56) in an application of the chromium trioxide - acetic anhydride - acetic acid method. A standard sample of extracted cotton linters was mercerized in 11 per cent sodium hydroxide solution at 0°, exhaustively washed with water at 0°, and its chromium trioxide accessibility determined. A part of this material was boiled in water for one-half hour and similarly tested. The first sample gave an accessibility value of 1.70 (the highest value recorded for any cellulose), and the second an accessibility of 1.28.

the ratio increased at low regains. The fact that the sorption ratio increased slowly suggested that the water involved in Hydrate I formation was less strongly bonded in the crystallites than in the amorphous regions. If the bonding were the same in magnitude in both regions, the adsorption ratio should be higher at very low regains. The probable distribution of hydrate water in regenerated and in native fiber is shown in Table XIV.

TABLE XIV

THE DISTRIBUTION OF WATER IN NATIVE AND REGENERATED CELLULOSE[a]

Native Fiber (amorphous fraction, 0.4)

Bound as Hydrate I in amorphous part:	(0.4)(3.7)	1.5%
Bound as Hydrate II in amorphous part:	(0.4)(11.1)	4.4%
	Total	5.9%

Regenerated Fiber (amorphous fraction, 0.75)

Bound as Hydrate I in the whole fiber:		3.7%
Bound as Hydrate II in amorphous part:	(0.75)(11.1)	8.4%
	Total	12.1%

c-11. The Sorption Isotherm in Terms of Hydrate Formation:

Hermans explains the shape of the cellulose sorption isotherm in terms of hydrate formation, as discussed above, and capillary condensation. The addition of water in excess of that involved in hydrate formation leads to swelling, caused by the dissolution of 'anchored' macromolecules. Between 6% and 12% regain for a native cellulose, and between 12 and 24% for regenerated cellulose, water is considered to be adsorbed in a monomolecular layer,

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a. Hermans, P. H. (21).

and further water retention is a consequence of capillary condensation. The three factors involved: formation of Hydrates I and II, the formation of monomolecular layers, and capillary condensation, do not procede as separate, sharply differentiated processes. Successive mechanisms overlap, and the effect of each is spread over a wide range of regains. An interpretation of the cellulose - water sorption isotherm cannot be based exclusively upon the crystalline-amorphous ratio, because, as already explained, there is no precise distinction between the two.

The fact that the heat of adsorption calculated for 1 mole of water adsorbed by a large body of cellulose is approximately the same as the heat liberated in the formation of the monohydrate of b-glucose, or in the mixing of ethyl alcohol and water, was advanced by Lauer (57) as substantiation of the theory that cellulose and water form a definite hydrate. Lauer (58) has further suggested that only this non-solublizing (or nicht lösendes) water of true sorption involves a change in internal energy, and that the water molecules are bound to the hydroxyl groups in the amorphous regions only.

c-12. The Sorption Isotherm in Terms of Hydrogen Bonding:

Purves and co-workers (59) employed the thallous ethylate method to calculate the accessibility of dry, highly swollen, mercerized linters (p. 61), and gave reasons to justify their belief that the result showed

24.4 per cent of all the hydroxyl groups to be accessible in water. The initial rapid rise (up to 2 - 3 per cent regain) was attributed to strong hydrogen bonding between water molecules and the hydroxyl groups accessible to water in the amorphous regions. The intermediate, essentially linear portion of the curve from 2 - 3 to 8 - 9 per cent regain (for native cotton) was attributed to the formation of multimolecular layers of water or capillary condensation within the fine capillary system. The steep, final portion of the curve was considered to be due to condensation within the coarser capillaries.

Since three hydroxyl groups per glucose unit were available for hydrogen bonding to water, 100% accessibility would be equivalent to 33.3% water[a], and thus the 24.4% accessibility would be equivalent to 24.4÷3 or 8.1% water. This value corresponded to the second inflection point (Point D, Figure VII) on the adsorption isotherm, and not to the first (Point B). If it is assumed that primary hydroxyl groups bond water more readily and more strongly than do the secondary hydroxyl groups, then the initial regain must be attributed to primary hydrogen bonding. The first inflection point, at 2.4% regain, actually does correspond closely to the calculated amount of water bonded to primary hydroxyl groups, ie, 8.1/3 or 2.7 per cent. The intermediate portions of the isotherm may be attributed to

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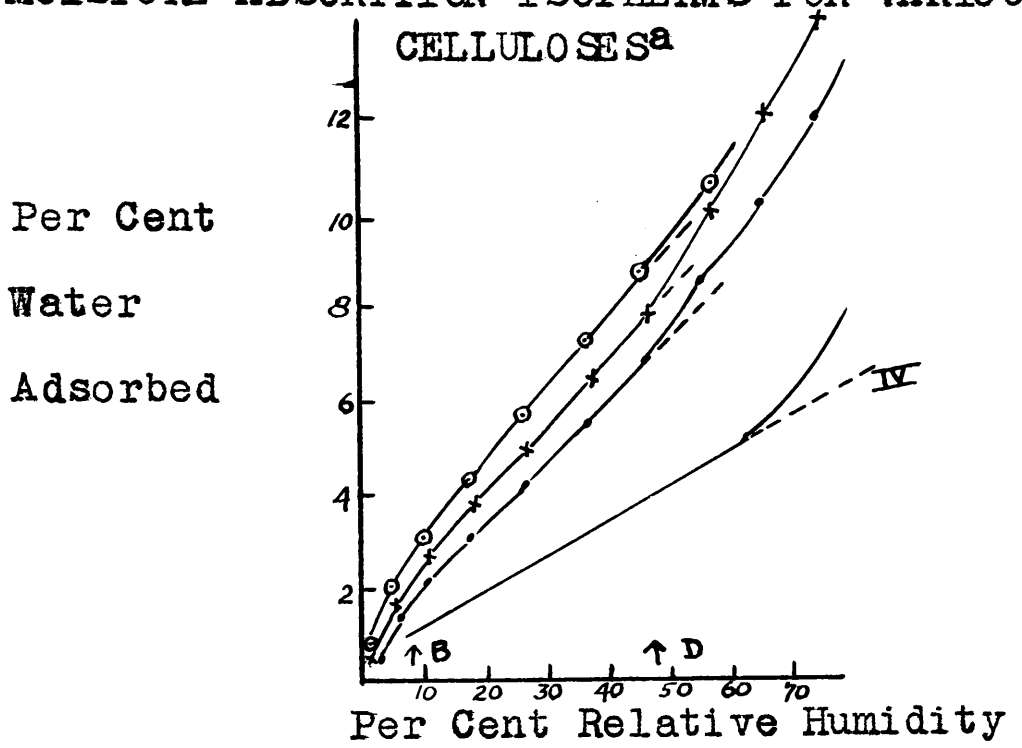
a. The per cent of water in $C_6H_{10}O_5 \ 3H_2O$ is (3)(18)÷(162) or 33.3 per cent.

FIGURE VII

MOISTURE ADSORPTION ISOTHERMS FOR VARIOUS CELLULOSES[a]



Cellulose I at 25°. . . . .
Cellulose II at 20°. o o o o
Cellulose II at 25°. x x x x
Plot IV is Urquhart and Williams' data for unswollen cotton at 80°.

bonding between water molecules and secondary hydroxyl groups, and the regain at the inflection points should be in the exact ratio of 3 to 1: the values determined experimentally lie close to this ratio.

Because cellulose may be brought to a bone-dry state by heating to 100°, the primary hydroxyl-water bond must be broken under these conditions. From the fact that the boiling point of a secondary aliphatic alcohol is approximately 20° lower than the boiling point of its

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a. Assaf, A. G., Haas, R. H. and Purves, C. B. (59)

primary isomer[a], it may be assumed that the water-secondary hydroxyl group bonding in cellulose will be broken at 80° approximately, and a cellulose-water adsorption isotherm at 80° should be a function of the primary alcohol groups only. One such isotherm, obtained by Urquhart and Williams (Plot 4, Figure VII) is essentially linear up to the point of distortion by swelling and capillary condensation.

Another indication of the weaker hydrogen bonding ability of secondary alcohol units was found in the pasting of starch at 65 to 85°. Hydrogen bonds between secondary hydroxyl groups break down in this temperature range and are unable to take part in hydrogen bonding. Below this temperature range the secondary hydroxyl groups are in a position to hydrogen bond with each other, with primary hydroxyl groups, or with water, and as a consequence the paste becomes rigid.

d. The Accessibility of Cellulose as Measured by Acetylation:

Extensive and precise acetylation studies, carried out by Staudinger and co-workers (26)(60), were intended originally to determine whether or not heterogeneous acetylation could be considered as a topochemical[b] reaction,

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a. The boiling-point of heptanol-1 is 176°, and that of its isomer heptanol-2 is 159°.

b. When two samples of cellulose with the same average degree of polymerization but with different structural arrangements of the cellulose chains possess different reaction velocities in the same heterogeneous reaction under identical conditions, then such a reaction is termed topochemical, and differences in reactivity or accessibility are attributed solely to differences in macromolecular arrangement.

or whether it would be affected by degree of polymerization. The pretreatments used were quite similar to those employed in the present nitration studies, and it seemed advisable to consider the work in some detail.

The dependency of cellulose reactivity upon supermolecular structure has been long known. For example, a regenerated cellulose with a D. P. of 1000 is soluble in 10% NaOH at 0°, whereas a native fiber cellulose with the same or even a lower D. P. is mercerized but remains essentially insoluble. Cellulose acetate with a D. P. of 500, made from a native cellulose, is almost completely insoluble in a mixture of m-cresol and chloroform, whereas an acetate with a D. P. range from 500 to 2000, made from a regenerated cellulose, dissolves completely in the same solvent mixture. These differences have been explained on a basis of the presence in a native cellulose of transverse bonds of unknown nature which are broken during the solution of the cellulose, and the absence of such bonds in a regenerated cellulose[a] (43).

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a. A number of accessibility studies carried out on various modifications of cellulose, involving the use of the thallous ethylate reagent (p. 61), chromium trioxide (p. 39) and acetylation (p. 44) have shown that a cellulose with a high crystalline content (such as native cotton) is virtually impervious to penetration by an organic liquid when in a collapsed state, and is only partially penetrated in a highly swollen state. A cellulose with a low per cent of crystalline component, such as viscose rayon, is impervious to organic liquids in the collapsed state, but is

Staudinger and co-workers utilized polymer-homologous series of cellulose obtained by subjecting cotton, ramie, hemp

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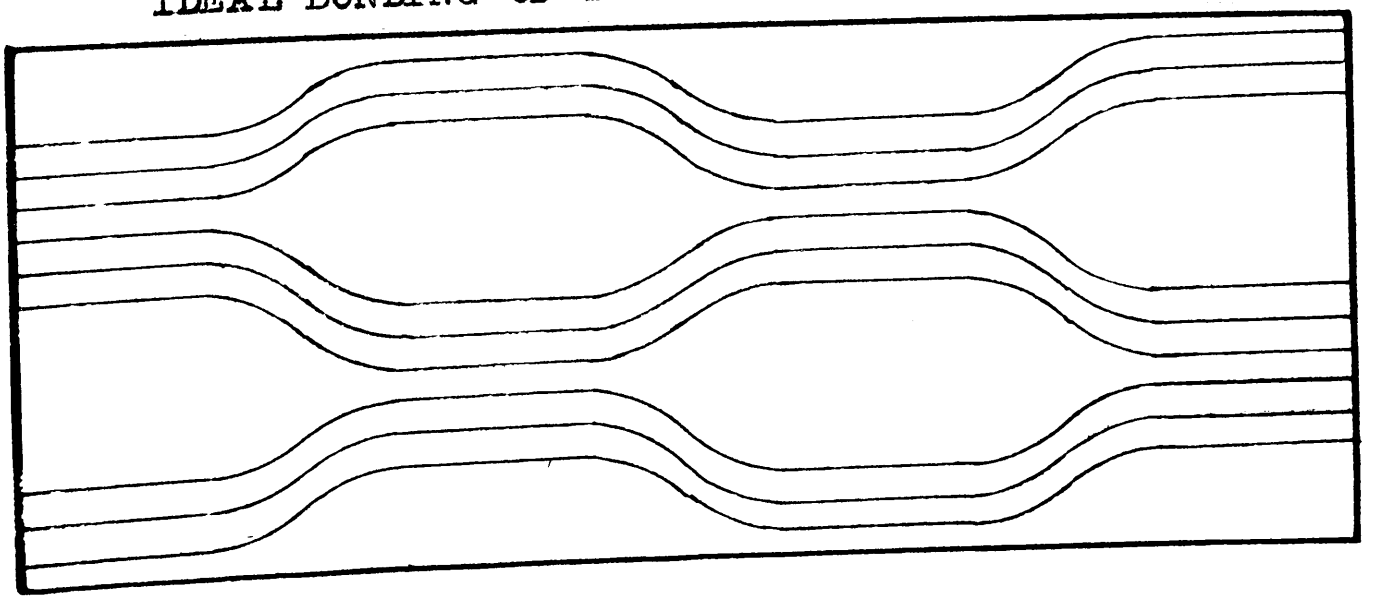
readily penetrated in the swollen state. By extension of these results it might be assumed that a swollen, 100% amorphous cellulose should be quite readily penetrated, whereas a 100% crystalline native cellulose should be almost completely impenetrable to organic solvents or to water in either a swollen or collapsed state, and should show only limited solubility in caustic soda solution over a wide range of D. P.'s.

If it is assumed that the crystallites are more reactive in nitration, and that the amorphous regions are more likely to contain variations in fine structure leading to a decrease in nitration reaction velocity, then a nitrating reagent should penetrate readily a 100% crystalline cellulose and thus result in a high nitration reactivity whether the cellulose was dried from water or through solvent exchange. A cellulose with a low crystalline-amorphous ratio, such as a regenerated cellulose, should possess a high nitration reactivity when dried through solvent exchange, and when dried from water a lower nitration reactivity than any found in the present nitration studies.

The alkali insolubility of a native cellulose, even at a low D. P., might be attributed not to transverse bonding between adjacent chains, but rather to the fact that the whole mass of a cellulose fiber is strongly bonded in a three dimensional network by cellulose macromolecules from one crystallite traversing a number of other crystallites as indicated in Figure VIII.

FIGURE VIII

IDEAL BONDING OF THE CELLULOSE CRYSTALLITES



with acetone-benzene for 8 hours and then for 2 hours with a hot 2 per cent solution of sodium hydroxide in the absence of air. A 25 ml. mixture made up of acetic anhydride (10 parts by volume) and pyridine (15 parts) was employed for the heterogeneous acetylation of 0.1 - 0.2 g. samples of cellulose for 24 hours at 60°. The reagent was selected because it was known to be non-degrading under the conditions used. Cellulose samples ranging in D. P. from 300 to 2500 were mercerized for 24 hours with an excess of a 20 per cent sodium hydroxide solution at 0° with careful exclusion of air, were neutralized, washed and dried. All samples were dried at 100° and 0.1 mm. of mercury except in those cases where drying conditions were being examined as a variable, and all samples were immersed in dry pyridine for 3 hours prior to acetylation. All products were analyzed for acetyl content by the method of Kuhn and Roth (61).

A summary of the quantitative results (Appendix I) forms the basis for the following inferences.

1. The most important factor determining accessibility toward acetylation was the method of drying. The variation between maximum and minimum per cent of hydroxyl groups acetylated ranged from 12-fold for native cotton (51, 52)[a] to 80-fold for viscose cellulose (61, 62).

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a. All number in brackets on pages 47, 48 and 49 refer to the run numbers as given in Appendix I.

2. The second most important factor was the crystalline-amorphous ratio. The maximum per cent of hydroxyl groups acetylated was 15% (39) for native cotton, 29% (56) for alpha-sulfite pulp, and 83% (62) for a regenerated cellulose.

3. A variable closely associated with the crystalline-amorphous ratio and of marked influence on acetylation characteristics was the cellulose modification. Mercerization increased the maximum acetylation from 15% (39) to 57% (54) for cotton, and from 29% (56) to 65% (59) for a sulfite pulp[a]. Mercerization had little effect in the case of a regenerated cellulose, since the regenerated fiber crystallites already possessed the hydrate form.

4. The native celluloses (cotton or wood pulps) differed fundamentally from their mercerized analogues in that the latter were rendered inactive by drying from water (1, 3, 6, 9, 15, 20-23, 28, 31, 35, 48, 58) whereas under precisely the same conditions cotton, ramie or wood pulp in the native form showed little or no reduction in the per cent of hydroxyl groups acetylated (45, 55, 57).

5. Cellulose could be dried from a wide variety of different solvents to yield a highly acetylatable product (11-14, 16-19).

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a. See footnote, p. 54, for a discussion of this phenomenon.

6. A cellulose which was rendered inactive by drying from water (28, 31, 51) could be reactivated by drying through solvent exchange (29, 32, 52), the latter deactivated by redrying from water (30, 33, 53) and these re-collapsed samples again activated by solvent exchange drying (34, 54). No trend toward an increase or decrease in acetylation accessibility upon alternate activating and deactivating was found.

7. The behaviour of a cellulose toward heterogeneous, non-degrading acetylation was a function of the conditions of drying for a given method of drying (24-27, 39, 40). The results obtained were not consistent and could not be correlated with any known variable, but there was some indication that the degree of acetylation rose with increased severity of drying.

8. The type of cellulose, cotton, ramie, etc., had little effect upon behaviour toward the acetylating reagents used, provided that each type was subjected to the same treatment (Tables XV and XVI).

9. Accessibility to the acetylation reagent was independent of the degree of polymerization within the range of 250 to 2500 for flax, hemp, ramie, cotton, sulfite and sulfate pulps and a number of regenerated fibers.

TABLE XV

ACETYLATION OF NATIVE AND MERCERIZED PULPS AFTER VARIOUS PRETREATMENTS[a]
(Acetylation after drying samples for 2 days at room temperature, 0.1 mm.)

Preparation	D. P.	Per Cent of Hydroxyls Acetylated					
		Native Pulps			Mercerized Pulps		
		I	II	III	I	II	III
Fir Sulfate	740	28	32	29	1	69	1
Spruce Sulfite	1710	20	28	22	2	66	2
	1720	20	29	24	2	66	2
Beech Sulfite	720	27	34	25	2	60	2
Acid-alkaline Treated Pulp	270	28	34	34	3	61	2

I. Dried from water.
II. I treated in turn with water, methyl alcohol, ether and cyclohexane, and dried.
III. II dried from water.

TABLE XVI

INFLUENCE OF THE CYCLOHEXANE TREATMENT ON THE ACETYLATION OF REGENERATED CELLULOSE[b]
(Acetylation after drying samples for 2 days at room temperature, 0.1 mm.)

Preparation	D. P.	Per Cent of Hydroxyls Acetylated					
		Native			Mercerized.		
		I	II	III	I	II	III
Lanusa Pulp	510	1	67	1	1	65	0.8
Schwarz Viscose	440	1	61	1	1	63	0.8
Vistra Viscose.	375	1	84	1	1	74	1.0
Cupram. Silk	210	2	84	1	1	74	0.5

I. Dried from water.
II. I treated in turn with water, methyl alcohol, ether and cyclohexane, and dried.
III. II dried from water.

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a. Staudinger, H., Döhle, W., and Heick, O. (60)
b. The same.

It was essential for satisfactory reproducibility of results to protect the solvent exchange dried samples from moisture, and to use moisture-free solvents. All the active celluloses were exceedingly sensitive to moisture and were partially converted to inactive cellulose when exposed for any length of time to atmospheric moisture. If the water was not completely removed from samples dried from water, the maximum decrease in activity was not attained. If water was present in a low-boiling solvent such as ether, then upon drying, the ether was removed first, and in the final stage of drying only water remained in the sample, the cellulose was dried essentially from water, and was thus rendered inactive.

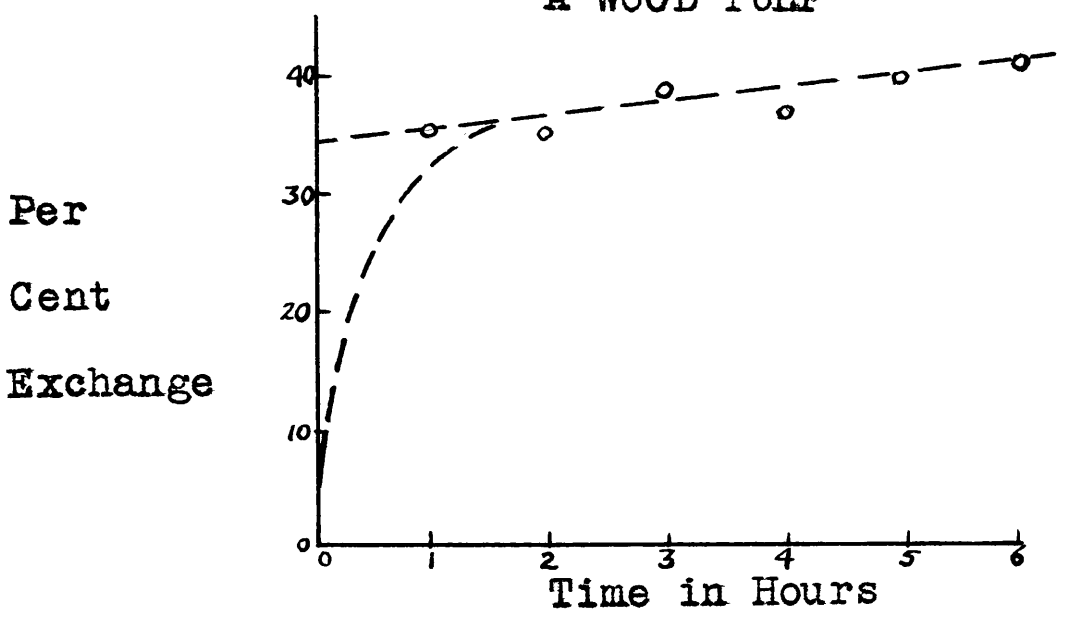
e. <u>The Accessibility of Cellulose as Measured by Deuterium Exchange</u>.

In 1938 Champetier and Viallard (62) observed that deuterium oxide was able to replace up to three hydrogen atoms in each glucose residue of cellulose with deuterium. The rate of this exchange was later used by Badgley, Frilette and Mark (63) to determine the accessibility of the cellulose. A sample of wood pulp was immersed at 25^{o} in a 37 per cent solution of deuterium oxide in water. After a period of 1 hours, 10 ml. of the liquid was removed and its specific gravity was determined accurately; the liquid was replaced and the operation repeated at regular intervals. From the specific gravity of the deuterium oxide - water mixture

the per cent exchange could be calculated. The results are shown in Figure IX. According to the authors, the

FIGURE IX

RATE OF EXCHANGE OF DEUTERIUM FOR HYDROGEN IN A WOOD PULP[a]



exchange rate plot might be interpreted in one of three ways:

1. If the primary hydroxyl groups in the amorphous and crystalline regions reacted at a faster rate than the secondary hydroxyl groups, the initial rapid exchange would be 33 per cent (value actually found, 33 per cent).

2. If the initial rapid exchange took place on the primary and secondary hydroxyl groups in the accessible regions only, then the per cent accessible material would be 33.

3. If all the hydroxyl groups in the amorphous regions and

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a. Badgley, W., Frilette, V. J. and Mark, H. (63).

all the hydroxyl groups on the exposed faces of the crystallites exchanged at the initial rapid rate, the per cent of amorphous cellulose would be less than 33 by some indeterminate fraction.

In a later communication Frilette, Hanle and Mark (64) found that the shape of the exchange-time curves for a number of cellulose modifications was the same as that shown in Figure VIII. Extrapolation of the plots (a) to zero time, (b) to 4 hours and (c) to one week gave 'characterization values', among which the 'b' values, with an average deviation of ± 0.005 were considered to be the most reliable. The per cent crystallinity in the cellulose was calculated from the relationship:

$$a = \frac{100 - F'}{1 - s} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (III)$$

where 'a' was the per cent crystallinity, F' the per cent of all hydroxyl groups exchanged (the 'b' values discussed above) and s the fraction of all the hydroxyl groups in the crystallites available for exchange, assumed to be 0.28 on a basis of a crystallite consisting of an infinitely long, square prism with a base of between 50 to 100A units on edge.

The results obtained on a number of cellulose modifications are presented in Table XVII.

TABIE XVII

ACCESSIBILITY AS ESTIMATED FROM DEUTERIUM OXIDE EXCHANGE FOR A NUMBER OF CELLULOSE MODIFICATIONS[a]

Cellulose Sample		Accessibility (in %) by:	
		D_2O Exchange.	HCl - $FeCl_3$[b]
Cotton		41	..
Cotton Linters		61[c]	5
Wood Pulp:	beech	54	12
	pine	55	10
	hemlock	55	9
	pine	68	8
	pine	74	15
'Cordura' Rayon		86	30
Fiber 'G'		67	15
Textile Rayon		68	27
Special Rayon		81	..

a. Frilette, V. M., Hanle, J., and Mark, H. (64).

b. Values determined by the method of Conrad and Scroggie (71)

c. No satisfactory explanation has been advanced as to why cellulose with a native lattice (cotton linters, ramie or wood pulps) should yield acetylation accessibilities only half as large as those given by the same cellulose when mercerized. It is known that a small amount of material is dissolved during the mercerization process, and it is possible that the material removed is responsible for some unknown type of transverse bonding which renders the whole native structure unreactive. It is likewise possible that the material removed during mercerization is composed of short chains which serve to block off a large fraction of the capillary system in the native fibers. The per cent of such material required to block off some appreciable fraction of the capillaries, say a half, and thus reduce penetration by an acetylation reagent, would not necessarily be high, and the low acetylation values could be thus accounted for by steric hindrance.

The water molecules within the cellulose, even when coordinatively bonded to the cellulose chains, are apparently quite mobile, and pass freely through regions not penetrable by acetic anhydride or pyridine molecules. Because water is a strong swelling agent for cellulose, it might be expected that the deuterium exchange accessibility values for a native cellulose

f. The Accessibility of Cellulose as Measured by Hydrolytic-Oxidation:

The measurement of cellulose accessibility by combined hydrolysis and catalytic-oxidation was developed by Nickerson (65)(66) together with Haberle (20)(67)(68) and adopted with modifications by a number of other workers (69)(70)(71). The method originally involved boiling the samples in a solution 2.45 N in hydrochloric acid and 0.6 M in ferric chloride. This treatment degraded the cellulose rapidly and severely, and therefore failed to provide information on the first stages of degradation. The progress of the reaction was followed by measuring the amount of carbon dioxide evolved at various time intervals; the large number of variables involved necessitated a rigid standardization of conditions.

The initial rapid rate of the hydrolysis-oxidation was accompanied by a rapid decrease in moisture regain and was attributed to the destruction of the amorphous component. After a reaction time of approximately 4 minutes the rate of hydrolysis began to decrease, whereas the moisture regain showed an increase. Reaction from 4 minutes to 1/2 hour was assumed to occur primarily in the mesomorphic or semi-crystalline regions. The remainder of the reaction-rate curve was attributed to attack on the cellulose crystallites.

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would correspond to acetylation values for its mercerized homologue. As may be seen from the data collected in Table XXVII this inference is strengthened by a comparison of the accessibility values obtained experimentally by the two methods.

The fact that the initial rapid removal of the amorphous component, a small fraction of the whole, was accompanied by a marked decrease in viscosity suggested that these regions occurred periodically, and that a large number of the macromolecules present in the original cellulose must extend through a series of amorphous areas. The high degree of hygroscopicity of the amorphous regions was considered to be due to the large number of free hydroxyl groups they presumably contained. In the latter stages of hydrolysis-oxidation, decomposition of the cellulose continued smoothly, moisture regain rose, and chain-length remained substantially constant. During this period the action of the reagent was restricted principally to the lateral surfaces of the intact crystallites. The increase in moisture regain might be accounted for on a basis of increased specific surface. The fact that the presumed attack on the mesomorphic regions was not accompanied by any marked change in viscosity or regain, as contrasted with the regain and viscosity changes during attack of the true amorphous regions, suggested that the semi-crystalline regions had a closer resemblance to the crystallites than to the disordered regions.

Unmodified linters cellulose and purified wood pulp exhibited similar behaviour during the first half hour of hydrolysis with sulfuric acid alone, and mercerization greatly increased the susceptibility of cotton to attack. The absence of breaks in any of the sulfuric acid hydrolysis

curves was interpreted as evidence that the cellulosic materials studied contained all gradations in macromolecular arrangements from completely disordered regions hydrolyzed with ease to highly order regions hydrolyzed with difficulty. Since hydrolysis continued with no abrupt changes, and with no decrease in average degree of polymerization in what was assumed to be the mesomorphic component, the latter was presumed to occur mainly on the crystallite surfaces.

Because the viscosities of all materials studied reached approximately the same value (1.36 to 1.75 cp. at 6 hours reaction time and 1.38 to 1.92 cp. at 1 hour reaction time), the degree of polymerization represented by this viscosity might be assumed to correspond to the average crystallite length. Calculated values for the chain-length of the crystallites of some cellulose modifications are presented in Table XVIII.

If it is assumed that hydrolysis soon ceased on the ends of the crystallites (since the viscosity remained substantially unchanged after 5 minutes of severe degradation or thirty minutes of mild degradation, and proceded only on their sides, the total amount of non-crystalline material present might then coincide with the total amount of cellulose hydrolyzed before a constant hydrolysis rate was attained. On this basis the amount of crystalline component present in a given cellulose would be equal to 100 minus its accesibility as measure by the hydrolysis - oxidation method.

CUPRAMMONIUM VISCOSITIES OF VARIOUS CELLULOSES AFTER 30 MINUTES IN BOILING 2.5 N. H_2SO_4, AND DERIVATED ESTIMATE OF CRYSTALLITE LENGTHS[a, b]

Material	Viscosity of 0.5% Cupram. Soln.(in cp)	Average Crystallite Length[c]
Egyptian Cotton	1.86	283
Linen	1.82	270
Unmercerized Cotton	1.76	253[d]
Acetate-grade Linters	1.75	248
No. 175 Linters	1.74	244
Mercerized Cotton	1.54	179
High Tenacity Saponified Acetate	1.40	132
High Tenacity Viscose Rayon	1.34	110

The hydrochloric acid - ferric chloride method was applied by Conrad and Scroggie (71) to linters and wood pulps used in the manufacture of viscose rayon in order to determine if, in a comparative study of various cellulose modifications, it would reveal differences not shown up by standard testing methods. Refinement of technique improved reproducibility to within a maximum error of 8 - 10%, with an average of 3 - 5%. The accessibility was found to decrease with increasing

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a. Nickerson, R. F., and Habrle, J. A. (68)
b. Calculated from D. P. by use of Battista's Equation (72).
c. As glucose anhydride units.
d. If it is assumed as a first approximation that the length of the crystallite is proportional to the per cent of crystalline material present, the ratio of crystalline components for viscose and native cotton would be 110/253 or 0.435. The same ratio on a basis of X-ray analysis would be 30/70 or 0.429. It is unlikely that this agreement is more than fortuitous, since by the same reasoning mercerization would reduce the per cent of crystalline material from 70 to (179)(70)/(253) or 49.5, and in actual fact the degree of crystallinity is assumed to increase upon mercerization. Further, evidence resulting from small-angle scattering studies suggests that the average crystallite diameters for different types of cellulose are quite variable (p. 8).

alpha-cellulose content (No's. 1 to 4, Table XIX). Xylose is known to evolve carbon dioxide more rapidly than does glucose or cellulose, and a high hemicellulose content in the low alpha-cellulose pulps would account for the differences found.

The increase in the hydrolytic - oxidation values resulting from mercerization (No's. 4 and 6, Table XIX) was attributed to swelling of the lattice structure or to the formation of shorter chain-length fragments. Drying of cotton through solvent exchange (water - methyl alcohol - benzene) led to some increase in accessibility (No's. 4 and 7, Table XIX), a result which is in agreement with the findings of Goldfinger, et al (73).

TABLE XIX

ACCESSIBILITY OF RAYON GRADE WOOD PULPS AND LINTERS[a]

No.	Cellulose	% Alpha-Cellulose	D. P.	% Accessibility
1	Wood Pulp from Beech Wood	89	....	11.5
2	Wood Pulp from Southern Pine	93	....	10.5
3	High Alpha-content Pulp " "	95	....	7.5
4	Cotton Linters	99	1000	5.3
5	High-viscosity Linters, unmerc.	..	1450	5.0
6	No. 3, treated with cold NaOH	..	....	14.5
7	No. 4, dried through water - methyl alcohol - benzene	..	1000	7.5

Goldfinger, Mark and Siggia (73) determined the accessibility of several cellulose samples by oxidation with periodic acid. The samples were treated with potassium

a. Conrad, C. C., and Scroggie, A. G. (71).

metaperiodate in the presence of sulfuric acid, for various periods of time, and the amount of periodate consumed was determined by analysis. The per cent of conversion plotted against reaction time in hours resulted in curves of the general shape shown in Figure IV, and the per cent of accessible[a] component was determined by extrapolation of the reaction-rate plot to zero reaction time. The results (Table XX) were somewhat lower than the same values obtained by the hydrochloric acid - ferric chloride method.

TABLE XX

ACCESSIBILITY OF CELLULOSE AS DETERMINED BY PERIODIC ACID OXIDATION[b]

Cellulose	Accessible Component [%]
Cotton Linters	6.0
Regenerated Cellulose	
Dried from Water	7.4
Dried from water - acetone - benzene	19.5

The increase in per cent accessibility obtained by solvent-exchange drying of a regenerated cellulose (7.4 to 19.5) as compared to the increased for native cellulose determined by Nickerson (5 to 7.5) for the same treatment, agains illustrates one of the fundamental differences between native and regenerated cellulose. Interpretation of the results obtained by periodic acid oxidation is rendered

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(a) The term 'amorphous component' us used by the authors (73)

(b) Goldfinger, G., Mark, H., and Siggia, S. (73)

difficult by the complicated course of the reaction as well as by the uncertainties involved in the extrapolation of reaction-rate curves.

g. The Accessibility of Cellulose as Measured by the Thallous-ethylate Method:

Assaf, Haas and Purves (27) made a detailed study of the thallous ethylate accessibility method as developed by Harris and Purves (74). The cellulose was immersed in a solution of thallous ethylate in a given solvent such as ether. Thallous ethylate, like thallous hydroxide, is a strong base, and hydroxyl groups with which it comes in contact are converted to thallous alcoholate:

$$\text{Cellulose-OH} + \text{TlOEt} \longrightarrow \text{Cellulose-OTl} + \text{EtOH} \quad \ldots \quad (IV)$$

The Cellulose-OTl was heated with excess of methyl iodide, resulting in the methylation of the thallous cellulosate:

$$\text{Cellulose-OTl} + \text{MeI} \longrightarrow \text{Cellulose-OMe} + \text{TlI} \quad \ldots \quad (V)$$

and the methoxyl groups were determined by a standard method. Accessibilities were determined for various samples, a variety of solvents being used for the thallous ethylate. The value obtained for any given solvent would be the accessibility of the cellulose to the liquid in which the reagent was dissolved. It was suggested that absolute accessibility[a] might be defined as the per cent

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a. The term 'amorphous cellulose' was used by the authors (27).

of hydroxyl groups accessible to a non-swelling reagent with a molecular volume of 0, and could be obtained by extrapolation of the molecular volume - per cent accessible plot (Figure I). The magnitude of the variation between accessibility values found for cotton linters with presumably identical prehistories showed the sensitivity of the method to changes in fine structure.

TABLE XXI

THALLOUS ETHYLATE ACCESSIBILITY VALUES FOR VARIOUS CELLULOSES[a]

Cellulose.	Accessibility (%)
Linters[b]	22, 17, 9, 27
Linters, Regenerated[b]	3.3
Ramie[b]	18
Unswollen Linters	0.4
Unswollen Ramie	0.25

The thallous ethylate method of measuring cellulose accessibility is one of the most difficult to carry out, and is probably the one most sensitive to changes in macromolecular arrangement in the amorphous regions.

Of the various accessibility measurements which have been discussed, the thallous ethylate and the acetylation methods should be most directly comparable.

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a. Assaf, A. G., Haas, R. H., and Purves, C. B. (27)

b. Swollen in caustic soda and dried through solvent exchange.

Both methods involved the use of an essentially non-swelling, non-degrading medium. In both studies cotton linters were solvent extracted, swollen with mercerization strength alkali, and dried either from water or through solvent exchange. None of the values found for the per cent of hydroxyl groups thallated in a swollen cellulose (maximum of 33%) agreed with the average, comparable value for the number of hydroxyl groups acetylated in a swollen, solvent-exchange-dried cellulose (ca 50%). However, it is of interest to note that in a study of swollen cotton linters by the thallous ethylate method, Glegg (75) obtained accessibility values of over 40%, which is in closer agreement with the 50% of hydroxyl groups acetylated in a comparable cellulose preparation. It is possible that all thallous-ethylate accessibilities were obtained on mercerized samples which had suffered some indeterminate degree of collapse.

In a discussion of the hydrochloric acid - ferric chloride and the thallous ethylate methods, Glegg (75) suggested that the anomalous results were related to the fact that the thallous ethylate was dissolved in an inert, non-swelling solvent, whereas the former measurement was carried out in water. The complicated nature of the acid degradation of cellulose has been demonstrated (76) by the fact that the shape of the reaction-rate curves can be markedly altered by treatment of the degraded fiber with alkali. A part of the decrease in reaction velocity

with time was attributed to the formation of short chains which hindered further attack. The short chains were removed by treatment of the hydrolyzed fiber with alkali and the rate of reaction increased upon re-hydrolysis.

h. The Accessibility of Cellulose as Measured by Water Regain:

In a recent paper Howsmon (77) discussed moisture regain under standardized conditions (58 per cent relative humidity and 75°F. as a measure of cellulose accessibility, and compared the results with accessibility values obtained by deuterium oxide exchange and by hydrolytic oxidation. The sorptive power of a cellulose was considered to be a function of the number of hydroxyl groups available for hydrogen bonding in the amorphous regions and upon the surfaces of the crystallites. Thus a given regain could result from a large per cent of amorphous material and large crystallites, or from a small per cent of amorphous material and small crystallites with a large surface. On the assumption that moisture regain (and consequently the sorption ratio) was proportional to the accessibility and that the value of the latter recorded for cotton by Frilette, Hanle and Mark (64) was valid, the relative accessibilities were calculated by multiplying the sorption ratios by 44[a]. The results are shown in Table XXII for a number of cellulose modifications.

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a. The same result would be obtained by multiplying the water regain values by the ratio: 44/6.70, ie, the deuterium oxide accessibility for cotton divided by the water regain for cotton.

TABLE XXII

COMPARISON OF ACCESSIBILITY AS MEASURED BY DEUTERIUM OXIDE EXCHANGE, WATER REGAIN AND HYDROLYTIC - OXIDATION OF CELLULOSE[a]

Cellulose	H_2O Regain at 58% R.H.	Sorpt. Ratio[b]	Density at 20°.	Accessibility in %		
				D_2O Exch.	H_2O Regain	Hydrol.-Oxidation
Cotton	6.70	1.00	1.544	44[c]	44	14[d]
Wood Pulp	8.05	1.20	1.541	55	53	19
Mercerized Pulp	10.45	1.56	1.534	74	69	30[e]
Experimental Rayon	11.50	1.71	.....	..	75	
Textile Rayon.	12.00	1.79	1.522	68	79	55
High Tenacity "	13.25	1.98	1.509	86	87	

The correlation between the two sets of values for cellulose accessibility from deuterium exchange and water regain was quite good, as might have been expected from the fact that both sets of values measured the accessibility of cellulose to water.

Howsmon has also discussed in detail the measurement of accessibility by the hydrolytic - oxidation method, and the relationship between moisture regain and weight

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a. Howsmon, J. A. (77).

b. The ratio of water regain for a given cellulose to the regain for cotton under the same conditions.

c. From (64)

d. Selected values from Nickerson's data: 100 - % crystallinity (corrected). The corrected values for crystallinity were obtained by assuming that recrystallization occurred during hydrolytic - oxidation, and that the increase in crystallinity was proportional to the decrease in regain upon hydrolysis.

e. Value actually recorded for mercerized cotton.

loss upon hydrolysis, as shown in Table XXIII.

TABLE XXIII

WEIGHT LOSS AND CHANGE IN MOISTURE REGAIN UPON HYDROLYSIS OF CELLULOSE[a]

Hydrolysis Time (min)	Moisture Regain	Weight Loss in %	Mols of H_2O per Mol Glucose Lost
0	13.35	....	..
30	11.42	0.43	41
60	10.56	0.67	37
90	10.18	0.91	31
120	9.86	1.42	22

If the decrease in moisture regain upon hydrolysis were to be attributed solely to the per cent of the material removed, then each glucose unit removed would have to be associated with 20 to 40 molecules of water as shown. X-ray analysis of these same hydrocelluloses revealed strong indications of an increase in crystallinity with increased degree of hydrolysis. The hydrolysis-oxidation data, the change in moisture regain upon hydrolysis, and the more clearly defined X-ray patterns from hydrocelluloses were accepted as constituting conclusive proof that hydrolysis in an queous medium was accompanied by an increase in crystallinity. The same opinion has been expressed by Brenner, Frilette and Mark (78).

Magne, Portas and Wakeman (79) made use of a calorimetric technique in a determination of the amount of freezing and non-freezing water present in several fiber

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a. Howsmon, J. A. (77).

modifications over a wide range of moisture contents. In this method a capsule containing the material under investigation was cooled to a specific temperature, placed in a calorimeter, and a measurement made of any heat change of the contents. The inflection points of the various plots obtained when the per cent of non-freezing water was plotted against the per cent of freezing water were used to obtain the results shown in Table XXIV. The per cent of crystalline component was calculated by assigning three molecules of water to each glucose units in the non-crystalline regions plus one-half molecule of water for each glucose unit in the crystalline regions of hydrate cellulose and calculating the per cent of non-crystalline material required to give a moisture content equal to the bound water.

The total non-freezing water (second inflection point) was found to decrease when the temperature was lowered, owing to freezing in smaller capillaries; the bound water (first inflection point) did not change with decreased temperature. This point of inflection was quite sharp, and possibly represented the truest measure of the chemically bound water. The value of 19% for the total freezing-resistant water in the case of a viscose fiber coincided nicely with the value of 20% of water which could not be removed from a regenerated cellulose by any application of pressure (p. 34).

TABLE XXIV

AMOUNT OF BOUND WATER AND TOTAL NON-FREEZING WATER AS DETERMINED BY CALORIMETRIC MEASUREMENT[a]

	Cellulose	Bound Water %	% Crystallinity Calorimetric	% Crystallinity By X-ray Analysis	Total Non-Freezing H_2O[b] %
I	Native Cotton[c]	4.3	87	70	20.3
II	Native Cotton[d]	6.4	81	70	19
III	Mercerized "[e]	12	77	70	22.3
IV	Viscose Rayon	19	52	40	39

The total non-freezing water for a viscose rayon (39 per cent) checks equally well with the desorption saturation point of 39.6 per cent for a viscose rayon as discussed by Matthes (53) (p. 35).

i. Calculation of the Per Cent of Theoretically Accessible Hydroxyl Groups:

This calculation requires estimates of the per cent amount of the amorphous component, of the hydroxyl groups on the crystallite surfaces, and of hydroxyl groups accessible within the crystallites.

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a. Magne, F. C., Portas, H. J. and Wakeman, H. (79)

b. Second inflection point, from curves for freezing temperature of -4.5°.

c. Recorded as 'linear fiber'.

d. Recorded as 'roundish fiber'.

e. Recorded as 'elliptical fiber'.

Per Cent of Amorphous Component:

The most recent values given by Hermans (5) will be accepted as the most accurate available.

Native Cotton.	30%
Wood Pulps	40%[a]
Regenerated Cellulose. . .	60%

Per Cent of Hydroxyl Groups Available for Bonding On or Within the Crystallites:

The hypothesis of hydrate formation within the crystallites is based upon the fact that an expanded lattice was observed upon mercerization of ramie fiber. Howsmon (77) suggested an alternative interpretation to that of hydrate formation within the crystallites, namely, the formation of hydrates from imperfect crystallites to give coherent X-ray scattering. Nevertheless, in the present analysis it will be assumed that the hydrate $C_6H_{10}O_5$ 1/2 H_2O is formed within the crystallites, that is, that 1/6 of the hydroxyl groups within the crystallites are available for hydrate formation or reaction.

Per Cent of Hydroxyl Groups on the Crystallite Surfaces Accessible for Bonding or Reaction[b]:

A careful examination of the work of Frilette, Hanle and

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a. The values actually obtained for per cent crystalline material by X-ray analyses were 70±2% for native cotton and 39±3% for regenerated cellulose (Table II). The only figure available for a wood pulp was 50%, based on density determinations. Because the per cent crystallinity determined for native cotton by the same method was 60% (compared with 70% by X-ray analysis), the value for pulps was increased from 50% to 60%, giving the 40% amorphous component recorded above.

b. With reference to the question of the fraction of hydroxyl groups available on the crystallite surfaces, Lauer (58) has suggested that no answer can be given, since two of the crystallite faces may carry no hydroxyl groups in the outer layer.

Mark (64), as well as that of Howsmon (77), led the present author to abandon any attempt to calculate precisely the fraction of the crystallite hydroxyl groups available on the crystallite surfaces for hydrogen bonding or for reaction. Instead, values of 30, 20 and 10 per cent were arbitrarily assumed for regenerated cellulose, mercerized cellulose, and native cotton linters, respectively. These values should correspond fairly closely to crystallite diameters of 50, 100 and 150A units.[a]

Indirect evidence that these relative values are probably of the correct order of magnitude was provided by data given by Kratky (80). Distribution curves for the frequency of the crystallite diameters, based on small-angle scattering measurements indicated an average crystallite diameter of 45A units for a regenerated cellulose and 65A units for native ramie. The value of 45A units for a regenerated cellulose agreed well with the value of 50 assumed above, and the value of 65A units for native ramie checks well the value of 68A units given by Heyn (Table III).

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a. According to Howsmon (77) a crystallite 50A units wide would have approximately 17% of surface hydroxyls (compared with the 30% assumed above). However, the value of 17% was based upon the assumption that the crystallite was of infinite length, and the per cent of hydroxyl groups on the surface of a crystallite of finite length and 50A units in diameter would be appreciably higher than 17%. If Heyn's assumption that the average period determined by small-angle scattering measurements is approximately equal to crystallite diameter for cotton (p. 7), then the approximate average crystallite diameters for native and mercerized cotton should be 146 and 95A units, respectively, and for viscose, something less than 70A units. The values recorded above have been selected on the assumption that this hypothesis is valid.

On a basis of the considerations discussed above, the per cent of hydroxyl groups theoretically accessible for hydrate formation has been calculated for several types of cellulose. The actual calculations are given in Appendix II, and the results are collected in Table XXV.

TABLE XXV

PER CENT OF HYDROXYL GROUPS THEORETICALLY ACCESSIBLE

Cellulose Modification	Crystallite Diam. A Units	Crystallite Per Cent	Fraction of OH Groups on Crystals	Per Cent OH Groups Theor. Accessible	Accessibility Ratio[a]
Cotton					
Native	150	70	0.10	37	1.00
Mercerized	100	70	0.20	53	1.44
Wood Pulps					
Native	150	60	0.10	46	1.25
Mercerized	100	60	0.20	60	1.62
Regenerated	50	40	0.30	77	2.08

j. A Comparison of Accessibility Values Obtained by Several Methods:

If the assumptions used in the above calculations are valid, then the ratio between the hydroxyl groups accessible for various modifications of cellulose should be approximately equal to the sorption ratio, since water sorption should be a direct function of the accessible hydroxyl groups. Similarly, the accessibilities should be in proportion to the integral heats of sorption, which,

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a. Obtained by equating to unity the accessibility of native cotton linters (37%).

as discussed by Hermans (21) is the 'capacity factor' of sorption.

TABLE XXVI

A COMPARISON OF THEORETICAL ACCESSIBILITY RATIOS, OF SORPTION RATIOS AND INTEGRAL HEAT OF SORPTION RATIOS

Cellulose	OH Group Accessibility Ratio[a]	Sorption Ratio Value	Reference	Integral Heat of Sorption Ratio. Value	Reference
Cotton					
Native	1.00	1.00		1.00	
Mercerized	1.44	1.49	(21, p.17)	1.5	(81)
		1.50	(10)		
Wood Pulp					
Native	1.25	1.3	(10)	1.25	(57)
Mercerized	1.62	....		....	
Regenerated	2.08	2.08	(21, p.17)	2.16	(57)

Agreement between calculated and experimental ratios is considered to be quite good, particularly in the light of the fact that the sorption ratios vary[b] with the type of cellulose (mercerized cotton = 1.49, mercerized ramie = 1.66), with the type of regenerated cellulose (viscose rayon = 2.12, Lilienfeld fiber = 2.08), and with the degree of stretch (0% stretch = 2.12, 70% stretch = 2.04.).

Values for a number of other accessibility tests, reduced wherever possible to a strictly comparable basis, have been collected in Table XXVII. Where a choice of values

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a. Native cotton equated to unity.

b. All values selected from data given by Hermans (21).

was possible, the highest value was usually chosen, since it has been amply demonstrated during the course of the present discussion that a variety of causes can lead to an inadvertent reduction in accessibility.

TABLE XXVII

A COMPARISON OF VARIOUS ACCESSIBILITY VALUES

Cellulose	Accessibility (Expressed as % of OH's reacting)					
	Calc.	HCl-$FeCl_3$	Acetyl-ation.	D_2O Exchange	Water Regain	Non-Freezing Water.
I	II	III[a]	IV	V	VI	VII
Cotton						
Native	37	26	25	44	44	26
Mercerized	53	48	53[b]	..	..	49
Wood Pulps						
Native	46	37	33	55	53	..
Mercerized	60	53	63[c]	74	69	..
Regenerated	77	77	74[d]	77[e]	83	77

Sources of Values in Table XXVII:

II	Table XXV.
III	Appendix III.
IV	Notes b, c and d, below, and Appendix I.
V	Table XXII.
VI	Table XXII.
VII	Table XXIV. Value recorded for viscose rayon equated to 77 and all other values scaled accordingly. Value for Native Cotton II selected.

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a. Method of calculation given in Appendix III.

b. Average of 10 values for a mercerized cotton linters: Numbers 2, 17, 18, 19, 29, 32, 34, 49, 50 and 54, Appendix I.

c. Average of values given in Table XV.

d. Average of values given in Table XVI.

e. Average for a textile rayon and for a high-tenacity rayon.

It should be emphasized that the various accessibilities shown in Table XXVII have been selected, in some cases from a wide range of values. Deuterium exchange accessibilities, for example, varied from 61% to 62% for cotton linters, from 54 to 74% for wood pulps, and from 66 to 86% for regenerated celluloses (64). Most of these accessibilities are higher than would have been predicted on a basis of the above calculations. Agreement between the varied results, when they are reduced insofar as possible to a common basis, appears to be generally close. The greatest deviation from theory occurred in the case of cotton or wood pulps in the native form, where in three separate types of accessibility measurements the experimentally determined values (26, 25, 26) were appreciably and unaccountably lower than the calculated value (37). It seems apparent that some variable of unknown nature is operative here. In their acetylation studies Staudinger and co-workers (26)(60) found that when a native cellulose was dried from water, it did not become inactive[a], and when dried through solvent exchange did not become activated, in direct contradiction to the results found for Hydrate Cellulose. No explanation was offered by Staudinger for these phenomena.

In the case of native cellulose from cotton or wood pulps there is a considerable body of opinion which holds that

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a. The native forms could be inactivated by heating at high vacuum and 100° for several days.

small, but indeterminate fraction of the glucose anhydride rings are cross-linked by bonds of an unknown type (49)(58) (82 to 87). If in addition to the well-known biochemical structure, a native cellulose contains a type of transverse bonding, sufficiently small in amount as to be immeasurable by analysis but sufficiently large to alter appreciably the reaction characteristics of the fiber, and of such a nature as to be destroyed upon mercerization, then the anomalous behaviour of native cellulose might receive at least a qualitative interpretation.

k. Reactivity of Cellulose Toward Nitration:

Because the object of the present investigation was primarily a study of cellulose structure and reactivity, no effort has been made to discuss in detail the mechanism and the variables of cellulose nitration. The literature of cellulose nitration is voluminous and a number of excellent reviews are available (2)(3)(4)(89)(90)(91).

The results obtained by Brown and Purves (1) in a study of the nitration characteristics of swollen, collapsed and untreated cotton linters may be summarized briefly as follows. Samples from each of the three modifications prepared as described later in the present work, were nitrated under standardized conditions. Both a phosphoric acid - nitric acid nitration mixture and a technical mixture made up of sulfuric acid - nitric acid - and water were used, and parts of the technical nitrates

were re-nitrated with the phosphoric acid mixture.

In four individual experiments there was close agreement between the nitrogen contents of samples nitrated directly with phosphoric anhydride - nitric acid or nitrated first with the technical mixture (to about 12% nitrogen) and then with phosphoric acid - nitric acid. The technical nitrates from the collapsed linters, however, were found to possess nitrogen contents lower than the nitrates from the swollen linters by 0.6, 0.4, 0.3 and 0.15 per cent nitrogen.

The intrinsic viscosities of the various samples were measured in butyl acetate: the nitrates from collapsed linters gave values higher than the nitrates from the swollen analogues. The lower nitrogen contents and the higher intrinsic viscosities of the nitrates from the collapsed modifications were attributed to the presence within the amorphous component of vitrified localities of low hygroscopicity, high density and low accessibility. The presence of these vitrified localities would lead to lower over-all nitrogen contents, and the persistence in solution of poorly nitrated and hence imperfectly dissolved fragments would result in an increased intrinsic viscosity. This supposition received support from the fact that

nitrogen determinations made on fractions obtained by careful fractional precipitation of the various nitrates from solution showed lower nitrogen contents in the low molecular weight fractions.

EXPERIMENTAL PART

DETERMINATION OF NITRATE SUBSTITUTION

The methods used are described in detail because strict attention to the details mentioned was necessary to secure the precision and reproducibility claimed for the hundreds of determinations made.

Preparation of Samples for Nitrogen Determinations:

All nitrates were brought to less than 3 per cent moisture by placing them in a desiccator over phosphorus pentoxide (a fresh surface of which was exposed every 24 hours) at room temperature for at least one week prior to the determinations. Where the nitrogen contents of the nitrated samples were to be determined by the yield method as well as by analysis the moisture content of the desiccator-dried cellulose nitrates was less than 1 per cent.

Five samples of the cellulose nitrate, each weighing approximately 30 mg., were placed in weighing flasks of approximately 1 ml. capacity and 3 to 4 g. in weight. These weighing flasks could be handled quite conveniently by means of two pairs of small forceps. The open weighing flasks together with contents were stored in a desiccator over fresh phosphorus pentoxide for 24 hours under 2 mm. vacuum. The desiccator was then opened and the ground-glass stoppers placed tightly in the weighing flasks. The average time

for this operation for a set of five samples was fifteen seconds approximately. The individual weighing flasks plus cellulose nitrate samples were weighed on a semi-micro, magnetically damped balance to the nearest 0.00003 g. Each nitrocellulose samples was transferred in one piece to a 25 ml. micro Kjeldahl flask by means of a pair of small forceps. The weighing flasks were reweighed, and particles of cellulose nitrate remaining on the walls of the weighing flasks were included in the weights of the flasks.

The amount of moisture remaining in the cellulose nitrate samples at the time of the final weighing was then determined by drying 50 to 60 mg. samples at 65° and 1 mm. pressure for 24-hour periods until consecutive weighings differed by no more than 0.0001 g.

Digestion of Samples:

Nitrogen determinations were by the modified micro Kjeldahl method used by Brown and Purves (1)(92). Salicylic acid, 0.1 ± 0.005 g., was added to the nitrate sample in the micro Kjeldahl flask. Two ml. of concentrated sulfuric acid was added and the flask allowed to stand until all solids had dissolved. After the addition of 0.3 g. (± 0.005 g.) sodium thiosulfate, the flask was heated gently for five minutes. Finally, 0.6 g. (± 0.005 g.) potassium sulfate was added to the contents of the flask and digestion was continued at a strong heat until a colorless solution was obtained, the time being standardized at 16 to 18 hours. At one stage in the

in the present studies considerable difficulty was encountered in obtaining reproducible micro Kjeldahl nitrogen values. The analytical method was thoroughly checked by analyzing a sample of pure urea. It was found that reproducible, accurate results could be obtained by doubling the quantity of reagents, and this was done in all subsequent nitrogen determinations (beginning with Run No. 39).

Distillation of the Digested Samples:

To the cooled, viscous liquid was added 8 ml. of distilled water; the contents of the flask, together with four 5 ml. volumes of distilled water and 12 ml. of 35 to 40% sodium hydroxide solution, were transferred to a standard Kemmerer-Hallett distillation apparatus (93). The ammonia was distilled into 10 ml. of a 2 per cent solution of boric acid containing 5 drops of a mixed indicator which consisted of 10 ml. of a 0.1% solution of brom-cresol green in ethyl alcohol mixed with 2 ml. of a 0.1% solution of methyl red in the same solvent. The time of distillation was standardized at five minutes from the first appearance of a green color in the boric acid solution, and the ammonia in the distillate was titrated directly with 0.02857 N hydrochloric acid. As a precautionary measure, at the end of the standard 5-minute period, the distillation was continued for approximately 1 minute into a second 10 ml. portion of boric acid plus indicator. Absence of a color change within 1 minute indicated that distillation was complete.

A number of blank determinations gave an average value of 0.11 ml. of the acid, and the per cent nitrogen was calculated from the relationship:

$$\% \text{ Nitrogen} = \frac{(\text{ml. sample} - \text{ml. blank})(N)(14)(100)}{(\text{Weight of sample in grams})(1000)} \quad \ldots \quad (VI)$$

or

$$\% \text{ Nitrogen} = \frac{(\text{ml. sample} - 0.11)(0.40)}{(\text{Weight of sample in grams})(10)} \quad \ldots \quad (VII)$$

where the factor 0.40 represents the product of the acid normality (0.02857) and the atomic weight of nitrogen (14).

The number of nitrogen determinations carried out on any individual cellulose nitrate sample was conditioned by several factors, including the agreement between 'yield' nitrogen and the micro Kjeldahl nitrogen values, the equipment available at the time, and the reproducibility of the results on one or more samples in a series of comparable runs. In the initial stages of the work (up to Run No. 11), five or six determinations were made on each nitrated cellulose; if for any reason one result varied from the mean of the others by more than 0.05%, it was rejected, and if two samples varied in per cent nitrogen by more than 0.1 per cent, a new set of determinations was made. In those cases where four nitrogen determinations were carried out on a given cellulose nitrate, only those values were accepted where three agreed to within 0.05%. Occasionally, particularly in the case of nitrates with less than 10 per cent

nitrogen, it was not possible to obtain values agreeing to within 0.1 per cent. The explanation almost certainly was that grossly heterogeneous nitration had introduced appreciable sampling errors.

'Yield' Nitrogen Determinations:

As a check on the micro Kjeldahl method, the nitrogen contents of many of the nitrated celluloses were also obtained in the following way. A sufficient number of swollen, collapsed and untreated linters samples for a set of nitration together with at least three samples to determine the moisture content of each type of cellulose, were weighed into weighing flasks. The sample weights in all cases were 1.05 ± 0.01 g., and the container weights were approximately 20 g. The open weighing flasks were placed in a desiccator over phosphorus pentoxide which was renewed every 24 hours, and the samples were weighed every several days over a period of 2 to 3 weeks, or until such time as two consecutive weighings varied by no more than 0.0005 g. All weighing flasks were tightly stoppered during the weighing operations. Each sample was weighed to within 0.0001 g., and all but the samples for moisture determinations were transferred to the 250 ml. iodine flasks in which the nitrations were to be carried out, or to the apparatus in which they were to be heat-treated prior to nitration. Finally, the containers were weighed to within 0.0001 g. The samples for moisture determination were dried at 100° and 20 to 30 mm. pressure (or at 0.1

to 1.0 mm. beginning with Run No. 32) over fresh phosphorus pentoxide for 24- or 48-hour periods until two consecutive weighings varied by no more than 0.0001 g. The values for the moisture in each type of starting material (swollen, collapsed and untreated cotton linters) determined in this way were used to calculate the bone-dry weights of the cellulose samples used in the nitrations.

All moisture determinations of the starting materials were carried out on 1 g. samples heated for 48 hours at 100 to 105° at less than 1 mm. vacuum over phosphorus pentoxide. Since this oxide is unstable at 100°, it had to be kept outside of the heating chamber but as close to the same as was convenient. Table XXVIII. records the amount of water retained by samples of viscose rayon when dried in a stream of dry nitrogen at the temperatures shown.

TABLE XXVIII

MOISTURE CONTENT OF VISCOSE RAYON FIBERS VARIOUSLY DRIED[a]

Temperature (°C)	Sample	24 hrs.	48 hrs.	72 hrs.
75	1	0.49	0.40	.....
	2	0.52	0.37	.....
87	1	0.15	0.12	0.10
	2	0.16	0.16	0.10
98 - 100	1	0.04	0.04	0.04
	2	0.04	0.04	0.04
115	1	(0.00)	0.00	0.00
	2	(0.00)	0.00	0.00

a. Hermans, P. H. (21)

Data are not available for the precise conditions used in the present work, but the moisture content of the samples after the drying procedure was probably less than 0.04%, and the samples so treated were considered to be bone-dry.

The cellulose nitrates were recovered on 25 ml., coarse sintered glass filters which had been weighed to within 0.0001 g. prior to use. All filtrations were carried out on these tared filters, and the nitrates, still on the filters, were dried over fresh phosphorus pentoxide at 20 to 30 mm. (or at 0.1 to 1.0 mm. beginning with Run No. 32) until two consecutive weighings made at 24 - hour intervals varied by no more than 0.0005 g. The moisture contents of the dried cellulose nitrates were determined on samples weighing approximately 50 mg. each, dried at 65° and 20 to 30 mm. (or at 0.1 to 1.0 mm.) until successive weighings checked to within 0.0001 g. From the bone-dry weights of the initial cellulose sample and of the final cellulose nitrate, the per cent nitrogen could be calculated from the relationship:

$$\% \text{ Nitrogen} = \frac{(W_{\text{nitrocell.}} - W_{\text{cellulose}})(0.311)(100)}{(W_{\text{cellulose}})} \quad \text{(VIII)}$$

where the factor (0.311) is the quotient of the atomic weight of nitrogen (14) by the increase in base molecular weight (45) accompanying the nitration of a hydroxyl group.

In the present work the yield nitrogens are not

recorded for the preliminary nitrations because sufficient precautions were not taken in the drying of the starting material and the cellulose nitrates, and the weights were therefore not known with sufficient accuracy to permit of reliable calculations.

By means of refinements applied to both methods of determining nitrogen it is possible that a closer check could be obtained between micro Kjeldahl and yield values than was actually obtained in the present work. However, the primary purpose of the present investigation was to compare the results of nitrating similar cellulose samples after pretreatments. While no claims are made as to the absolute values recorded, the difference between duplicates in a given series of nitrations covered in a study of one variable was probably less than 0.05%. The highest degree of reproducibility obtained in the micro Kjeldahl determinations was ± 0.02% for pure, crystalline compounds, and ± 0.05% on the average for the cellulose nitrates.

PREPARATION OF CELLULOSE SAMPLES FOR NITRATION

Extraction of Cotton Linters:

High-grade cotton linters, obtained from the Hercules Powder Company and from the same lot as used by Brown and Purves (1) in their studies, were extracted in 100 - g. lots with a 1:2 ethanol - benzene mixture in a Soxhlet extractor of 2 liters capacity for two days. The

extracted linters, while protected against contamination by dust, were air-dried for one week at room temperature.

Preparation of Alkali for Mercerization:

A forty per cent solution of sodium hydroxide was made up and allowed to stand for several weeks in order to permit any sodium carbonate present to settle. From this stock solution the required amount of 10% or 11% sodium hydroxide solutions was made up immediately prior to use.

Mercerization:

(a). In all preliminary experiments the method outlined by Brown and Purves (1) and Glegg (75) was used in the preparation of mercerized cellulose. Approximately 15 g. of air-dried dewaxed cotton linters were added to 540 g. of a 10% solution of sodium hydroxide cooled to 0 to 5°, and the mixture was left standing for two and one half hours. The alkali solution was neutralized by the addition of a calculated amount of 10% acetic acid. After recovery the linters were made slightly acid by the addition of a 1 per cent solution of acetic acid and finally washed with distilled water until the wash water was neutral to litmus. This method was found to produce swollen celluloses possessing various accessibilities as measured by the chromium trioxide and by the thallous ethylate methods.

(b). More uniform products were obtained upon adoption of the following procedure[a]. The linters were mercerized with 11 ± 0.1% sodium hydroxide at 0-5° and neutralized by washing over a period of several hours with repeated changes of distilled water at 0-5° until the washings were neutral to litmus. The linters were then boiled in distilled water for half an hour, the product serving as a starting material for the subsequent preparation of swollen and collapsed samples.

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a. This procedure was adopted after it was found that mercerization according to method (a) yielded products possessing a range of accessibilities. At this time and in these laboratories Dr. Jorgenson was conducting an extensive series of investigations in a study of the accessibility of a number of cellulose types and modifications, employing an acetic anhydride - acetic acid solution of chromium trioxide as the reagent. He found that if cotton linters or wood pulps were mercerized and subjected to a half hour treatment with boiling water as described above, reproducible accessibility values could be obtained.

It would have been desirable to nitrate a sample in the highly reactive 'water cellulose' state prior to the boiling and conversion to the stable Hydrate I allotrope, but this was impossible by any nitration method which necessitated the use of a dried material. One possibility would have been to use the method of nitration in a homogeneous medium developed by Rogovin and co-workers (94). It should be possible to solvent exchange the water cellulose into nitromethane or a mixture of nitromethane and methylenechloride or dichlorethane and then to nitrate with fuming nitric acid. The method was not attempted, since it would have involved a preliminary investigation of considerable length.

Preparation of Sulfite Pulp:

A sample of bleached, purified sulfite pulp, 'Novocel', which had never been dried, was extracted with alcohol-benzene, air-dried and mercerized according to method (b). When air-dried or vacuum-dried from water or from benzene, the pulp samples formed small, hard pellets which were found to possess exceedingly low nitration reactivities (Runs 43 to 48). In order to obtain results comparable to those given under similar conditions by cotton linters, it was necessary to convert the dry pulp samples to a form comparable to cotton linters. This object was accomplished by subjecting the dry pulp samples (swollen, collapsed and untreated) to the action of a Waring Blender for approximately 20 seconds. The best results were obtained by placing approximately 0.1 g. of dry pulp pellets in the Blender, which was of approximately 2 liters capacity.

Preparation of Swollen Cotton Linters:

The wet, mercerized and stabilized cotton linters were immersed in 500 ml. of 99% methanol. In 30 minutes the methanol was removed (most conveniently by means of a filter-stick made from the bottom of a sintered glass funnel) and the alcohol-wet linters were added to 500 ml. of fresh 99% methanol. This procedure was carried out five times in all. The alcohol-wet linters were then immersed in 500 ml. of

thiophene-free benzene, left standing for approximately one-half hour, and the benzene removed. This procedure was carried out five times in all. Care was taken to insure that the entire mass of cellulose was moist at all times in order to avoid local collapse of the fibers. Whenever it was necessary to leave the samples standing overnight in one of the liquids, they were left under a ground-glass seal in order to avoid the possibility of the samples or the immersion liquid picking up moisture from the air. The swollen fibers were dried in a desiccator over phosphorus pentoxide and paraffin shavings at 25 mm. pressure for at least one week.

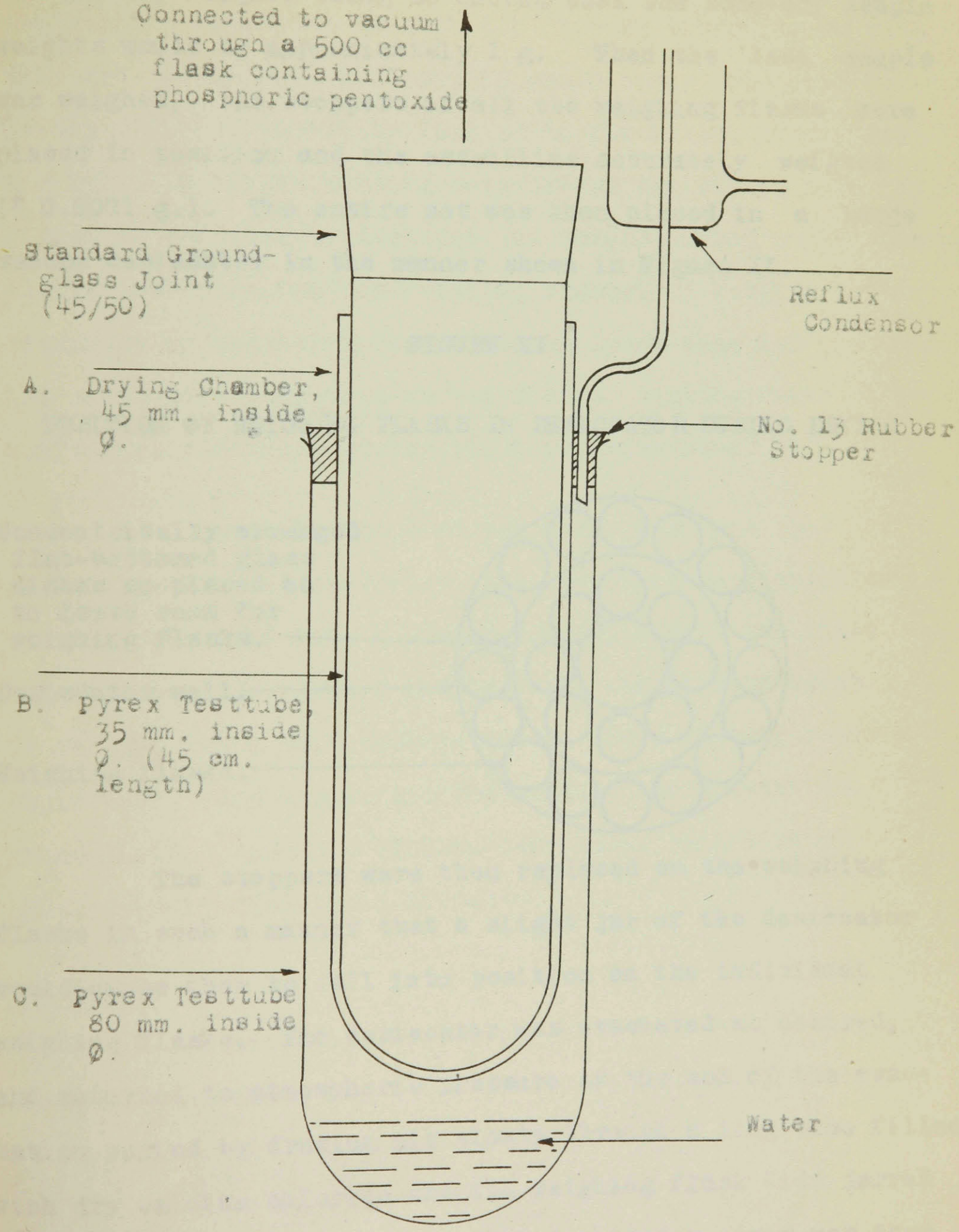
Preparation of Collapsed Linters:

Approximately one-half of the swollen, dried linters was immersed in distilled water for 1 week at room temperature. The excess water was drained off and the linters were dried for one week over phosphorus pentoxide at 20 mm. pressure thus causing collapse of the swollen structure and yielding an unreactive, or 'collapsed' cellulose.

Heat Treatment and Drying of Samples:

It was found most convenient to heat-condition the 1-g. samples of linters in a constant temperature drying apparatus of the type shown in Figure X. The same type of equipment was also used for determining the moisture contents of various samples, the technique being the same

FIGURE X

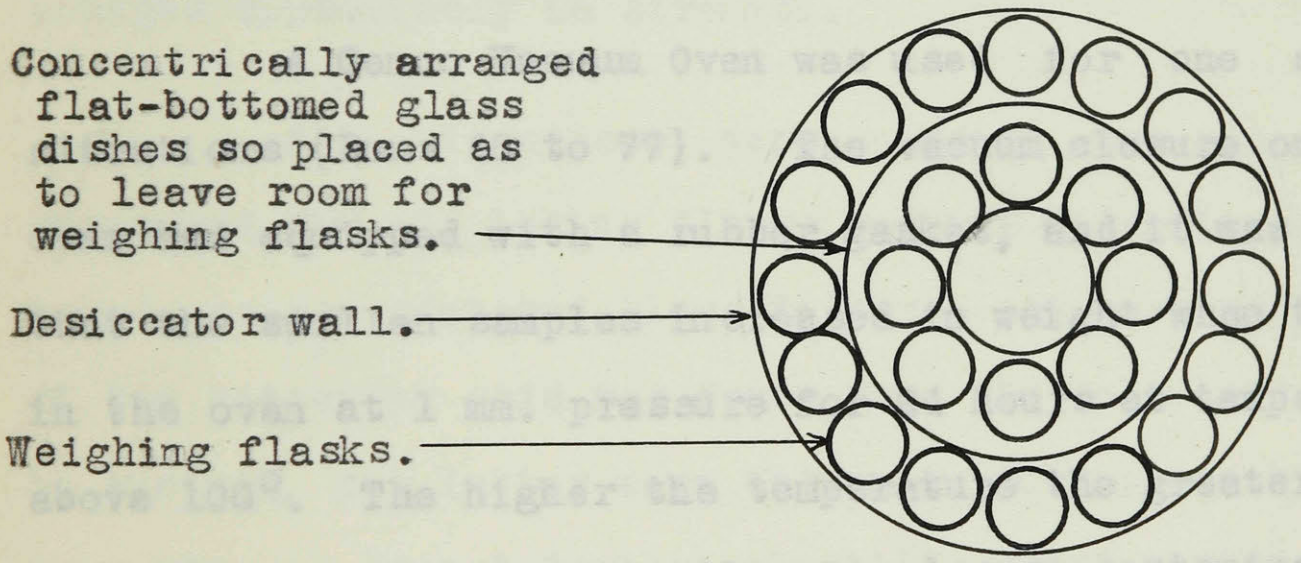


APPARATUS FOR CONSTANT-TEMPERATURE DRYING

in all cases. The various samples, occasionally numbering as many as 30, were all weighed during the same time period, the air-dry weights being so chosen that the bone-dry sample weights would be approximately 1 g. When the last sample was weighed, the stoppers of all the weighing flasks were placed in position and the assemblies accurately weighed (± 0.0001 g.). The entire set was then placed in a large vacuum desiccator in the manner shown in Figure XI.

FIGURE XI

POSITION OF WEIGHING FLASKS IN DESICCATOR DURING DRYING



The stoppers were then replaced on the weighing flasks in such a manner that a slight jar of the desiccator would cause them to fall into position on the individual weighing flasks. The desiccator was evacuated as desired, and returned to atmospheric pressure at the end of the evacuation period by drawing air slowly through a long tube filled with dry calcium chloride and the weighing flask lids jarred tight to the weighing flasks. The desiccator cover was then removed and the lids were pressed firmly on the weighing

flasks.

In the case of the samples dried in the constant-temperature apparatus (Figure X), the weighing flasks with balanced covers were enclosed in small cages made from wire screen and were carefully lowered to the bottom of the drying tube. A slight shaking movement of the drying tube (B, Figure X) sufficed to dislodge the covers, which would then settle into place on the weighing flasks. For the heat treatment of samples at temperatures lower than 100°, standard constant temperature drying flasks, together with solvents boiling at the temperatures required, were used.

A Cenco Vacuum Oven was used for one set of nitrations (Runs 68 to 77). The vacuum closure on this oven was equipped with a rubber gasket, and it was found that the swollen samples increased in weight when treated in the oven at 1 mm. pressure for 24 hours at temperatures above 100°. The higher the temperature the greater the contamination, and all swollen samples so contaminated gave strongly discolored nitrates.

Nitrations:

All nitrations specified as being carried out under standard conditions involved the use of a nitrating mixture of the following composition by weight (95):

Nitric Acid:	30 per cent
Sulfuric Acid:	53.2 per cent
Water:	16.8 per cent.

When other nitration levels were desired in the products, nitrating acids were made up according to tables given by Doree (89).

Nitrating acid (3000 g.) was prepared sufficient in amount for a large number of nitrations. The nitrating acid was adjusted in composition as required to give a cellulose nitrate with 12.2 ± 1 per cent nitrogen when untreated cotton linters were nitrated for one half hour at 15 to 18° and with a bath ratio of 1 g. of cellulose to 100 g. of nitrating acid. The nitrating acid was stored at - 10° and was checked occasionally by a trial nitration to insure that it had not changed appreciably in strength.

All nitrations were carried out in tightly stoppered 250 ml. iodine flasks and all filtrations were on tared, coarse sintered glass filters. As soon as the bulk of the nitrating acid was drawn from the cellulose nitrates by suction, the latter were thrown quickly piece by piece into 250 ml. of a 1:1 ethyl alcohol - water mixture at -10° (96). As a precautionary measure the nitrating acid was always disposed of at this point in order to avoid the possibility of inadvertently mixing it with the alcohol - water mixture. The nitrates were left immersed for 15 to 30 minutes, recovered on filters, covered with an additional 250 ml. of 1:1 alcohol-water, and the immersions repeated until the liquors were neutral to litmus. The nitrates were stabilized by boiling for four successive 30-minute intervals

in 250 ml. volumes of fresh 1:1 ethyl alcohol - water. All products were dried in a desiccator as previously described.

The micro Kjeldahl nitrogen determinations were carried out in most cases within one to two weeks after the formation of the nitrates, and when these determinations were considered satisfactory, the nitrates were immersed in distilled water and stored in a room maintained at 5 to 10°. When it was necessary to re-examine any of the cellulose nitrates so stored, small samples were withdrawn and dried under vacuum at room temperature.

Study of 'Inclusion' Celluloses:

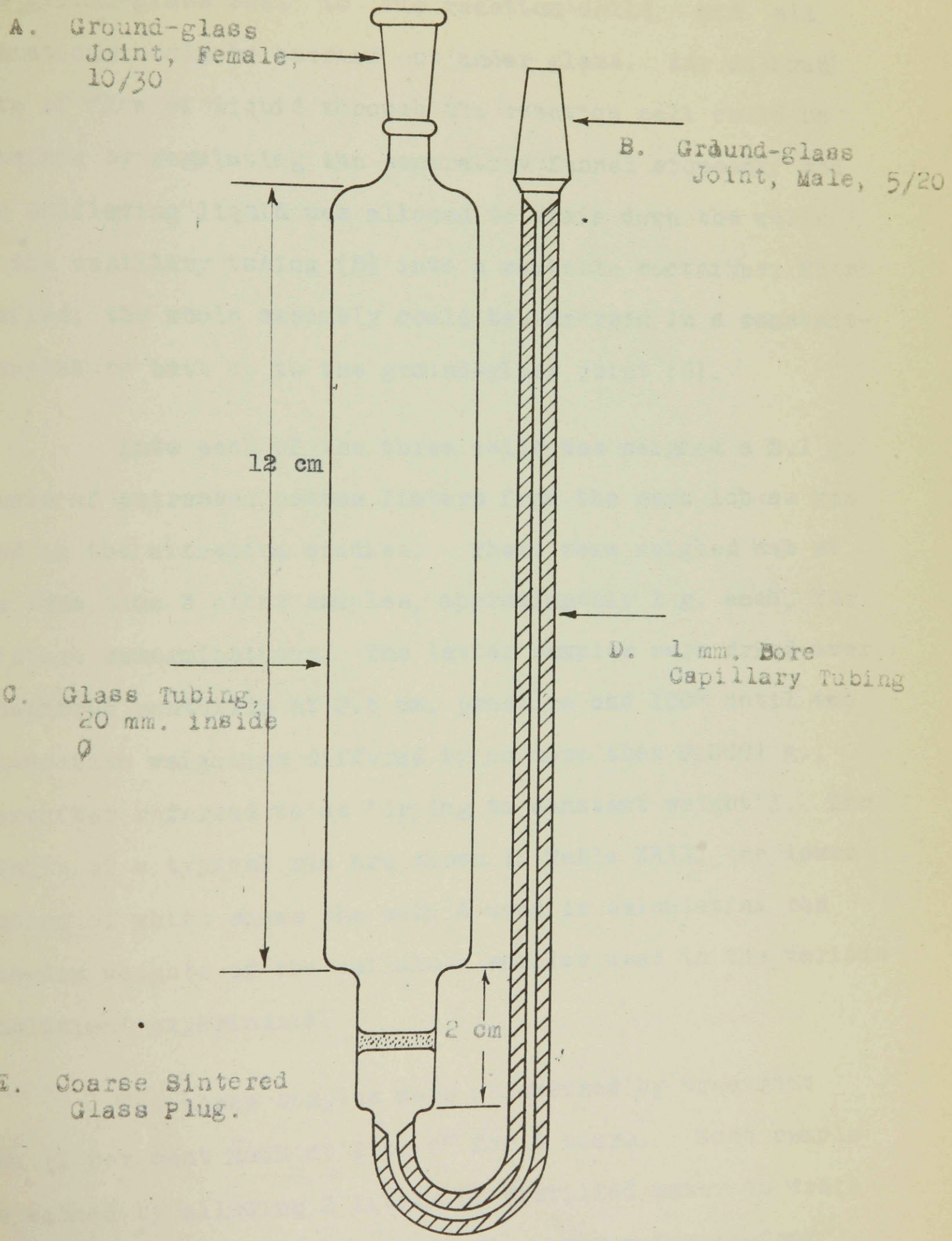
Reactions cells of the type shown in Figure XII were thoroughly cleaned, dried, weighed and carried through the series of operations to which the cellulose would be subjected in subsequent investigations, ie, mercerization, washing, solvent exchange and drying, in order to determine the loss in weight of the cells. Typical results were as follows:

	Cell 1.	Cell 2.
Initial Weight	59.6698 g.	60.2745 g.
Final Weight	59.6689	60.2735
Weight Loss	0.0009	0.0010

The weight of each cell was therefore corrected for a loss of 0.001 g. during the various operations.

Reagents and solvents used were placed in a 500-ml.

FIGURE XII



REACTION CELL USED IN 'INCLUSION' STUDIES

Pyrex separatory funnel provided with a 10/30 male ground-glass joint. The separatory funnel was connected through the ground-glass seal to the reaction cells, and all operations could be carried out under glass. Any desired rate of flow of liquid through the reaction cell could be obtained by regulating the separatory funnel stopcock, and the outflowing liquid was allowed to drain down the walls of the capillary tubing (D) into a suitable container. When desired, the whole assembly could be immersed in a constant-temperature bath up to the ground-glass joint (B).

Into each of the three cells was weighed a 2.1 g. sample of extracted cotton linters from the same lot as was used in the nitration studies. There were weighed out at the same time 3 other samples, approximately 1 g. each, for moisture determinations. The latter samples were dried over phosphorus pentoxide at 0.5 mm. pressure and 100° until two consecutive weighings differed by no more than 0.0001 g., (hereafter referred to as 'drying to constant weight'). The details of a typical run are shown in Table XXIX, the lower section of which shows the method used in calculating the bone-dry weights of the cellulose samples used in the various 'inclusion' experiments.

The three samples were mercerized by treatment with 11 per cent NaOH at 3 to 5° for 2 hours. Each sample was washed by allowing 2 liters of distilled water to drain through the cellulose by gravity flow over a twenty-four

TABLE XXIX

DETERMINATION OF BONE-DRY WEIGHTS OF CELLULOSE SAMPLES USED IN INCLUSION STUDIES

Weights (g.)	Sample 1	Sample 2	Sample 3
Flask - air-dry cellulose	18.2501	21.9034	18.5844
Flask - bone-dry cellulose	18.1832	21.8388	18.5080
Moisture in sample	0.0669	0.0646	0.0764
Flask - bone-dry cellulose	18.1832	21.8388	18.5080
Flask alone	16.9880	20.6827	17.1581
Bone-dry cellulose	1.1952	1.1561	1.3499
Per cent moisture	6.69	6.46	7.64
	1.195	1.156	1.350
	5.60	5.59	5.66
Average % moisture in starting materials	5.62 ± 0.04%		
Average % bone-dry in starting materials	94.38 ± 0.04%		
Cell - air-dry cellulose	61.6532	62.0676	56.3735
Empty reaction cell	59.5705	59.9864	54.2882
Air-dry cellulose in cell	2.0827	2.0812	2.0853
Bone-dry cellulose in cell = (air-dry weight)(0.9438)	1.966	1.964	1.968

hour period. Sample No. 1 was then dried directly from water. Through each of the other two samples two liters of 99.5% methyl alcohol was drained over a 24-hour period[a]. Sample No. 2 was solvent-exchanged through methyl alcohol and Sample No. 3 through methyl alcohol followed by thiophene-free benzene, and dried. All samples were dried over phosphorus pentoxide and paraffin shavings at room temperature and 12 mm. pressure for 72 hours, then at 1 mm. for

a. This operation will be referred to hereafter as 'solvent exhanged through alcohol' (or benzene, etc.).

24 hours, and at 0.1 mm. to constant weight. The results are collected in Table XXX.

TABLE XXX

CALCULATION OF PER CENT 'INCLUSION' OF METHYL ALCOHOL AND BENZENE IN A MERCERIZED CELLULOSE

Weights and Calculations:	Sample Dried From Water	Sample Dried From Methyl Alcohol	Sample Dried From Benzene
	Sample 1	Sample 2	Sample 3
Cell + mercerized cellulose	61.5148	61.9356	56.2470
Cell alone[a]	59.5695	59.9854	54.2872
Mercerized cellulose	1.9453	1.9502	1.9598
- 0.5% for moisture content[b]	0.0097	0.0098	0.0098
Bone-dry Wt. of mercerized cellul.	1.9356	1.9404	1.9500
Bone-dry Wt. of unmercerized " [c]	1.966	1.964	1.968
Bone-dry Wt. of mercerized "	1.936	1.940	1.950
Wt. loss during mercerization	0.030	0.024	0.018
Per Cent Wt. Loss During "	3.0	2.4	1.8
	1.97	1.96	1.97
	1.52	1.22	0.91
Per Cent of 'Included' Material[d]	....	0.30	0.61

a. Corrected for 0.001 g. loss in weight of reaction cell during all operations, as described in the Experimental Part.
b. Three samples of linters approximately 1 g. each in weight were mercerized and dried directly from water under the same conditions as used for the material in the reaction cells, and were then dried to constant weight for 96 hours (100^{o} - 0.3 mm. - P_2O_5). (This abbreviation for drying at 100^{o} and 0.3 mm. pressure over phosphorus pentoxide will be used extensively throughout the present discussion in order to conserve space.
c. From Table XXIX.
d. Columns 2 and 3 subtracted from Column 1. No analyses were made to determine the chemical nature of the 'included' material.

Through each sample was drained 2 liters of distilled water over a period of 24 hours. Samples 2 and 3 were then solvent exchanged through alcohol - benzene and Sample 3 was dried (100° - 0.4 mm. - P_2O_5) to constant weight. The amount of material retained by the cellulose when dried under these more severe conditions is shown in Table XXXI. The amount of retention is slightly higher than that found for drying at room temperature (0.86% at 100°, 0.61% at 25°) but was still

TABLE XXXI

AMOUNT OF MATERIAL 'INCLUDED' IN A MERCERIZED CELLULOSE SOLVENT EXCHANGED THROUGH METHANOL - BENZENE AND DRIED AT 100°

Weights and Calculations	Sample Dried From Water Sample 1	Sample Dried From Benzene Sample 3
Wt. of cell + mercerized cellulose	61.5060	56.2420
Wt. of reaction cell alone	59.5695	54.2872
Wt. of bone-dry mercerized cellulose	1.9365[a]	1.9548
Wt. of bone-dry starting material	1.966	1.968
Wt. of bone-dry mercerized cellulose	1.936	1.955
Loss in Wt. upon mercerization	0.030	0.013
Per cent loss in Wt. upon mercerization	3.0 / 1.97	1.3 / 1.97
	1.52	0.66
Per Cent Inclusion[b]	....	0.86

much lower than the value of 3.4% recorded by Staudinger and co-workers for benzene inclusion (Appendix V).

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a. It may be noted that this value for the bone-dry weight of the mercerized cellulose checks the value calculated on a basis of 0.5% moisture determined on separate moisture samples (Table XXX).
b. Column 2 subtracted from Column 1.

Sample No. 2 was dried for 1 week (25° - 10 mm. - P_2O_5 plus paraffin shavings), 48 hours (100° - 10 mm. - P_2O_5) and then to constant weight (100° - 1 mm. - P_2O_5). The amount of included material was found to 0.40%, suggesting that the less severe the conditions of drying, the less material was retained by the cellulose. The same sample was then extracted with 2 liters of distilled water over a 24-hour period and dried to constant weight (100° - 0.5 mm. - P_2O_5). As may be seen from Table XXXII, no material was retained under these conditions.

Finally, Sample No. 2 was washed with 12 liters of distilled water over a 6-day period and dried to constant weight (100° - 0.5 mm. - P_2O_5). The per cent weight loss was 1.58, from which it may be assumed that the triple washing and drying, the results for which are shown in Table XXXII, gives a material with no more than 0.02% of included solvent. As shown by Table XXXII, washing a sample of cellulose which has been dried through solvent exchange for 4 days should be sufficient to remove substantially all of the included solvent.

Prior to the use of the reaction cells as described above, the same values were determined in a series of separate operations. Three samples of cotton linters of accurately known weight were mercerized, washed and dried from water, methyl alcohol and benzene. The conditions of these tests differed from those in which the reaction cells were used in that the drying schedule was considerably milder. The

TABLE XXXII

AMOUNT OF MATERIAL RETAINED BY MERCERIZED CELLULOSE AFTER EXTRACTION WITH WATER

Weights and Calculations:	Sample 2
Wt. of cell + mercerized cellulose dried for 1 week (25° - 10 mm. - P_2O_5 - paraffin), etc	61.9270
Wt. of cell alone	59.9854
Wt. of mercerized cellulose so dried	1.9416
Wt. of bone-dry starting material	1.964
Wt. of bone-dry mercerized cellulose	1.942
Wt. loss upon mercerization	0.022
Per cent weight loss upon mercerization = 2.2/1.96 =	1.12%
Sample treated with 2 liters of distilled water and dried to constant weight (100° - 0.5 mm. - P_2O_5)	
Wt. of cell + mercerized cellulose:	
Treated once as described above	61.9241
Treated twice " " "	61.9200
Treated three times as " "	61.9197
Wt. of reaction cell	59.9854
Wt. of mercerized cellulose	1.9343
Wt. of bone-dry starting material	1.964
Wt. of mercerized cellulose treated as above	1.934
Wt. loss upon mercerization and treatment as above	0.030
Per cent loss in weight upon mercerization and treatment as above = 3.0/1.964 =	1.52
Per cent 'Inclusion' = 1.52 - 1.52 =	0.00 a

weighed cellulose samples were transferred to the iodine flasks in which the mercerization was carried out. All filtrations were carried out on tared, coarse sintered glass filters. The samples were transferred from the filters to weighing flasks immediately before drying. The filters were dried at 100° for 24 hours and weighed to determine the amount

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a. Weight loss of sample treated as described above was exactly equal to the weight loss of the sample mercerized and dried directly from water.

of cellulose adhering to them. All three mercerized samples were dried over paraffin shavings and fresh phosphorus pentoxide at room temperature for 48-hour successive periods at each of the following pressures: 200, 100, 50, 20, 20 and 20 mm. The samples were then transferred quantitatively to weighing flasks sufficiently small to permit drying at 100° in the apparatus available, and dried to constant weight (100° - 1 mm. - P_2O_5).

The weight loss on mercerization was 1.74%. The amount of material 'included' after drying from methanol was 0.14% and from benzene was 0.19%. Owing to slight manipulative losses, the data are not considered to be as accurate as those obtained in the reaction cells, which yielded the values of 1.52, p.30 and 0.61 respectively. Nevertheless, the results substantiate the hypothesis previously advanced, namely, that the less severe the conditions of drying, the less the amount of solvent that will be retained by the cellulose.

The work on the inclusion of amines, described later in 'Experimental Results', was carried out by substantially the same methods as those just described.

Attempted Determination of Particle Size:

The method adopted was that of Heller, Klevens and Oppenheimer (97). In light scattering systems, the optical density is related to the wave length of the incident light by the relationship (98):

$$D = c\lambda^{-n} \quad \ldots\ldots\ldots\ldots\ldots\ldots \text{(IX)}$$

or

$$\log D = -n.\log\lambda + c \quad \ldots\ldots\ldots\ldots \text{(X)}$$

where c is a constant, D is the optical density (I_o/I, where I_o is the intensity of the incident and I that of the transmitted beam), λ is the wave-length of the light used, and n is a constant for a given system. The value of n varies slightly with the concentration of the particles, and for precise work n is determined at a number of concentrations and n_o is obtained by extrapolation to zero concentration. Haller, et al (97) have presented a calibration curve of n (0.5 to 4) plotted against corresponding particle diameters (2500 to 500A units) (Figure XIII). The plot was claimed by the authors to be valid for any type of dispersed system in which the ratio of the refractive index of the light-scattering spherical particles to the refractive index of the dispersing medium was 1.24 ± 0.01. The method was considered valid for particles with diameters greater than one tenth of the wave length of the light used, and the exponent n varies from 4 for particles of less than 500A units to negative values for those with diameters exceeding 5000A units.

The exponent n was determined in the following way:

a. Approximately 0.1 g. samples of cellulose nitrates from the swollen, collapsed and untreated linters (Runs 4, 5 and 6) were placed in weighing flasks, covered with approximately 10 ml. of the solvent selected, and shaken gently for 48

hours. The solutions were then left standing for 48 hours, and approximately 5 ml. of each was removed from the upper portion and transferred to another set of ground-glass flasks.

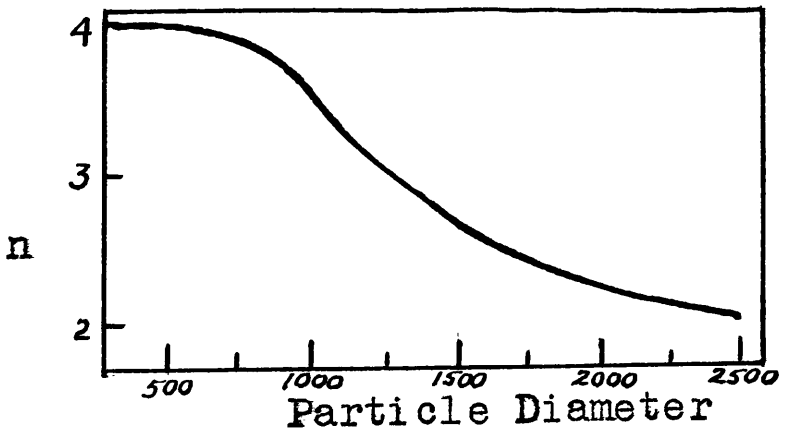
b. Corex spectrophotometer cells were filled with the solutions being examined or with the solvent used.

c. Values of D were determined for wave lengths of 6000, 5500, 5000 and 4000A units on a Beckmann Spectrophotometer.

d. D was plotted against λ on log-log paper and the slope of the line, or n, was measured.

FIGURE XIII

VARIATION OF n WITH THE DIAMETER OF SPHERICAL PARTICLES[a]



Microscopic Examination of Nitrated Fibers:

The instrument used in the studies of the various nitrated products was a Winkel-Zeiss microscope fitted with polarizing prisms. Most of the examinations were carried out at a magnification of 20. Where it was desired to examine individual fibers, magnifications of 80 and 470 were used. The slides, cover glasses, etc., were those normally used in microscopy.

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a. Heller, W., Klevens, H. B., and Oppenheimer, H. (97).

Most of the nitrates were examined in pairs, the swollen and collapsed samples from a given nitration being selected. The fibers were deposited on a microscope slide at a density of approximately 20 fibers per square cm. by holding a small clump of the nitrated fibers in a pair of forceps and tapping the latter slightly over a slide. During the course of swelling, solution or application of stains, each slide was examined alternately under ordinary light and under polarized light. Where it was desired to preserve a given sample, the solvent was allowed to evaporate completely and the specimen mounted in Canadian Balsam.

The solvents studied included acetone, methanol, ethyl, butyl, isobutyl, amyl and isoamyl acetates, dioxane, glycol, and dibutylphthalate, either as such or with the addition of Crystal Violet dye in 0.01 per cent concentration, and finally, with Hertzberg stain prepared according to the method given in Schorger (99).

The time required to prepare an individual slide and make the examination was approximately 1 minute, and in consequence a large number of solvents and nitrates could be examined in a relatively short space of time. A typical series of observations made with the Hertzberg stain is shown in Table XXXIII.

TABLE XXXIII

OBSERVATIONS ON A STAINED CELLULOSE NITRATE

Nitration No. 8-b (from untreated Novocell Sulfite pulp), 7.3 per cent nitrogen, one-half hour nitration, nitration level of 12.2 per cent.

Appearance of the fibers after ten minutes in contact with the Hertzberg stain:

Less than 7 % Nitrogen:

Under Ordinary Light:

Ten % of the fibers stained a dark brown. Some fibers showed scattered patches, light brown or yellow in color.

Under Polarized Light:

The same fibers showed up a brilliant scarlet. Patches of light green gave a mottled appearance to some of the fibers.

Between 7 and 10% Nitrogen:

Under Ordinary Light:

Seventy per cent of the fibers were a fairly uniform light brown or yellow in color, containing a few lighter or darker patches.

Under Polarized Light:

The same fiber showed up light or dark green, with patches lighter or darker than the bulk of the fiber.

More than 10% Nitrogen:

Under Ordinary Light:

Twenty per cent of the fibers not stained at all, or only in spots unevenly distributed along the fibers.

Under Polarized Light:

The same fibers barely detectible, the spots showing up as clearly defined green areas even at high magnification (x 470).

EXPERIMENTAL RESULTS

'INCLUSION' OF LIQUIDS IN CELLULOSE.

1. The 'Inclusion' of Methanol and Benzene in Mercerized, Dried Linters:

The amount of benzene retained by cellulose samples dried by solvent-exchange from water through methanol to benzene was of paramount importance in the determination of the nitrogen content of nitrated samples by the yield method, for the latter depended upon an accurate knowledge of the bone-dry weight of the starting material. Staudinger, et al (60) found that a cellulose dried through solvent-exchange retained large amounts of the last liquid used in the solvent-exchange series. A number of preliminary calculations, by the yield method, of the nitrogen contents of cellulose nitrates prepared from swollen linters showed an agreement with the micro Kjeldahl results that appeared incomprehensible on a basis of the amount of benzene included according to Staudinger (3.4%, Appendix V). Agreement between the two sets of nitrogen values was, however, sufficiently irregular that it became desirable to obtain a quantitative measure of the amount of benzene retained by the swollen linters under the conditions employed in the present studies.

Several attempts to determine the benzene content of dried, swollen celluloses by conversion of the benzene to the m-dinitrate and a colorimetric determination of the latter (100) were unsuccessful, although it appeared that

the amount was less than 1 per cent. The amount was determined finally by the two laborious gravimetric methods outlined in the Experimental Part, with the results shown in Table XXXIV.

TABLE XXXIV

PER CENT OF METHYL ALCOHOL AND BENZENE RETAINED IN CELLULOSE MERCERIZED AND DRIED BY SOLVENT EXCHANGE

Method of Inclusion Detn.	% Methanol Included.	% Benzene Included.	% Wt. loss upon Merc.[a]
Individual Operations	0.14	0.19	1.74
Reaction Cells	0.30	0.61	1.52 1.51

Both methods involved a knowledge of the loss in weight occasioned by mercerization (Column 3, Table XXXIV) and of the bone-dry weight of the mercerized sample obtained by drying directly from water in a vacuum at 100°. The increases in weight resulting from drying thoroughly in the same way from methanol (Column 2) and from benzene (Column 3) were obtained by individual operations in the first method and in special reaction cells in the second. These cells made it possible to carry out the entire series of treatments and weighings without transferring the cellulose, and the results are considered to be quite accurate. Although the weight increases shown were retained presumably indefinitely when the samples were maintained in vacuum at 100°, prolonged steeping in water was found to eliminate them and to recover products which, when dried, had the exact weight of the controls.

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a. Matthes (53) reports the solubility of native cellulose fiber in 10 per cent solution of sodium hydroxide as 1.4%.

As a result of these experiments it was concluded that a thorough washing of the swollen samples to be used in moisture determinations would be sufficient to remove any organic liquid. Accordingly, this method was adopted for the determinations of the bone-dry weights of swollen linters samples. Collapsed samples were also prepared by immersion of swollen linters in distilled water for approximately one week. During this time the water was withdrawn several times a day by means of a filter stick and the material re-immersed in distilled water. These precautions, adhered to in subsequent work, made it unecessary to consider errors that might theoretically arise from inclusion of benzene or methanol.

2. <u>The Inclusion of Amines in Untreated Cotton Linters</u>:

A series of amines was chosen for a further study of the phenomenon of liquid inclusion in cellulose. The amines were selected because they provided a series of low boiling liquids varying in molecular length (methyl-, ethyl-, propylamines, etc.) and in molecular diameter (primary, secondary or tertiary amines), and because a nitrogen analysis would provide a ready means of determining what part of any included material was actually amine.

In a preliminary experiment duplicate samples of cotton linters whose bone-dry weights were accurately known

were immersed for 48 hours in 25 ml. volumes of ethylamine (72% in water), diethylamine and triethylamine. The samples were freed from excess amine and were dried to constant weight (100° - 10 mm. - P_2O_5). Those which had been immersed in ethylamine and diethylamine were slightly discolored, for the most part on the surface. Samples immersed in triethylamine were brown in color throughout and showed numerous brown, burnt-looking patches on the surface. The original bone-dry weight of the starting materials and the presumably bone-dry weights of the treated materials being known, the per cent of included amine could be determined readily. These values were confirmed by micro Kjeldahl nitrogen determinations.

TABLE XXXV

PER CENT INCLUSION OF AMINES IN NATIVE CELLULOSE

	Amine Included					
	Ethylamine (72% in H_2O)		Diethylamine		Triethyl-	
% of amine included	0.9,	0.7	2.7,	2.7	1.7,	1.7
% Nitrogen, based on % amine included	...	0.23	...	0.52	...	0.24
% Nitrogen, determined by micro Kjeldahl analysis	...	0.18	...	0.47	...	0.22

The quantity of amine included appeared to be sufficiently high to warrant continuing the experiments. Samples from the same lot of extracted cotton linters were weighed out in duplicate and their bone-dry weights accurately determined. Two 1 - g. samples were immersed in 20 ml. portions of ethylamine, diethylamine, triethylamine and butylamine for 1 week. They were then placed in a desiccator and dried for ten days (25° - 0.3 mm. - P_2O_5), each sample being weighed every 2 days. Those immersed in ethylamine and diethylamine attained constant weight within 2 days, but the others were still decreasing in weight after 10 days.

Sufficient material was drawn from each sample for three micro Kjeldahl nitrogen determinations. The samples were then dried to constant weight (100° - 1 mm. - 5 days). The per cent of amine included at 25° and 100°, as calculated from the final weights and from the nitrogen analyses are presented in Table XXXVI.

The check determinations by the micro Kjeldahl method show without doubt that the inclusion causing the increase in weight was amine. The amount of triethylamine included in the native cellulose dried for 10 days at 25° followed by drying directly at 100° was appreciably and unaccountably higher (5.6%) than the amount included in the native cellulose dried directly at 100° (1.7%).

TABLE XXXVI.

PER CENT OF AMINES RETAINED BY A NATIVE CELLULOSE AT 25° AND 100°

% Amine or Nitrogen	Amine Included			
	Ethylamine 72% in H_2O	Diethyl-amine	Triethyl-amine	Butyl-amine.
	%	%	%	%
% Amine Included at 25°	1.1, 0.9	2.8, 2.4	9.0, 7.8	16.7, 17.2
% " " at 100°	0.7, 0.8	2.5, 2.3	5.5, 5.7	7.2, 7.2
% N. in sample dried at 25°:				
a. From % inclusion	0.34 ...	0.54 ...	1.25	3.20 ...
b. From micro Kjeldahl analyses.	0.31 ...	0.50 ...	1.07	3.11 ...

3. Inclusion of Amines in Mercerized Cotton Linters:

In order to determine if mercerization would have an effect upon the degree of inclusion, a 2 - g. sample of mercerized linters was treated in a reaction cell with 20 ml. of ethylamine (72% in water) for a 24-hour period and dried to constant weight (100° - 0.5 mm. - P_2O_5). The increase in weight was found to be 1.65%, or somewhat higher than the value of 0.97% found for a native cellulose, and a systematic investigation of the inclusion of amines in mercerized cellulose was then undertaken.

Five samples of native cotton linters, each approximately 2 g. in weight, were placed in the reaction cells and the bone-dry weight of each sample was accurately determined on separate samples. Each sample

was heated with 11% sodium hydroxide solutions for 2 hours at 0 to 5° and washed with ice-water until the washings were neutral to litmus. One sample was dried directly from water in order to check the amount of material (1.51%) removed by the mercerization alkali; each of the remaining samples was covered with one of the selected amines and left standing for 24 hours. All samples were dried for 8 days at room temperature (0.5 mm. - P_2O_5). Finally, each of the amine-treated linters was washed with 4 liters of distilled water over a period of 6 days and dried to constant weight (100° - 0.5 mm. - 8 days). The amount of each amine included is shown in Table XXXVII.

TABLE XXXVII

PER CENT OF AMINES RETAINED BY A MERCERIZED CELLULOSE AT 25°, 100° AND AFTER WASHING

Amine Included	Ethylamine 72% in H_2O %	Diethyl-amine %	Triethyl-amine %	Butyl-amine %
At 25°	3.3	3.3	3.1	18.2
At 100°	2.3	2.5	2.3	6.4
After Washing	0.0	0.0	0.46[a]	0.41

Amines, therefore, which could not be removed by prolonged heating in vacuo were removed, either

a. After washing and drying this sample showed a few areas of dark brown discoloration, indicating that the washing was probably imperfectly carried out.

completely or nearly so, by prolonged extraction with water.

The study of amine inclusion was extended to several additional amines, including amyl-, octyl- and hexadecylamine. The general technique used was identical with that described above, with two important modifications.

a. Mercerization, washing and solvent exchange were all carried out at 0 to 6°, thus ensuring the retention of Cellulose Hydrate II allotropic modification throughout all operations.

b. The water in the mercerized fibers was replaced by methyl alcohol and the methyl alcohol was replaced in turn by a solution of the given amine in methanol (in 1:1 volume ratio where possible, otherwise a saturated solution of the amine), each amine solution being left in contact with the cellulose for 48 hours at 0 to 5°.

A suction line was attached to the capillary tubing of the cells and all superficial liquid was drained off. The samples were then dried at room temperature (0.2 mm. - P_2O_5) for six weeks. As may be seen from Table XXXVIII, six week's drying under these conditions was sufficient to reach constant weight in the case of ethyl-, triethyl- and hexadecylamine only. An approximate value is given in the last line of Table XXXVIII for the amount of amine inclusion which would be approached

asymptotically in each case. The high boiling point of the octylamine (b. p. = 179°) might account for the fact that it was removed at such a slow rate compared with the amylamine (b. p. = 104°).

TABLE XXXVIII

PER CENT OF VARIOUS AMINES INCLUDED BY A MERCERIZED CELLULOSE DRIED AT 25°

Time of	AMINE INCLUDED (IN %)							
	Ethyl	Di-ethyl	Tri-ethyl	Ethyl	Butyl	Amyl	Octyl	Hexa-decyl
2	3.26	7.55	6.44	3.26	12.3	13.5	33.2	14.6
3	2.86	7.05	5.96	2.86	11.3	13.0	17.9	12.8
4	2.86	6.90	5.96	2.86	11.1	12.5	17.3	12.7
5	2.82	6.75	5.93	2.82	10.9	12.2	16.2	12.7
6	2.83	6.65	5.93	2.83	10.7	12.0	15.6	12.6
n[b]	2.8	6.0	5.9	2.8	10	11	11.5	12

All samples were discolored: the cellulose treated with octylamine, in particular, was dark brown throughout, that treated with amylamine was a lighter color throughout, and others were principally discolored on the surface, or outer portions.

All samples were then dried to constant weight (100° - 0.1 mm.) for 1 week. As seen from the results shown in Table XXXIX, the per cent of amine retained

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a. Dried at 25° and 0.2 mm. pressure over phosphorus pentoxide.

b. Extrapolation to infinite drying time.

TABLE XXXIX

PER CENT OF VARIOUS AMINES INCLUDED BY A MERCERIZED CELLULOSE DRIED AT 100°

Amine	Density	Molec. Weight	Molec. Volume	b. p. of Amine (°C)	% Amine Included[a]
Ethyl	0.706	45.1	64	16.6	2.2
Diethyl	0.711	73.1	103	55.5	4.3
Triethyl	0.723	101.2	140	89.5	5.6
Ethyl	0.706	45.1	64	16.6	2.2
Butyl	0.740	73.1	99	77	6.3
Amyl	0.761	87.2	115	104	7.7
Octyl	0.777	129.2	165	179	9.5
Hexadecyl	0.8?	241.5	300?	322	11.5

increased with molecular diameter (ethyl - diethyl - triethyl) and with chain length (ethyl - butyl - amyl - octyl and hexadecyl). The relationship between per cent amine included and the number of carbon atoms in the amines is shown more clearly in Figure XIV.

Sufficient material was withdrawn from each cell for at least 4 micro Kjeldahl nitrogen determinations. The cells were the filled with distilled water for 48 hours in order to swell the samples, and all samples were washed over a period of 1 week with methanol and over a period of 1 week with distilled water. All samples were then dried to constant weight (100° - 0.2 mm.). Corrections being made for the material removed for nitrogen analysis, the bone-dry weight of the material was calculated. The results are shown in

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a. The per cent of amine included was calculated on a basis of the weight of cellulose plus amine dried to constant weight at 100° and the bone-dry weight of the mercerized cellulose, taking into account the 1.5% of cellulose removed by the mercerization process.

FIGURE XIV

PER CENT INCLUSION AND NUMBER OF CARBON ATOMS FOR A SERIES OF AMINES

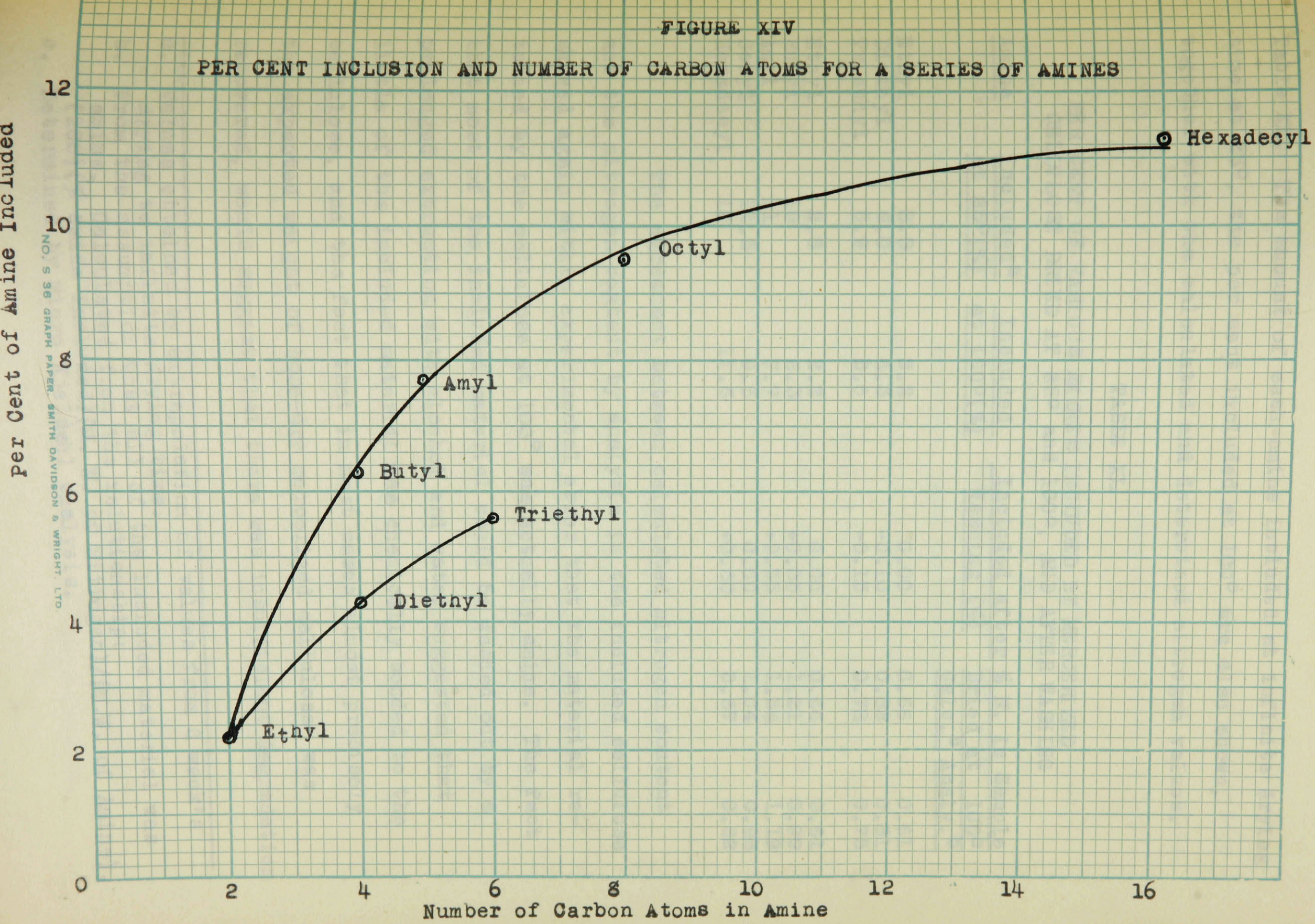

Table XL. The amount of each amine included at infinite drying time at 25°, the per cent included at 100° are also shown, together with the calculated and determined nitrogen values.

TABLE XL

PER CENT OF VARIOUS AMINES INCLUDED BY MERCERIZED CELLULOSE DRIED AT 25° and 100°, AND AFTER WASHING

Amine	Included[a] at 25°(%)	Included at 100°(%)	Included after Washing (%)	% N. in Sample Dried at 100°	
				Calc.[b]	Analy.[c]
Ethyl	2.8	2.2	0.00	0.66	0.61
Diethyl	6.0	4.3	-0.10	0.82	0.81
Triethyl	5.9	5.6	-0.15	0.78	0.75
Ethyl	2.8	2.2	0.00	0.66	0.61
Butyl	10	6.3	+0.35	1.21	0.99
Amyl	11	7.7	+0.55	1.24	1.19
Octyl	11.5	9.5	0.00	1.04	0.98
Hexadecyl	12	11.5	+0.60	0.67	0.62

The agreement between calculated nitrogen content and the nitrogen comtent by analysis in the included cellulose showed again within experimental error that the material retained by the cellulose at 100° was actually amine. The fact that most of the included material could be washed out by a prolonged extraction with alcohol and water suggested that little of the included material was chemically bonded to the cellulose, and the fact that in most cases almost precisely the expected weight of bone-dry mercerized cellulose was recovered, would suggest that there was insufficient degradation

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a. Values obtained by extrapolation of values from 6 week's drying to infinite drying time.
b. From the assumption that all of the included material was amine. Calculated from the relationship: (100)(% amine included)(M. W. of Nitrogen)/(M.W. of Amine).
c. Determined by micro Kjeldahl analysis.

to form any appreciable amount of methanol- or water-soluble products. Thus it was probable that the bulk of the cellulose remained substantially unaffected during the studies, in spite of the marked discoloration of the samples when dried at 100°.

Most of the cellulose samples, after having been washed with alcohol and water and dried at 100°, were only slightly discolored, and those samples which had been treated with ethyl-, diethyl-, and triethylamine could scarcely be distinguished from the original linters. The cellulose from the treatment with octylamine, however, was a medium brown in color throughout, and the sample from treatment with hexadecylamine showed considerable surface darkening.

When the amine-treated samples were covered with water after the drying procedure at 100°, they showed normal wetting and swelling characteristics, especially those dried from the low molecular weight amines. In the case of the sample which had been dried from hexadecylamine, however, not only did the whole mass of cellulose, but also individual fibers, remained suspended for 48 hours and showed no signs of swelling. Upon the addition of methanol the whole mass became rapidly swollen and moist, and sank to the bottom of the reaction cell. This observation has little bearing on the present studies of inclusion, but is recorded as being of possible interest in the preparation of completely water-proof fibers. Hexadecyl-amine would, of course, be impractical for this purpose,

but there is no obvious reason why any of the normal straight-chain paraffin hydrocarbons with more than 18 carbon atoms, or mixtures of them, could not be used for the impregnation of cellulose fibers by some such solvent-exchange process as discussed above.

EFFECT OF PRETREATMENTS ON THE NITRATION OF CELLULOSE

1. Confirmation of the Results Obtained by Brown and Purves (1):

In the preliminary part of the present investigation, the effect of collapsing the fiber structure by wetting with water and re-drying upon the nitration reactivity was confirmed under essentially the same conditions as were used by Brown and Purves (1). This effect, which will be referred to as 'decreased nitration reactivity' was never of a large order of magnitude, in contrast to the numerous variations discussed in the Historical Introduction, and seldom caused a decrease of more than 0.5% in nitrogen content. In these experiments (Table XLI) the nitrated products displayed definite variations in nitrogen content and in the per cent decrease caused by 'collapsing' the swollen celluloses prior to nitration. These samples were then mercerized by method (a) (p. 86), which probably yielded a metastable mixture of Hermans' Cellulose Hydrates I and II. Mercerization by method (b) probably recovered the swollen samples entirely in the more stable cellulose Hydrate I form and the decrease in nitrogen content caused by

'collapsing' the starting material was uniform at 3.1 to 3.3 per cent.

TABLE XLI

A COMPARISON OF THE NITROGEN CONTENTS OF SWOLLEN, COLLAPSED AND UNTREATED COTTON LINTERS NITRATED UNDER STANDARD CONDITIONS

Work by:	Cotton Linters			
	Untreated	Swollen	Collapsed	% Decrease
	% N[a]	% N[a]	% N[a]	in % N.[b]
Brown and Purves	12.20	12.04	11.42	5.2
	12.20	12.19	11.84	2.9
	12.26	12.16	12.00	1.3
	12.26	12.05	11.77	2.3
Present Author: [c]	12.20	12.06	11.74	2.7
	11.89	11.80	11.55	2.1
	12.21	12.21	12.00	1.7
[d]	12.10	12.06	11.69	3.1
	12.24	12.20	11.84	3.3
	11.95	11.85	11.47	3.1

It should be emphasized that these nitration reactivities were determined for cotton linters. The effect of the gross physical structure of the starting material upon the nitration characteristics was found to be

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a. Nitrogen contents determined by micro Kjeldahl analysis.

b. $$\frac{\%\ N\ (\text{Swollen Linters}) - \%\ N\ (\text{Collapsed Linters})}{\%\ N\ (\text{Swollen Linters})}$$

c. Determined in preliminary investigations to check results obtained by Brown and Purves. Samples mercerized by method (a) (p. 86).

d. Obtained incidental to later studies of nitration variables. Samples mercerized by method (b) (p. 86).

of a higher order of magnitude (p. 141) and would effectively mask any reactivity decrease caused by changes in fine structure.

2. The Effect upon Nitration Reactivity of Alternate Wetting and Drying of Collapsed Linters:

In an effort to determine if the decrease in nitration reactivity resulting from the drying of a swollen cellulose from water could be magnified, a sample of swollen linters was alternately immersed in water for 48 hours and dried (25° - 20 mm. - P_2O_5) for a total of nine times. Samples were withdrawn after the first, fifth and ninth drying and nitrated under standard conditions.

As may be seen from Table XLII, there was a

TABLE XLII

THE EFFECT ON THE NITRATION OF COLLAPSED LINTERS OF ALTERNATE WETTING AND DRYING

Treatment Prior To Nitration.	% N Micro Kjeldahl
Untreated	12.2
Collapsed: once	12.00
5 times	11.89
9 times	11.78

progressive decrease in reactivity upon wetting and drying which apparently approached a limit of approximately 5%. This estimate was based on a nitrogen content of 12.21% for the swollen linters nitrate and on an extrapolated value of 11.60 per cent for an infinite number of wetting and drying procedures on the collapsed linters. Although the ultimate decrease from 12.2 to 11.6 per cent nitrogen

was not impressive, the corresponding change in nitrate substitution, from 2.31 to 2.13 moles per glucose residue, represented the inactivation of (2.31 - 2.13)/(2.31) or approximately 8 per cent of all the hydroxyl groups entering into substitution at a nitrogen level of 12 per cent.

The same type of decrease in activity upon alternate wetting and drying of a viscose cellulose was found by Matthes, et al (p. 31). The effect was considered to be due to a restricted syneresis of the cellulose gel structure. The fact that the same limiting Q-value for retained water could be attained by a single immersion of the dry fiber in liquid ammonia, followed by evaporation of the ammonia, was credited to the great expansion of the crystalline unit cell in the presence of liquid ammonia and to the reversion to the native modification upon its removal. The expansion and contraction of the whole cellulose structure apparently permitted maximum mobility or flexibility of the macromolecules and a maximum realignment with subsequently a maximum degree of hydrogen bonding. It should be of interest to determine the nitrating characteristics of cotton linters similarly treated with liquid ammonia.

3. The Effect of Nitration Time Upon the Nitration Reactivity of Swollen, Collapsed and Untreated Linters:

Standard samples of swollen, collapsed and untreated cotton linters were nitrated under standard conditions for

five hours in order to determine whether prolonged nitration would overcome the inactivation caused by wetting with water and direct re-drying. The preliminary results in Table XLIII show that such indeed was the case.

TABLE XLIII

NITROGEN CONTENTS OF SWOLLEN, COLLAPSED AND UNTREATED COTTON LINTERS NITRATED UNDER STANDARD CONDITIONS FOR ONE HALF AND FOR FIVE HOURS

Cotton Linters	Nitration Time	
	1/2 Hour	5 Hours
	% N[a]	% N[a]
Untreated	12.23	12.24
Swollen	12.21	12.24
Collapsed	12.00	12.26

The dependence of the nitrogen level upon the nitration time was then investigated more fully by nitrating standard samples of swollen, collapsed and untreated cotton linters under standard conditions for times ranging from 2 hours to 1 to 2 minutes. Both the micro Kjeldahl and the yield nitrogen values are given in Table XLIV, from which it may be seen that the two sets of values agreed within ± 0.08 per cent in all but a single nitration, the collapsed sample of Run No. 3, where for some unaccountable reason the variation was + 0.23%. The error was probably in the yield nitrogen value, possibly because of the introduction of some foreign body into the filtering crucible containing the nitrated product.

A. Nitrogen contents determined by micro Kjeldahl analysis.

TABLE XLIV

THE NITROGEN CONTENTS OF NITROCELLULOSES FROM SWOLLEN, COLLAPSED AND UNTREATED COTTON LINTERS NITRATED FOR VARIOUS TIMES

Run No.	Nitn. Time (min.)	Nitrocellulose obtained from Swollen Linters		Collapsed Linters		Untreated Linters	
		Yield % N	Micro Kj. % N	Yield % N	Micro Kj. % N	Yield % N	Micro Kj. % N
1	120	12.29	12.33	12.07	12.03	12.36	12.38
2	60	12.16	12.20	11.96	11.88	12.22	12.25
3	30	12.03	12.06	11.91	11.68	12.15	12.13
4	15	11.90	11.90	11.47	11.52	11.98	12.00
5	5	11.60	11.52	11.03	11.10	11.63	11.67
6	1[a]	11.20	11.12	10.16	10.24	10.97	10.93

The results shown in Table XLIV are quite similar to those obtained by a number of other workers on nitration (2)(101) and are also comparable to the effect of prolonged immersion in water upon the Q-value of cellulose deactivated or collapsed by drying (p. 23).

4. Validity of Nitrogen Determinations:

The validity of the results obtained in the present nitration studies depends primarily upon the reliability of the nitrogen determinations. The micro Kjeldahl method of analysis was checked in the initial phases of the work by means of a sample of recrystallized urea (nitrogen content = 46.6 per cent). The same sample

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a. Difficulties in manipulating the nitrated samples made this time indeterminate between 1 and 2 minutes for any one of the three samples.

of urea was analyzed at intervals, or, as occasionally happened, at such times as the yield nitrogen values and the micro Kjeldahl nitrogen values were in poor agreement. In one case it was desired to test the purity of a sample of sym-diethyldibenzyl urea (nitrogen content of 9.62%). Analysis by the standard method used throughout the present work gave the following results: 9.39, 9.40, 9.41, 9.40 and 9.39 per cent. Reproducibility was excellent, although the absolute values was probably 0.2 per cent low.

The degree of reproducibility obtained upon pure organic nitrogen containing compounds (± 0.01%) was seldom achieved for cellulose nitrates at any level of nitration. A typical set of results from the micro Kjeldahl analyses is shown in Table XLV.

TABLE XLV

REPRODUCIBILITY OF NITROGEN CONTENTS AS DETERMINED BY MICRO KJELDAHL ANALYSIS

Sample	Linters Modification (Run No. 1)		
	Swollen	Collapsed	Untreated
	% N	% N	% N
1	.....	11.93	12.28
2	12.23	11.96	12.23
3	12.22	11.89	12.30
4	12.24	11.91	12.29
5	12.21	11.95	12.30

In Table XLVI is shown the difference between micro Kjeldahl and yield nitrogen values for a complete series of nitrations.

TABLE XLVI

DIFFERENCE BETWEEN MICRO KJELDAHL AND YIELD NITROGEN VALUES FOR CELLULOSE NITRATES PREPARED FROM SWOLLEN, COLLAPSED AND UNTREATED LINTERS

Run No.	Nitration Level(% N)	Cellulose Modification		
		Swollen	Collapsed	Untreated
		Diff.%[a]	Diff. %[a]	Diff. %[a]
1	12.4	-0.04	+0.04	+0.02
2	12.3	-0.04	+0.08	-0.03
3	12.1	-0.03	+0.23	+0.02
4	12.0	0.00	-0.05	-0.02
5	10.9	+0.08	-0.07	-0.04
6		+0.08	-0.08	+0.04

There may be more than a fortuitous regularity in the difference between yield and micro Kjeldahl values in the case of the swollen linters. As the nitration level decreased the yield nitrogen values increased fairly regularly over the others, perhaps because of an increase in hygroscopicity of the nitrate with a decrease in the degree of nitration. The lower the nitrogen content, the more free hydroxyl groups will be present in the nitrated cellulose, and the greater will be the amount of hydrate water postulated by Hermans (21). Since this water can be removed only by severe drying conditions, the drying of nitrates for the determination of nitrogen contents by the yield method would be incomplete, and would result in a high value. The moisture present in the nitrates used for micro Kjeldahl analysis was checked periodically by drying samples of the cellulose nitrates at 100° or 86° and in a high vacuum for several days. It may be assumed that the hydrate water would be removed by this drying procedure; consequently the micro Kjeldahl nitrogen values should be

the more correct.

If the above assumptions are valid, then it is difficult to understand why the order of difference between the two sets of nitrogen values should be reversed in the cases of nitrates prepared from collapsed linters (Table XLVI). One possible explanation is that the hydrate water effect is operative in the case of the collapsed linters, but there is an additional vitrification effect which is sufficiently strong to reverse the relationship between yield and micro Kjeldahl nitrogen values. The lower the degree of nitration, the greater the per cent of vitrified regions present in the collapsed samples, and the less the number of hydroxyl groups available to retain water. It is not unreasonable to suppose that the small number of vitrified regions remaining after nitration of collapsed linters might alter the equilibrium moisture relationships, since such vitrified regions have a much more marked effect upon the cellulose - water relationship than they do upon nitration reactivity.

Calculations showed to what extent a slight amount of moisture tenaciously retained by the cellulose could cause a variation in the difference between micro Kjeldahl and yield nitrogen determinations. In the case of Sample No. 6 from swollen linters (Table XLIV) the difference between yield and micro Kjeldahl nitrogen was 11.20 - 11.12 = 0.08%. A decrease of 0.25% in the moisture content of the nitrate

would decrease the yield nitrogen value to 11.15% and would increase the micro Kjeldahl value to 11.14%, that is, would reduce the difference between the two values from 0.08% to 0.01%. In practice, the moisture samples were weighed to constancy within ± 0.1 mg., and this weight represents ± 0.25% on a 50 mg. sample of cellulose nitrate.

The above considerations are of a qualitative nature only, and a quantitative interpretation of the differences between yield and micro Kjeldahl nitrogen contents of a homologous series of celluloses must await more precise experimentation. It is quite possible that the heterogeneous nature of the fiber nitrates renders impossible any greater degree of accuracy in nitrogen determination than that obtained in the present work. In any case, the fairly wide spread in micro Kjeldahl nitrogen values (± 0.05%) and the marked sensitivity of the yield nitrogen determinations to moisture contents illustrate the caution that must be exercised in interpreting small changes in such data.

5. Variation in the Composition of Nitrating Acid in the Nitration of Swollen, Collapsed and Untreated Linters:

Standard samples of the three modifications of cotton linters were nitrated for one-half hour at 18° with a ratio of nitrating acid to cellulose of 100 to 1 by weight, and nitrating acids of various composition as shown in Table XLVII.

TABLE XLVII

NITROGEN CONTENT OF CELLULOSE NITRATES FROM SWOLLEN, COLLAPSED AND UNTREATED LINTERS NITRATED WITH NITRATING MIXTURES OF VARIOUS COMPOSITIONS

Run No.	Linters Modification					
	Swollen		Collapsed		Untreated	
	Yield % N	Micro Kj. % N	Yield % N	Micro Kj. % N	Yield % N	Micro Kj. % N
7[a]	13.50	13.56	13.22	13.13	13.61	13.62
8[b]	11.85	11.85	11.61	11.47	11.97	11.91
10[c]	6.76	6.68	6.80	6.47	6.76	6.69

a. H_2SO_4: HNO_3: H_2O = 45: 50: 5% by weight

b. " " " 41: 45: 14% " "

c. " " " 37: 40: 23% " "

There was a marked difference in the appearance of the nitrates obtained in Run No. 10; those from the swollen linters were superficially identical with the original cellulose. The nitrates from the untreated and collapsed linters, however, were hard, lumpy, and retained none of their original fibrous appearance in bulk form, although under the microscope the individual fibers did not differ in this way from other nitrated fibers. The nitrates obtained in Runs 8 and 10 discolored upon standing for several months, and the micro Kjeldahl determinations were more than ordinarily variable.

This preliminary study should be checked and extended because the agreement between yield nitrogen and micro Kjeldahl nitrogen contents was unaccountably poor in

the case of the collapsed samples. At a level of less than 7% nitrogen it was virtually impossible to obtain reliable nitrogen values by analysis; finally, because of the loss of one complete run, the gap between the 7 per cent and the 12 per cent nitrogen levels is too wide.

It is of interest to note, however, that the decrease in nitration reactivity of the collapsed modifications appeared to be independent of nitration level up to 13.6% nitrogen. As may be seen from Table XLVIII one of the results obtained by Brown and Purves would indicate that this apparently constant decrease in nitration reactivity extends to results at 13.9% nitrogen obtained by nitration in non-aqueous medium. The constant decrease in nitrogen reactivity obtained upon nitration of linters with sulfuric acid - nitric acid - water nitration mixtures, if verified,

TABLE XLVIII

DIFFERENCE IN PER CENT NITROGEN BETWEEN COLLAPSED AND UNTREATED LINTERS CELLULOSE NITRATES AT VARIOUS NITROGEN LEVELS

Run No.	Per Cent Nitrogen Untreated	Collapsed	Decrease in N Content(%)	% Decrease in N Content[a]
A[b]	13.95	13.61	0.34	2.4
B[b]	13.90	13.66	0.24	1.7
C[b]	13.76	13.63	0.13	1.0
D[b]	13.76	13.62	0.12	0.9
7	13.62	13.13	0.49	3.6
3	12.13	11.68	0.45	3.7
8	11.91	11.47	0.44	3.7
10	6.69	6.47	0.22	3.3

a. $\frac{\%\ N\ (Untreated\ Linters) - \%\ N\ (Collapsed\ Linters)}{\%\ N\ (Untreated\ Linters)}$

b. From data obtained by Brown and Purves (1). The same materials nitrated with a phosphoric acid - nitric acid mixture under standard conditions.

would mean that the vitrified areas postulated as one possible cause of the phenomenon are equally inacessible or unreactive to all technical nitrating mixtures.

6. Effect Upon Nitration of Heating Cellulose:

In a preliminary experiment, three samples of cellulose, one swollen, one collapsed and one untreated, were heated for 4 days at 20 mm. pressure and 100°. When these samples were then subjected to a standard 15 minute nitration, the nitrogen contents as determined by the yield method were 12.00, 11.94 and 12.07 per cent, respectively. These results would suggest that the heat treatment had altered the nitration characteristics of the three linters with respect to each other, because from the closely parallel results in Table XLIV, Run No. 4, the expected values were 11.90, 11.47 and 11.98 respectively.

In order to check this possibility further, a more precise study of the effects of heating was undertaken. Samples from each modification were heated at 56, 86 or 100° for 48 hours at 20 mm. pressure and nitrated for 5 minutes under standard conditions. A nitration time of 5 minutes was chosen in order to magnify any differences which might exist between the various samples. The results, shown in Table XLIX show that the difference between the swollen and collapsed samples was obliterated at 86°, but not at 56°.

TABLE XLIX

EFFECT OF HEAT ON THE NITRATION CHARACTERISTICS OF SWOLLEN, COLLAPSED AND UNTREATED COTTON LINTERS

Run No.	Heated at(°C)[a]	Linters Modification Nitrated[b]		
		Swollen % N[c]	Collapsed % N[c]	Untreated % N[c]
18	Unheated	11.65	11.00	11.65
16	56	11.69	11.33	11.78
14	86	11.20	10.20	11.30
12	100	11.26	11.26	11.28

The results of this series of nitrations made with a nitration time of one-half hour (Table L) supported the trend of the earlier experiment.

TABLE L

EFFECT OF HEAT ON THE NITRATION CHARACTERISTICS OF SWOLLEN, COLLAPSED AND UNTREATED COTTON LINTERS

Run No.	Heated[a] at (°C)	Linters Modification Nitrated[d]		
		Swollen % N[c]	Collapsed % N[c]	Untreated % N[c]
17	Unheated	12.10	11.80	12.28
15	56	12.20	11.91	12.30
13	100	12.20	12.22	12.30

a. Heated at 20 mm. pressure for 48 hours prior to nitration.

b. Standard 5 minute nitration.

c. Per cent nitrogen determined by calculation from yield of nitrate.

d. Standard 30 minute nitration.

In neither of these series of nitrations was the moisture content of the various starting materials known with precision, except that in all cases it was probably less than 1 per cent, and in Run 13 may have been close to 0%.

Because untreated and swollen cotton linters showed essentially the same behaviour toward nitration in all the preceding investigations, and because of the additional work necessary to determine the bone-dry weights of the swollen samples, no nitrations of this modification were carried out in the following and many of the subsequent nitration series.

A sufficient number of untreated and collapsed linters samples for several series of nitrations and precise determinations of moisture contents were weighed out. All samples were brought to the same moisture content at room temperature under vacuum in a desiccator, and then subjected to a 48-hour heat treatment prior to nitration in the apparatus and according to the procedure outlined in the Experimental Part (p. 89). Each sample was weighed after 48 hours at the temperature selected and then nitrated within several minutes of the weighing. The various samples were exposed to atmospheric moisture for no more than a few seconds, and the moisture contents determined upon removal of the samples from the heating chambers corresponded quite closely to the moisture content at the time of nitration. The results of this more detailed and more precisely controlled investigation

are presented in Table LI.

TABLE LI

THE EFFECT OF HEAT ON THE NITRATION OF UNTREATED AND COLLAPSED COTTON LINTERS

Run No.	Heated[a] at (°C)	Linters Modifications Nitrated[b]			
		Untreated		Collapsed	
		% H_2O[c]	% N[d]	% H_2O[c]	% N[d]
19	Unheated	0.80	12.01	1.30	11.53
20	56	0.32	12.09	0.46	11.79
21	66	0.39	12.11	0.39	11.79
22	76	0.19	12.13	0.29	11.87
23	86	0.07	12.20	0.06	11.86
24	100	0.00[e]	12.21	0.00[e]	11.87

Table LI shows that the failure of the samples from the collapsed cellulose to attain the same nitrogen level as the untreated series under identical conditions of nitration cannot be attributed to variation in moisture content. In samples 21 to 24 the latter in both series varied from 0.39 to zero without changing the nitrogen levels by more than 0.1%.

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a. Samples heated for 48 hours over phosphoric pentoxide at 1 mm. pressure and the temperature recorded.

b. Standard 15 minute nitration.

c. Per cent water in the sample at the time of nitration.

d. Per cent nitrogen by calculation from the nitrate yields.

e. Weights obtained by heating for 48 hours at 100° and 1 mm. pressure are assumed to represent bone-dry weights and the moisture content of the samples so treated to be zero.

The nitration time was then increased to 30 minutes. The nitrating acid used contained approximately one-third less water than the standard acid in order to obtain a somewhat higher nitrogen level. There was no particular purpose to be served in nitrating at any exact nitrogen level, and it was considered desirable to have samples with nitrogen contents spread over a fairly wide range to serve for later investigations.

As may be seen from Table LII, the effect of

TABLE LII

THE EFFECT OF HEAT ON THE NITRATION CHARACTERISTICS OF SWOLLEN, COLLAPSED AND UNTREATED COTTON LINTERS

Run No.	Heated[a] at (°C)	Linters Modification Nitrated[b]					
		Untreated			Collapsed		
		% H_2O[c]	Per Cent N.		% H_2O[c]	Per Cent N.	
			Yield[d]	Micro Kj.		Yield	Micro Kj.
31	Unheated	0.52	12.50	12.50	0.83	12.08	12.05
32	56	0.38	12.52	.....	0.53	12.21	.....
33	66	0.39	12.60	.....	0.52	12.29	.....
34	76	0.31	12.54	.....	0.41	12.31	.....
35	86	0.19	12.61	.....	0.10	12.39	.....
36	100	0.00	12.61	.....	0.00	12.42	12.37

a. Samples heated for 48 hours over phosphoric pentoxide at 3 mm. pressure and at the temperature recorded.
b. Standard half-hour nitration.
c. Per cent moisture in sample at time of nitration.
d. Per cent nitrogen calculation from the yield of nitrates.

preheating upon the nitrogen level of the products from untreated and collapsed linters was confirmed.

It was desirable to check the nitrogen values by analysis as well as by the gravimetric method. This was done, but in order to reduce to a minimum the time-consuming micro Kjeldahl analyses, only the extremes within the series were so analyzed. As may be seen from Table LII, the correspondence between the nitrogen contents of the products determined by the two methods was within the limit of accuracy of the analytical method (± 0.05%).

In a further series of nitrations it was intended originally to eliminate the variable of moisture content by heating the samples over the same range as had been used in the previous series (unheated and at 56, 66, 76, 86 and 100°) and then allowing all samples to attain the same moisture content by exposure to the atmosphere for approximately 24 hours. However, differences in the hygroscopicity of the various samples depending upon the intensity of the heat treatment as well as upon the cellulose modification made it difficult to bring all samples to the same moisture content within a reasonable time after the heat treatments. All samples were therefore nitrated at the moisture contents shown in Table LIII.

As might have been expected, the nitration level attained by the untreated linters was little effected by heat treatments up to 100° provided that the final moisture

TABLE LIII

THE NITRATION OF UNTREATED AND COLLAPSED LINTERS HEATED AT VARIOUS TEMPERATURES AND ALLOWED TO PICK UP MOISTURE

Run	Heated[a]	Linters Modification Nitrated[b]					
		Untreated			Collapsed		
		% H_2O[c]	Per Cent N.		% H_2O[c]	Per Cent N.	
			Yield[d]	Micro Kjeld.		Yield[d]	Micro Kjeld.
31	Unheated	4.6	12.31	12.28	7.8	11.68	11.65
32	56	4.3	12.32	.....	6.5	11.69	.....
33	66	4.3	12.31	.....	6.5	11.72	.....
34	76	4.1	12.29	.....	6.2	11.72	.....
35	86	...	12.31	.....	5.3	11.77	.....
36	100	4.0	12.28	12.30	4.6	11.82	11.80

content was nearly constant. Irregular moisture contents made it difficult to interpret the data for the collapsed samples, although the last line of Table LIII clearly shows that at approximately the same moisture content (4 to 4.6%) the relative unreactivity caused by collapse depressed the nitrogen content from 12.3 to 11.8%.

Tables LIV and LV describe more drastic heat

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a. Samples heated for 48 hours over phosphoric pentoxide at 3 mm. pressure and the temperature recorded, allowed to stand for 24 hours exposed to the atmosphere and nitrated.

b. Standard 15 minute nitration.

c. Per cent moisture in sample at time of nitration.

d. Per cent nitrogen by calculation from the yield of nitrates.

TABLE LIV

THE NITRATION OF UNTREATED AND COLLAPSED LINTERS HEATED TO 100 AND 140° PRIOR TO NITRATION

Run No.	Heated[a] at (°C)	Linters Modification Nitrated[b]					
		Untreated			Collapsed		
		% H_2O[c]	Per Cent N.		% H_2O[c]	Per Cent N.	
			Yield[d]	MicroKj.		Yield[d]	MicroKj.
41	Unheated	0.4	12.51	12.36	0.6	11.89	
42			12.50			11.90	11.86
						11.92	
39	100	0.0	12.52	12.49	...	.....	.....
			12.54				
37	140	0.0	12.62	12.61	0.0	12.40	12.38
38			12.64	12.65			

TABLE LV

THE NITRATION OF SWOLLEN, COLLAPSED AND UNTREATED LINTERS HEATED TO 125 AND 150° PRIOR TO NITRATION

Run No.	Heated[a] at (°C)	Linters Modification Nitrated[b]		
		Swollen	Collapsed	Untreated
		% N[d]	% N[d]	% N[d]
70	100	12.69	12.48	12.71
75	125	12.65	12.58	12.83
76	150	12.74	12.58	12.86
77	150	.....	12.47[f]	.....

a. Samples in Run 39 heated for 48 hours over phosphoric pentoxide at 100°. Samples in Runs 37 - 38 heated in an open, standard Cenco drying oven maintained at approximately 140°.

b. Standard 15 minute nitration.

c. Per cent moisture in sample at time of nitration.

d. Per cent nitrogen by calculation from the nitrate yields.

e. Sample opened immediately after heating and allowed to pick up 0.7% moisture (in 5 minutes) and nitrated immediately.

treatments. Several points of interest are shown by the results in these tables. The agreement between the nitrogen contents of duplicate samples determined by the gravimetric method (± 0.02%) was somewhat better than that obtained in the micro Kjeldahl analyses (± 0.05%). It is apparent that the slight rise in nitrogen level increases for all three linters modifications upon heating at temperatures above 100°. The increase in nitrogen content of sample No. 77 indicates the extreme sensitivity of cellulose to small amounts of moisture in the nitration reaction.

7. The Nitration of Swollen, Collapsed and Untreated Cellulose from a Sulfite Pulp.

Swollen, collapsed and untreated samples were prepared from a bleached, refined sulfite pulp (Novocel[a]) which had never been dried. The same methods were used in the preparation of each modification as described for the corresponding linters samples. Approximately 1 - g. samples of each of the three pulp modifications were dried to constant weight (25° - 1 mm. pressure - P_2O_5). A number of each type sample were then heat-treated for 48 hours (1 mm. - P_2O_5), weighed, and all samples nitrated. As may be seen from Table LVI, the results were exceedingly erratic and the checks between duplicate samples were poor.

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a. The author wishes to thank Dr. S. Wang, of Cellulose Industrial Research Ltd., Hawkesbury, Ontario, for the gift of sulfite pulp used in the experiments described.

TABLE LVI

NITRATION OF SWOLLEN, COLLAPSED AND UNTREATED 'NOVOCEL' SULFITE PULPS

Run No.	Heated[a] at (°C)	Pulp Modification Nitrated[b] Swollen % N[c]	Collapsed % N[c]	Untreated % N[c]
43a	100°	8.2	9.6	7.8
b		10.8	11.0	7.2
46a	Unheated	11.0	7.8	8.8
b		11.0	8.9	7.3

It is quite apparent from Table LVI that the coarse pellet form of the pulp inhibited nitration to a quite marked degree. In order to ensure macrohomogeneity of the starting materials, all three modifications were treated dry in a Waring blender to give a light, fluffy product no dissimilar in appearance to cotton linters (Runs 55 to 58). Approximately 1.04 g. (air-dry) of the samples so treated were dried to constant weight (over phosphoric pentoxide at 0.4 mm. pressure and 25 or 100°). Two samples of untreated cotton linters were included in the nitration series as a check on nitration level, which in Run 55 was quite close to this control.

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a. Samples heated for 48 hours over phosphoric pentoxide at 0.3 mm. pressure and the temperature recorded.

b. Standard half-hour nitration.

c. Per cent nitrogen by calculation from the yield of nitrates.

TABLE LVII

NITRATION OF SWOLLEN, COLLAPSED AND UNTREATED PULP PREPARED IN THE SAME FORM AS LINTERS

Run No.	Heated[a] at (°C)	Pulp Modification Swollen % N[c]	Collapsed % N[c]	Nitrated[d] Untreated % N[c]	Linters[d] Untreated % N[c]
55	25	12.20	11.30	12.03	12.31 12.29
58	100	12.08	12.00	12.20	

The yield values for per cent nitrogen correlated poorly with the per cent nitrogen as determined by the micro Kjeldahl analyses, being quite low in the former case for the swollen pulp samples, perhaps because of benzene inclusion.

It has long been known that the gross physical form of the starting material has an effect upon the nitration characteristics of a cellulose (90)(102), and a comparison of the results obtained in Runs 46 and 55 provides a semi-quantitative measure of the magnitude of the effect. The results suggest that in the use of a wood pulp cellulose for the preparation of cellulose

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a. Samples heated for 48 hour over phosphoric pentoxide at 100°.

b. Standard half-hour nitration.

c. Per cent nitrogen by micro Kjeldahl analysis.

nitrates, the physical form of the starting material is the most important single factor, followed by the amount and nature of non-cellulosic compounds, then conditions used in the enriching or refining process, and finally the conditions of drying for a given method of preparing the cellulose prior to nitration.

DISCUSSION OF RESULTS

THE EFFECT OF PRETREATMENTS ON THE NITRATION OF CELLULOSE

The retention of benzene and other organic liquids during the drying of cellulose, the reliability of the analytical methods employed, and other matters closely concerned with experimental technique were adequately discussed in the preceeding pages. So, too, was the fact that the decreased reactivity of collapsed linters to nitration could be completely overcome by prolonging the time of nitration from 30 minutes to 5 hours. Shortening the time to a few minutes grossly exaggerated the effect, which therefore depended upon the rate of diffusion of the nitrating acid into the fibers. The effect also approached a limiting value with repeated swelling and collapsing.

Brown and Purves (1) have already suggested that this decrease in reactivity might be accounted for by an increase in the amount of 'vitrified cellulose' postulated by Jayme (p. 25) produced by dense but unorganized hydrogen bonding in portions of the amorphous cellulose fraction. Whatever the distribution of these bonds within the fiber may be, they are stable to acetylation with acetic anhydride and pyridine (103), are very slowly broken by immersion for weeks in water, and are broken only with difficulty by the swift permutoid nitration reaction.

The following discussion concerns the effect of various other pretreatments upon the nitration characteristics of various celluloses.

1. Preheating of Nearly Dry Samples (100 to 150°):

There was found to be a slight but persistent increase in nitrogen content of cellulose nitrates prepared from untreated, nearly dry cellulose with increased temperature of preheating, as shown from a summary of the results shown in Table LVIII.

TABLE LVIII

THE EFFECT OF HEAT ON THE NITROGEN CONTENTS OF CELLULOSE NITRATES PREPARED FROM UNTREATED CELLULOSE

Run No.	Cellulose (Untreated)	Nitn.[a] Time(min.)	Preheated 48 hrs, 1 mm, at:	% H_2O at time of Nitrn	% N. Yield	% Increase in N Content[b]
17	Linters	30	Unheated	0.5	12.28	
13	"	"	100°	0.0	12.32	0.33
41	Linters	30	Unheated	0.8	12.50	
39	"	"	100°	0.0	12.54	0.32
19	Linters	15	Unheated	0.8	12.01	
24	"	"	100°	0.0	12.20	1.67
31	Linters	15	Unheated	0.52	12.50	
36	"	"	100°	0.00	12.60	0.8
68	Linters	15	Unheated	0.50	12.63	
70	"	"	100°	0.00	12.71	0.63
57	Sulfite Pulp	30	Unheated	0.8	12.03	
60	" "	"	100°	0.0	12.20	1.40
41	Linters	15	Unheated	0.4	12.50	
37	"	"	140°	0.0	12.63	1.04
68	Linters	15	Unheated	0.5	12.63	
75	"	"	125°	0.0	12.83	1.58
76	"	"	150°	0.0	12.86	1.82

a. The composition of the nitrating mixture varied slightly from pair to pair.

b. Per cent increase in nitrogen content:

$$= (100)\frac{(\%\ N_{heated} - \%\ N_{unheated})}{(\%\ N_{unheated})}$$

Although, for reasons already outlined (p. 134), the number of nitrations carried out on the swollen samples was considerably less than those on the untreated and collapsed modifications, the results were comparable to those for untreated linters. The swollen samples differed from the untreated samples, however, in always giving a nitrate with a greater tendency to become discolored and with a very slightly lower nitrogen content. This small but consistent difference may have been caused by the method of solvent exchange used in the preparation of the swollen samples. Hermans (21) has noted that when a moist, highly swollen viscose fiber was immersed in pure glycerol, the fiber shrank appreciably, because the water diffused into the glycerol more rapidly than the glycerol could penetrate into the fiber structure. If the same sample of viscose was immersed for 1 - hour periods in glycerol - water solutions of decreasing water content, the fiber could be saturated with 100 per cent glycerol with only slight attendant shrinkage. In all the procedures used in the present work, the swollen, moist samples were immersed in methyl alcohol of high concentration (95% or higher) and it is at least possible that some shrinkage (ie, collapsing) of the samples may have taken place. It should be well worthwhile checking this assumption by replacing the water in a freshly prepared swollen sample by the dropwise addition of methyl alcohol, preferably over a 24 - hour period, in the preparation of swollen cellulose.

The effect of heating nearly dry collapsed linters or sulfite pulp for 48 hours at 100° is shown by the data collected in Table LIX. In general, the increase in nitrogen

TABLE LIX

EFFECT OF HEAT ON THE NITROGEN CONTENTS OF CELLULOSE NITRATES FROM COLLAPSED LINTERS OR SULFITE PULP

Run No.	Cellulose Collapsed	Nitn. Time (min.)	Preheated, 48 hrs, 1mm at:	% H_2O at Time of Nitration	% N Yield	% Increase in N Content[a]
17	Linters	30	Unheated	0.8	11.80	
13	"	"	100°	0.0	12.10	2.52
19	Linters	15	Unheated	1.3	11.53	
24	"	"	100°	0.0	11.87	2.94
68	Linters	15	Unheated	0.6	12.24	
70	"	"	100°	0.6	12.48	1.96
56	Sulfite Pulp	30	Unheated	0.5	11.30	
59	" "	"	100°	0.0	12.00	6.2
39	Linters	15	Unheated	0.6	11.90	
38	"	"	140°	0.0	12.40	4.2
68	Linters	15	Unheated	0.6	12.24	
75	"	"	125°	0.0	12.58	2.78
76	"	"	150°	0.0	12.58	2.78

content upon heating is considerably higher than was found for untreated cellulose. In no case, however, was the nitrogen content of a nitrate, obtained with ordinary nitration periods from collapsed linters after heating

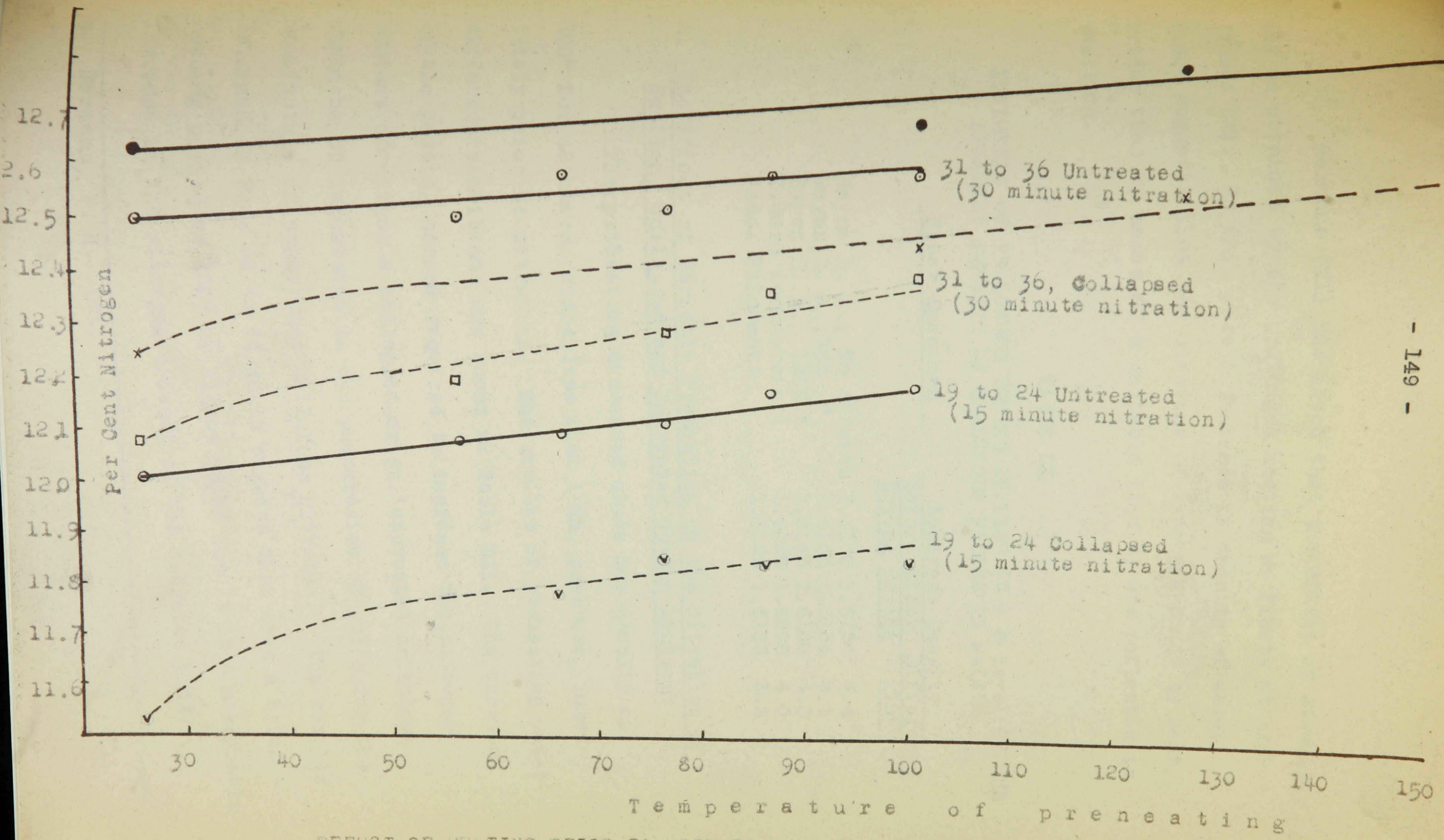
---

a. Per cent increase in nitrogen

$$= (100)\frac{(\%\ N_{heated} - \%\ N_{unheated})}{(\%\ N_{unheated})}$$

equal to the nitrogen content of the control samples of untreated linters. This discrepancy might have been due to slight errors in the moisture determination or to the fact that the decreased reactivity caused by the process of 'collapsing' of the cellulose during drying is not completely restored by heating. The effect of heating both untreated and collapsed linters upon the nitration level is shown in Figure XV.

If the decreased reactivity of the collapsed cellulose is caused by strong hydrogen bonding which retards the rate of nitration, then the above results may be interpreted as meaning that heating results in a marked decrease in hydrogen bonding. It might be assumed that severe thermal agitation would tend to break unorganized hydrogen bonds between primary or secondary hydroxyl groups on adjacent cellulose chains, but the present evidence supports the view that the effects of such cleavages are retained by the cooled cellulose. A similar, but rather inconclusive observation was made by Staudinger, et al, in their acetylation studies (p. 49). These workers found that the reactivity of an 'active' cellulose increased from 21 to 30 per cent acetylation upon preheating in high vacuum at 100°. An inactive cellulose, on the other hand, corresponding to the collapsed modification of the present discussion, did not increase appreciably in per cent acetylation when similarly treated, which is in direct contradiction to the results discussed above.



EFFECT OF HEATING PRIOR TO NITRATION ON THE NITROGEN CONTENT OF CELLULOSE NITRATES PREPARED FROM UNTREATED AND COLLAPSED COTTON LINTERS

Hermans (21) has noted that the effect of steaming may be obtained by the prolonged heating of fibers at 110° (Table LX). In this case a decrease in density of about 0.004 suggests that the cleavage of hydrogen bonds by heat, rather than by means of a suitable liquid, was reflected in swelling.

TABLE LX

INFLUENCE OF PROLONGED DRYING AT 110° (7 - 8 days) ON THE APPARENT DENSITY OF CELLULOSE FIBERS IN WATER[a]

Fiber Specimen	Apparent Density Before Drying	Apparent Density After Drying	Difference x10^3
Rayon L. A., No stretch	1.6178	1.6134	4.4
Rayon L. A., 70% "	1.6165	1.6134	3.1
Rayon H. A., 120% "	1.6143	1.6100	4.2
Sedura (commercial)	1.6138	1.6098	4.0
Model Filaments	1.6165	1.6123	3.2

2. The Effect of Variable Preheating on the Nitration of Swollen, Collapsed and Untreated Cotton Linters:

The preheating discussed above was usually at 100° for 48 hours, under less than 1 mm. pressure, immediately prior to nitration. The results of preheating under different conditions are shown in Table LXI. The question of the heating period required to increase the nitrogen content of either a collapsed or an untreated cellulose would be of importance in the preparation of pulps for the manufacture of commercial cellulose nitrates. The results obtained in Runs 68 to 74 would suggest that even a brief heating period at 100° or higher would result in a measurable increase in the nitrogen content of the nitrated product,

a. Hermans, P. H. (21)

TABLE LXI

THE INFLUENCE OF VARIABLE DRYING CONDITIONS ON THE NITRATION OF SWOLLEN, COLLAPSED AND UNTREATED LINTERS

Run No.	Nitn. Time (min.)	Conditions of Preheating	Linters Modification		
			Swollen % N[a]	Collapsed % N[a]	Untreated % N[a]
3	30	Unheated	12.06	11.68	12.13
11[b]	"	100°, 20 mm., 4 days	12.07	12.12	12.08
68	15	Unheated	12.62	12.24	12.63
69	"	4 hrs, 100°, 0.3 mm.	.....	12.42	12.68
		48 " " " "	12.69[c]	12.48	12.71
		2 weeks," " "	12.62	12.58	12.74

but that the increase in reactivity is not complete even upon prolonged heating. The effect is largest in the case of collapsed linters and least in the case of swollen linters.

An increase in the degree of crystallinity during heating perhaps offers an explanation for this phenomenon. Since the crystalline component of cellulose offers little if any resistance to penetration of the nitrating reagent, the causes of the decreased reactivity should lie almost exclusively within the amorphous regions. Any increase in crystallinity, either as defined by X-ray analysis or as an increase in molecular order which would lead to the formation of crystallites too small to change the X-ray diffraction pattern, should lead to an increase in

---

a. Per cent nitrogen determined by calculation from yield of nitrate.
b. A preliminary run in which the moisture contents of the starting materials was not known.
c. Sample contaminated during drying, and gave a badly discolored nitrate.

nitration reactivity. Waller, Bass and Roseveare (104) studied the effect of heat, with or without the presence of moisture, on native and regenerated cellulose, and found definite evidence that the heating of a regenerated cellulose in the presence of air and oxygen resulted in an increase in crystallinity (as measured by X-ray analysis) and a development of the native modification. Heating under anhydrous and oxygen-free conditions showed considerably less effect, it is true, but a lack of change in the X-ray pattern could mean that the recrystallization involved small areas. An increase in crystallinity would account for a lowered regain (104), a decrease in the apparent density in water (21) and an increase in nitration reactivity.

It has been reported (105) that 50% of native cellulose was converted to cellulose IV upon heating in glycerol, whereas the conversion reached approximately 90% when the cellulose was mercerized prior to heating. The increase in conversion was attributed to the higher degree of swelling in the mercerized cellulose. X-ray analysis of the heated products showed that the amount of crystalline material increased, and it was suggested that the lateral order of the amorphous regions increased. The heating of jute for 4 hours at 110° diminished the hygroscopicity, and the effect was attributed to an increased crystallization of the amorphous regions (106). It has been noted (107) that when cellulose was heated at 300 to 600°, it became

entirely amorphous.

The hypothesis that the rate of nitration depends upon the crystalline-amorphous ratio finds support in a presentation by Chedin on the mechanism of nitration of cellulose. Chedin (108)(109) together with Tribot (110) have suggested that during the course of technical nitration the nitric acid molecules alone penetrate the crystalline components, while the more bulky sulfuric acid molecules are capable of penetrating the more loosely packed amorphous regions only. All three nitrating components thus penetrate the amorphous regions; nitric acid and water penetrate the crystallites, and the water formed in the crystallites during nitration is withdrawn by attraction of exterior sulfuric acid. When equilibrium is reached, the crystallites should thus contain a slight excess of the hydrates of nitric acid; the amorphous regions should contain a slight excess of hydrated sulfuric acid and a slight deficiency of nitric acid. It was concluded that nitration proceded by way of a rapid reaction between the more readily accessible hydroxyl groups in the amorphous regions and by a slower reaction between less readily accessible hydroxyl groups within the crystallites. The latter assumption, however, is rendered doubtful by the well-founded view that the effective nitrating agent in a technical nitrating mixture is the small, mobile, positively charged nitronium ion (111)(112). Such an ion would be expected to penetrate a hydrogen bonded crystal lattice with great facility.

3. <u>The Effect of Moisture on the Nitrogen Content of Nitrates from Untreated and Collapsed Linters:</u>

This effect was studied by drying a number of samples to less than 1% moisture at 25° or to 0 per cent moisture at 100°, and then allowing each sample to stand exposed to the atmosphere until the desired moisture content had been reached. The weighing flasks were then tightly stoppered and left standing for 24 hours to permit equilibrium to be reached. The various samples, with a moisture content ranging from 1 to 12 per cent, were then nitrated under standard conditions. All samples showed a decrease in nitrogen content with increasing moisture content (Table LXII) greater than could be accounted for by dilution of the nitrating acid. The ratio of nitrating acid to cellulose was constant at 100 to 1 by weight. Five per cent moisture (based on the weight of the cellulose) would result in a dilution of 0.05 g. of water in 100 g. of nitrating acid, or of 1 part in 2,000. An 0.5% change in the concentration of water (ie, a dilution of 1 in 200) in a standard nitrating acid, such as used in the present series of investigations, would alter the nitration level by no more than 0.1%. On the other hand, there might be much greater dilution of the nitrating mixture within the cellulose structure. Diffusion of water from the cell structure is known to be slow, and in almost all cases the nitration time was in the technical range of 30 minutes, or at the more rapid nitration time of 15 minutes.

TABLE LXII

THE EFFECT OF MOISTURE ON THE NITROGEN CONTENT OF NITRATES PREPARED FROM UNTREATED AND COLLAPSED COTTON LINTERS

Run No.	Linters Modification Nitrated[a]					
	Collapsed			Untreated		
	% H_2O[b]	Per Cent N.		% H_2O[b]	Per Cent N.	
		Yield[c]	Micro Kj		Yield[c]	Micro Kj.
61	1.4	11.83	11.81	1.0	12.10	12.13
62	4.5	11.60	.....	3.7	12.00	.....
63	7.8	11.49	11.44	6.4	11.93	.....
64	11.1	11.47	11.43	7.8	11.92	.....
65	0.2	11.60	11.56	1.0	12.18	12.19
66	5.5	11.70	11.43	3.8	12.00	12.00
67	10.4	.....	11.36	7.2	11.88	11.90

The small amount of water present at the time of nitration would be, for the most part, strongly bonded to the cellulose chains, and would have a tendency to dilute the nitrating acid at points of nitration along the chain, thus resulting in a slight shift of the reaction equilibrium towards denitration.

---

a. Standard half-hour nitration.

b. The per cent moisture in the samples at the time of nitration.

c. Per cent nitrogen determined by calculation from yield of nitrates.

The nitration of the collapsed linters was also found to be sensitive to the moisture content of the samples at the time of nitration (Table LXIII). Again the reduction

TABLE LXIII

EFFECT OF MOISTURE CONTENT ON THE NITRATION OF COLLAPSED LINTERS

Run No.	Nitn. Time (min.)	Heated 48 Hrs, 0.3mm at: (°C)	% H_2O at Time of Nitration	% N (Yield)
61	30	Unheated	1.4	11.93
62	"	"	4.5	11.60
63	"	"	7.8	11.49
64	"	"	11.1	11.47
65	30	100	0.2	11.56[a]
66	"	"	5.5	11.43[a]
67	"	"	10.4	11.36[a]
30	15	100	4.6	11.82
29	"	86	5.3	11.77
28	"	76	6.2	11.72
27	"	66	6.5	11.72
26	"	56	6.5	11.69
25	"	Unheated	7.8	11.68
76	15	150	0.0	12.58
77	"	"	0.7	12.47

in nitration level is considerably greater than could be accounted for by dilution of the nitrating acid.

The decrease in nitrogen content with increasing moisture content of the nitrated cellulose is in agreement with the findings of Chedin and Tribot (110) that the nitration of linters with a nitric acid - sulfuric acid - water nitrating mixture was slow by omission of drying prior to nitration. It should be noted, however, that in a later

a. Nitrogen contents determined by micro Kjeldahl analysis.

contribution by the same authors (113) they reported that the addition of water to a sulfuric acid - nitric acid nitrating bath increased the nitration of a given cellulose, the maximum rate occurring at 11% moisture. It was suggested that the water acted as an activator by breaking secondary valence bonds between hydroxyl groups, thus rendering them more accessible to the nitrating agent. The rate therefore increased, although the degree of nitration decreased.

INVESTIGATION OF THE PHYSICAL HETEROGENEITY OF SELECTED CELLULOSE NITRATES

The hypotheses that have been advanced to account for the different degrees of nitration produced by a standard procedure from different celluloses reduce on the physical level to the assumption that the efficiency of diffusion of the nitrating agent into the cellulose is capable of change. It is also possible, of course, that variable degrees of denitration occurred at the surface of the fibers when the latter were recovered by 'drowning' the spent nitration liquors in aqueous ethanol. Heterogeneities in the distribution of nitrate groups caused in this way would presumably include some of microscopic dimensions. Unequal penetration of the nitrating agent within the fiber might also cause heterogeneities of the same order of magnitude, and it seems reasonable that very brief nitration times (5 minutes or less) tend to produce them.

Nitrate-poor regions could also exist on a submicroscopic scale and be of colloidal dimensions comprising a few short chains or limited sections of long chains, or even of large sections of the amorphous component. The concept of hornification or vitrification postulated by Jayme might produce this type of heterogeneity. Finally, heterogeneity on the molecular scale involves the distribution of nitro groups among the second, third and sixth positions of the glucose residues and between one glucose residue and another. This distribution results from the fact that technical nitrating mixtures produce an equilibrium between nitrated and unnitrated hydroxyl groups.

It was obviously desirable that, if possible, some idea be obtained of the nature of any heterogeneity in the nitration level of the nitrated celluloses prepared in this research.

An examination of the pertinent literature (2)(114) led to the conclusion that any chemical degradation of the nitrates would not prove particularly fruitful, at least not unless undertaken on a scale beyond the scope of the present work. In a detailed study of the degradation products obtained by treating cellulose nitrates with aqueous alkalis, Kenyon and Grey (115) pointed out that the alkaline degradation of nitrated cellulose was a complicated reaction, made up of oxidation, hydrolysis, and resinification.

Only a small fraction of the decomposition products were separated and identified, and it seemed probable that the series of concurrent, deep-seated reactions would mask effectively even gross variations in fine structure or distribution of nitrate groups or heterogeneously nitrated areas within the fiber. All the chemical degradations considered, for example methylation, reduction of the nitrate groups, hydrolysis and identifications of the partly methylated glucoses, involves exposure of nitrate groups to alkaline conditions at one stage of the process. Such a project, indeed, had been attempted with complete lack of success by two previous workers in this laboratory (116) (117). A recent investigation of the relative reactivity of the nitrate groups in nitrate methyl glucosides has proven more successful (118).

Hambraeus and Ranby (119) made an electron-microscopic examination of several cellulose nitrates precipitated from solution, and claimed to have been successful in distinguishing several morphological components. In the present work, however, solution followed by precipitation of the nitrates would not provide information on the original fine structure of the nitrates, since complete solution would probably destroy the very heterogeneity it was desired to examine. A more attractive alternative would be an examination of the nitrates in fiber form in the hope of distinguishing variations in structure at the higher magnifications. Such an examination, however, would entail the preparation of sample replicas by a one-stage or two-stage

replica techniques involving distillation of metals (120)(121). It was decided that more time would be required for the preparation of replicas for examination in the electron microscope than was available.

Brown and Purves (1) reported that solutions in acetone or butyl acetate of cellulose nitrates prepared from some collapsed linters possessed a 'grained' appearance. This phenomenon was verified for the nitrates obtained in Runs 4, 5 and 6 (p. 125), which also showed to the greatest extent the difference in nitrogen content between swollen and collapsed linters. Solutions of all three nitrates from the collapsed linters had the same almost imperceptible hazy or 'grained' appearance, while solutions of the nitrates prepared from swollen or collapsed linters appeared to be optically clear. An attempt to determine particle size in these solutions by the Tyndall spectra method of Heller, et al (96) was not successful. The values for D (light absorption at various specific wave lengths) were quite small, scarcely larger than the accuracy of the instrument at the higher wave-lengths (D = 0.003 at λ= 6,000A units), and the exponent n was found to be 4 or higher. Thus the dispersed particles giving rise to the grained appearance of the solutions from the collapsed linters nitrates were less than 500A units in diameter (Figure XIII) or alternatively the method simply broke down altogether under the conditions used. If the latter explanation was correct, the failure might lie in the fact that

the refractive indices of the solvent (acetone) and the solute particles (cellulose nitrate of unknown nitrate content) were too close together, and the ratio m = 1.56/1.36 = 1.15 lay far outside the range (1.24 ± 0.01), within which the method was claimed to be valid.

The standard microscope, in conjunction with ordinary light, polarized light and a variety of stains, has been used intermittently for years in studies of cellulose nitrates. The intensity and sign of polarization change with degree of nitration (122), and the uniform light blue interference colors of highly nitrated fibers can serve as a criterion of homogeneous nitration. As the nitration level decreases, the polarizing colors change through dark blue, indigo, red, orange and yellow, varying at any given nitrogen level with the refractive index of the nitrate, the composition of the nitrating acid, changes in fine structure, the degree of magnification and the source of light and the type of cellulose (123). The application of the polarizing microscope can be broadened by the use of dyes; Fensom and Fordham (124) for example, in a study of the solvent action of nitroglycerine on cellulose nitrates in the range 11.4 to 12.6 per cent nitrogen, used Crystal Violet dye to accentuate differences apparent in the appearance of the fibers under the polarizing microscope.

A number of the cellulose nitrates reported in the

present work were examined microscopically. It was possible to distinguish between samples differing in nitrogen content by approximately 1 per cent by a combination of solubility characteristics and relative polarization intensities. A nitrate containing 10.8% nitrogen would show approximately the same brilliance under crossed Nicols as a nitrate containing 12.8%, since the polarization sign changes at approximately 11.8% nitrogen, but the solubility characteristics would be considerably different.

It was likewise possible to distinguish gross heterogeneities such as were present in the nitrates resulting from a short nitration time (Nitration No. 6) or from the Novocel pulp nitrated in pellet form (No's. 43 to 48). Samples 10-s and 48-b possessed approximately the same nitrogen contents (6.7 and 7.3% respectively) but showed up entirely differently under polarized light. No. 10-s was nitrated with an acid to give an equilibrium nitrogen content of approximately 7% in a one-half hour nitration, while No. 48-b (from untreated sulfite pulp) was nitrated in pellet form for one-half hour with a nitrating acid which should have given 12.2% nitrogen. No. 10-s appeared quite bright under crossed Nicols and showed no change when covered with acetone. No. 48-b, on the other hand, showed marked variation in appearance when viewed under crossed Nicols, one half of the fiber being quite bright and the other half barely discernible, thus indicating a broad spread of nitrogen contents between fibers.

When covered with acetone, half of the fibers remained untouched and half were immediately dissolved or highly swollen; under crossed Nicols the undissolved fibers were quite brilliant. The latter fraction was therefore only superficially nitrated, while nitration in the other fraction was rather high.

The microscope studies were, however, largely negative as regards distinguishing between nitrates prepared from swollen or collapsed linters. The solubility characteristics of the nitrates, the amount of residue and its appearance under ordinary and polarized light, appeared to be a function of the total fiber rather than upon component parts of it. At a given nitrogen level and under conditions of limited solubility, a fraction of the fiber dissolved completely and another fraction was unattacked. In one case only was there any marked difference between nitrates from a swollen and collapsed linters. When the nitrate from the swollen linters in Run No. 4 (11.90% Nitrogen) was covered with amyl acetate, practically all of the fibers dissolved within a few seconds, leaving a few scattered, tiny fragments which showed up brilliantly under crossed Nicols. When the nitrate from the collapsed linters was examined, approximately 95 per cent of the fiber appeared to dissolve immediately and completely. Under crossed Nicols, however, there appeared, not the residue of a few brilliantly polarized, scattered

fragments, but rather a pattern of spots just barely visible (at magnifications of 20, 80 and 470). The individual fibers were outlined in a faint pattern quite similar in appearance to a star constellation.

It was thought that this phenomenon might provide a means of distinguishing between the nitrates from swollen and collapsed linters, and perhaps lead to some idea of the nature of the heterogeneities in the latter case. With this in mind, a large number of the products were treated with various pure and mixed solvents. No similar phenomenon was observed with any nitrate of approximately the same nitrogen content. However, the same type of pattern was observed when No. 6-c was covered with isobutyl acetate, and No. 3-c with a 1:1 mixture of isobutyl acetate and di-butylphthalate, and, to a much less marked degree, when all three samples from Run No. 8 was covered with butyl acetate alone. It was decided on a basis of these results that the scattering effect under polarized light was probably a matter of selecting the proper solvent to give some precise optimum degree of limited solubility, and was not the result of any fundamental difference between nitrates prepared from swollen and collapsed linters. Consequently the investigation was not carried further.

The best method for detecting heterogeneous nitration, both between fibers and across individual fibers,

was found to be the use of the Hertzberg Stain (125), under ordinary and polarized light. The method revealed no differences between nitrates prepared from swollen and collapsed linters, but a discussion of the method is included here because of its general interest in a study of cellulose nitrates. The effect of the stain was time-variable, the time required for staining being a function of the nitrogen level, and all colors fading after several hours. Fibers with a nitrogen content of 12% did not stain at all, and fibers with less than 8% nitrogen stained within one minute. A uniformly nitrated cellulose stained quite evenly, and the colors changed from a rich dark brown at less than 6% nitrogen through various shades of brown and yellow to a faint yellow at 11% nitrogen. Under crossed Nicols the colors ranged from a brilliant scarlet at 7% nitrogen to a faint green at 11% nitrogen.

The method was found to be not only effective in distinguishing between fibers of different nitrogen content, but also in detecting heterogeneous nitration across individual fibers. The effect was particularly marked under crossed Nicols and at a high magnification (470), and typical observations were included among the Experimental Results. Its failure to differentiate between typical pairs of swollen and collapsed nitrates, or between swollen and collapsed nitrates from different runs but at the same nitrogen content, suggested that the heterogeneities in the latter were not greater in size than 5000A units, or

the wave length of visible light. The failure to detect heterogeneities by the light-scattering method was consistent with the view that they were smaller than 500A units in diameter, or were almost below the colloidal range. Although the evidence was highly uncertain and negative, it was not inconsistent with the view that 'vitrification', rather than heterogeneities caused by gross variations in the diffusion of the nitrating agent, was responsible for the slightly lower nitrogen contents and less perfect solubility characteristics of nitrates prepared from collapsed celluloses.

SUMMARY

In Table LXIX is presented an outline of the principal points established in the present work. In order to simplify the presentation, the results of a hypothetical series of treatments prior to nitration are outlined. It was not feasible to carry out such a series of experiments in practice, since any one series involved numerous samples and analyses and was likely to be based on the results of the preceding one. The relative values, however, in each case represent transpositions from results actually obtained.

In brief, considering a swollen and a collapsed cotton linters, nitrogen values ranging from 11.4 to 12.5 may be obtained in a rigorously standardized nitration, depending upon the history of the fiber between mercerization and nitration. Subsidiary researches on the inclusion of organic liquids in cellulose and on the optical properties of cellulose nitrates were also carried out.

TABLE LXIX

SUMMARY OF RESULTS ON THE NITRATION OF SWOLLEN, COLLAPSED AND UNTREATED COTTON LINTERS VARIOUSLY TREATED.

Treatment Prior to Nitration[a] (on page 169)	% N
Untreated Cotton Linters[b] (on page 169)	
Unheated:	
Nitrated at 0.5% moisture.	12.2
" " 5 % "	12.1
" " 10 % "	12.0
Heated:	
At 100° - 0.3 mm. pressure - 48 hrs, nitrated at 0% H_2O	12.3
" 125° " " " " " " " " "	12.4
" 150° " " " " " " " " "	12.5
" 100° " " " " " " " 0% "	12.3
" " " " " " " " " 5% "	12.1
" " " " " " " " " 10% "	12.0
Collapsed Cotton Linters	
Collapsed once	11.8
" 5 times	11.7
" 10 "	11.6
" an infinite number of times.	11.4
Unheated:	
Nitrated at 0.5% moisture.	11.8
" " 5 % "	11.5
" " 10 % "	11.4
Heated:	
At 25° (ie, unheated)	11.8
" 100° - 0.3mm. pressure - 48 hrs., nitrated at 0% H_2O	12.1
" 125° " " " " " " " " "	12.3
" 150° " " " " " " " " "	12.4
" 100° " " " " " " " 0% "	12.1
" " " " " " " " " 1% "	12.0
" " " " " " " " " 5% "	11.9
" " " " " " " " " 10% "	11.8
" " " " " "	

Footnotes to Table LXIX.

a. Conditions of Nitration:

Nitrating acid: sulfuric acid, nitric acid and water = 53.7, 30.0 and 16.3 per cent by weight, respectively.

Nitration time: 1/2 hour.

Nitration temperature: 18 to 20°.

Ratio of acid weight to cellulose weight: 100 to 1.

Flask shaken vigorously at 5-minute intervals during nitration.

Stabilization: Five 1/2-hour boiling periods in 1:1 by volume ethyl alcohol - water.

Starting material: cotton linters extracted with 2:1 benzene - ethyl alcohol for 48 hours, air-dried for 1 week, vacuum-dried at 0.3 mm. pressure over phosphoric pentoxide at room temperature to 0.5 - 0.6% moisture, then swollen and collapsed as described in Experimental Part.

b. Substantially the same results would be obtained upon nitration of swollen linters.

APPENDIX I

ACETYL CONTENTS OF A NUMBER OF CELLULOSE MODIFICATIONS VARIOUSLY TREATED

(Staudinger, H., Döhle, W., and Heick. O. J. für prakt. Chem. 161, 8-10, 191 (1943).

No.	Cellulose	D. P.	Treated in Succession as Shown and Acetylated under Standard	Acetyl %	% of OH Acet'd.
1	Cotton, M[a]	1050	$-H_2O$ - SD[b]	0.5	1.1
2	"	"	$-H_2O$ - pyridine - SD	26.5	59.1
3	Ramie, M	860	$-H_2O$ - SD	0.45	1.0
4	"	"	(3) - pyridine - SD	0.42	0.9
5	"	"	(3) - H_2O - pyridine - SD	19.5	43.5
6	Ramie, M	800	$-H_2O$ - SD	0.45	1.0
7	"	"	(6) - cyclohexane - SD	0.43	1.0
8	"	"	(6) - H_2O-Me Alc-ether-cyclohexane-SD	21.4	47.6
9	Ramie, M	800	$-H_2O$ - SD	0.45	1.0
10	"	"	(9) - H_2O - Me. Alc - SD	2.56	5.7
11	"	"	(9) - H_2O - Me. Alc - ether-SD	24.6	54.9
12	"	"	(9) - H_2O - Me. Alc - ether - cyclohexane - SD	22.7	51.1
13	"	"	(9) - H_2O - Me. Alc - ether - petroleum ether - SD	21.6	48.2
14	"	"	(9) - H_2O - Me. Alc - ether - benzene - SD	25.5	56.7
15	Cotton, M	670	$-H_2O$ - SD	0.42	0.9
16	"	"	(15) - H_2O - pyridine	18.5	41.3
17	"	"	(15) - H_2O - Me. Alc. - ether - benzene - SD	22.5	50.2
18	"	"	(15) - H_2O - Me. Alc. - ether - carbon tetrachloride - SD	22.6	50.4
19	"	"	(15) - H_2O - Me. Alc. - ether - ethyl acetate - SD	24.3	54.2
20	Ramie, M	880	$-H_2O$, dried at 15mm, 35°, 3days	0.45	1.0
21	"	"	" " " 0.1mm, 20°, 6days	0.42	0.9
22	"	"	" " " " 60°, 6days	0.40	0.9
23	"	"	" " " " 100°, 6days	0.47	1.0

APPENDIX I (continued)

No.	Cellulose	D. P.	Treated in Succession as Shown and Acetylated under Standard Conditions	Acetyl %	% of OH Acet'd.
24	Ramie, M	880	-S.E.D.[a], dried, 15mm., 35°, 3days	21.4	47.7
25	"	"	" " 0.1mm., 20°, 6 "	28.4	63.4
26	"	"	" " " 60°, 6 "	29.3	65.4
27	"	"	" " " 100°, 6 "	30.2	67.4
28	Cotton, M	670	-H_2O - SD	0.42	0.9
29	"	"	-(28) - H_2O - Me. Alc. -Acetone-SD.	24	53
30	"	"	-(29) - H_2O - SD	0.63	1.4
31	Cotton, M	1050	-H_2O - SD	0.42	0.9
32	"	"	-(31) - H_2O - Me. Alc. - ether-cyclohexane - SD	22.8	50.8
33	"	"	-(32) - H_2O - SD	0.30	0.7
34	"	"	-(33) - H_2O - Me. Alc. - ether-cyclohexane - SD	23.9	53.3
35	Ramie, M	800	-H_2O - SD	0.45	1.0
36	"	"	-(35) - H_2O - Me. Alc. - ether-cyclohexane - SD	21.4	47.7
37	"	"	-(36) - H_2O - SD	0.41	0.9
38	"	"	-(37) - H_2O - Me. Alc. - ether-cyclohexane - SD	24.8	55.3
39	Cotton, N[c]	850	-Dried at 0.1 mm., 20°, P_2O_5, 2d.	6.8	15.2
40	"	"	" " " " " " 10d.	7.6	16.9
41	Cotton, N	850	-SD for 4 days	1.39	3.1
42	" , M	"	-SD " 4 "	0.45	1.0
43	Cotton, N	850	-(41) - H_2O, dried 0.1mm, 20°, 10d	8.9	19.8
44	"	M 860	-(42) - " " " " "	0.40	0.9
45	Cotton, N	830	-H_2O - SD	8.1	18
46	"	M 830	-H_2O - pyridine	11.3	25.2
47	"	"	-H_2O - Me. Alc. - ether - cyclohexane - SD	10.4	23.2

APPENDIX I (Continued)

No.	Cellulose	D. P.	Treated in Succession as Shown and Acetylated under Standard Conditions	Acetyl %	% of OH Acet'd.
48	Cotton, M	810	-H_2O - SD	0.70	1.6
49	"	"	-H_2O - Pyridine	24.6	54.9
50	"	"	-H_2O - Me. Alc. - ether - cyclohexane - SD	22.8	50.9
51	Cotton, N 140°, 63hrs	840	-H_2O - SD	0.98	2.2
52	"	"	-H_2O - pyridine	10.9	24.3
53	(51) M	"	-H_2O - SD	0.79	1.8
54	(51) M	"	-H_2O - pyridine	25.7	57
55	Pulp[e], N	720	-H_2O - SD	9.1	20.1
56	"	"	-(55) - H_2O - Me. Alc. - ether-cyclohexane - SD	12.8	28.6
57	"	"	-(56) - H_2O - SD	11.0	24.5
58	(55), M	720	- H_2O - SD	0.71	1.6
59	"	"	-(58) - H_2O - Me. Alc. - ether - cyclohexane - SD	29.1	65.0
60	"	"	-(59) - treated with H_2O-SD	0.79	1.8
61	Viscose, N	375	- H_2O - SD	0.43	1.0
62	"	"	-(61) - H_2O - Me. Alc. - ether - cyclohexane - SD	37.1	82.7
63	"	"	-(62) - H_2O - SD	0.4	0.9
64	(61), M	375	- H_2O - SD	0.55	1.2
65	"	"	-(64) - H_2O - Me. Alc. - ether - cyclohexane - SD	33.0	73.6
66	"	"	-(65) - H_2O - SD	0.55	1.2

a. M = mercerized at 0°, 20% NaOH, 24 hours, neutralized, washed
b. SD = Standard Dried, 48 hours, 100°, 0.01 mm. pressure.
c. S.E.D.= Solvent Exchange Dried: H_2O - methyl alcohol - ether - cyclohexane - SD.
d. N = native, or unmercerized form of cellulose.
e. A spruce sulfite pulp.

APPENDIX II

CALCULATION OF THE PER CENT OF HYDROXYL GROUPS THEORETICALLY ACCESSIBLE IN VARIOUS MODIFICATIONS OF CELLULOSE

Cellulose	Per cent Crystalline Component	Fraction of Crystallite OH's on " Surface	% Total OH access. on Cryst. Surfaces	Fraction of Cryst. OH's in Cryst. Interior	Fraction of Crystallite Interior OH Accessible
a	b	c	d	e	f
Cotton	70				
Native	70	0.10	70x0.10 = 7	0.90	0
Mercerized	70	0.20	70x0.20 = 14	0.80	1/6
Wood Pulps	60				
Native	60	0.10	60x0.10 = 6	0.90	0
Mercerized	60	0.20	60x0.20 = 12	0.80	1/6
Regenerated	40				
	40	0.30	40x0.30 = 12	0.70	1/6

Cellulose	Fraction of Cryst. OH's Accessible.	% of Total OH's acces. in Cryst.	% of OH's Accessible in Amorph. Regions.	Total % of OH's Accessib.	Accessibil. Ratio
	g	h	i	j	k
Cotton					
Native	0	0	30	37.0	0.00
Mercerized	0.80/6	9.2	30	53.2	1.44
Wood Pulps					
Native	0	0	40	46	1.25
Mercerized	0.80/6	8.0	40	60	1.62
Regenerated	0.70/6	4.7	60	66	2.08

Notes:

b. Per cent crystalline material as determined by X-ray analysis.

APPENDIX II (continued).

Notes: (continued)

c. The values shown are approximations, and their selection is discussed on page 70.

e. 1 minus the fraction of crystallite hydroxyl groups assumed to be accessible on the crystallite surfaces.

f. It is assumed that the crystallites of native cellulose are impervious to penetration. It is assumed that 1/6 of the hydroxyl groups within the crystallite lattices of hydrate cellulose are available for hydrate formation or reaction.

j. The total accessibility will be the sum of the per cent of hydroxyl groups accessible within the amorphous regions, on the crystallite surfaces, and within the crystallite interior.

k. Accessibility ratio = accessibility of a given cellulose divided by the accessibility of native cotton linters.

APPENDIX III

CONVERSION OF HYDROCHLORIC ACID - FERRIC CHLORIDE HYDROLYSIS CRYSTALLINITY VALUES TO ACCESSIBILITIES[a]

Cellulose	Accessibility =100-crystally.	Selected Values	Corrected[b] Accessibilities
Cotton			
Native	6 to 7.5	7	26
Mercerized	11 to 15	13	48
Pulps			
Native	9 to 11	10	37
Mercerized	14.5	14.5	53
Regenerated			
Rayon	21 to 31	21	77

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a. Values selected from Nickerson and Habrle (68) and Contrad and Scroggie (71)

b. Accessibility of rayon set equal to 77 and all other values scaled accordingly. Value of 21 chosen for rayon because it gave the best values for the other corrected accessibilities.

APPENDIX IV

SAMPLE CALCULATION OF PER CENT NITROGEN IN CELLULOSE NITRATES BY YIELD CALCULATION AND BY MICRO KJELDAHL ANALYSIS.

Run No. 39, carried out in duplicate.

Determination of Nitrogen by Yield Calculations[a].

Bone-dry Weight of Starting Materials:	Sample No. 39a	Sample No. 39b
Wt. flask + cellulose, dried (P_2O_5, 25°, 1 mm.)	21.5215	19.1566
Wt. flask + cellulose, dried (P_2O_5, 25°, 0.5 mm., 4 days)	21.5236	19.1562
Wt. of empty flask	20.5299	18.1616
Wt. of vacuum-dried cellulose	0.9937	0.9946
Samples treated for 48 hours at 100°, 0.5mm.		
Wt. of flask + bone-dry cellulose	21.5171	19.1519
Wt. of empty flask	20.5299	18.1616
Wt. of bone-dry cellulose	0.9872	0.9903
	0.987	0.990

Weight of Cellulose Nitrate (uncorrected):		
Wt. of filter + adhering cellulose nitrate.	28.8821	29.6361
	28.8721	29.6262
Wt. of filter alone	0.0100	0.0099
Wt. of cellulose nitrate lost	20.5310	18.1685
Wt. of weighing flask (uncorrected)	20.5210	18.1526
Wt. of weighing flask (corrected)		
Wt. of nitrate, dried 24 hrs, 16mm, P_2O_5	22.1952	19.8323
" " " " 1 week, 25°, 1mm "	22.1932	19.8307
Wt. of flask, corrected for lost nitrate	20.5210	18.1526
Wt. of cellulose nitrate (not bone-dry)	1.6722	1.6781

APPENDIX IV (continued)

A small sample of cellulose nitrate was removed from the flask, transferred to small weighing flasks in approximately 40 mg. lots, and dried 24 hours - P_2O_5 - 0.3 mm. 25°, weighed, then dried to constant weight at 86° - P_2O_5 - 0.3mm.

Wt. of Cellulose Nitrate + flask as weighed	3.62784	3.45539
Wt. " " " dried to constant Wt, 86°	3.62734	3.44492
Wt. of water in the cellulose nitrates:	0.00050	0.00047
Per Cent water in cellulose nitrates:	0.050/0.040	0.047/0.039
	average = 1.2%	
Wt. of flasks + cellulose nitrate, bone-dry	3.62734	3.44492
Wt. of flasks alone	3.58692	3.40610
Bone-dry weight of moisture samples	0.04042	0.03882
Wt. of cellulose nitrate + flask, dried 25°, 0.4 mm, P_2O_5, 24 hours	3.62770	3.45526
Wt. of cellulose nitrate + flask, bone-dry Wt	3.62734	3.44492
Wt. of water in sample used in micro Kjeldahl	0.00036	0.00034
Per Cent water in " " " " "	0.036/0.040	0.034/0.039
	average = 0.8%.	

Calculation of Per Cent Nitrogen

Wt. of cellulose nitrate, uncorrected	1.672	1.678
Wt. of water in nitrate (1.2% of bone-dry Wt)	20	20
Wt. of cellulose nitrate, bone-dry	1.652	1.658
Wt. of cellulose, bone-dry	0.987	0.990
Wt. increase upon nitration:	0.665	0.668
Per Cent Nitrogen in Samples:	31.1x0.665/1.652	31.1x0.668/1.658
	12.50	12.53

a. All calculations made on a side rule, and checked to = 0.02%

APPENDIX V

PER CENT OF VARIOUS ORGANIC SOLVENTS INCLUDED IN MERCERIZED AND UNMERCERIZED CELLULOSE

(Staudinger, H., and Mohr, R. J. prakt. Chem. 158, 9 - 12, 233(1941).

Solvent Included	Per Cent of Solvent Included In: Mercerized Cotton	Mercerized Ramie	unmercerized Cotton
Non-activating solvents			
glycol	3.4	5.1	1.9
methanol	0.3	0.3	0.8
Water-soluble activating solvents			
ethanol	2.4	3.3	1.6
propanol	3.6	...	3.1
butanol	4.0	...	...
tetrahydrofurfural	7.8	9.2	6.7
acetone	2.5	3.7	2.0
pyridine			
by weight	6.4	6.7	2.7
by analysis	6.89	6.66	...
Water-insoluble, activating solvents			
hexane	4.0	6.7	4.9
cyclohexane	8.1	8.7	3.6
benzene	3.4	7.8	2.7
toluene	4.6	10.3	2.8
chlor-benzene	5.8	....	3.3
bromo-benzene			
by weight	10.0	10.4	3.0
by analysis	12.17	....	...

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