EFFECTS OF THE ACCESSIBLE FRACTION OF CELLULOSE ON SOME PROPERTIES OF ITS NITRATES

A Thesis

by

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ABSTRACT

Ph. D. Chemistry

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This Thesis concerns the influence upon the properties of cellulose nitrate exerted by the moisture history of the original cellulose. It is shown that the wetting and direct redrying of highly swollen cotton linters, followed by technical nitration, yields a nitrate whose nitrogen content is perceptibly diminished from the normal value. Systematic fractionation of such nitrates suggested that degredation during nitration was slightly less severe.

In an effort to discover whether wetting and redrying of the cellulose eventually yielded nitrates in which the distribution of the nitrate groups in the cellulose macromolecule was abnormal, technically nitrated products were oxidized with lead tetraacetate. Although differences in the level of oxidation were observed, in these nitrates, and also in twelve commercial nitrocelluloses, the meaning of these differences was not clarified.

Published experiments to determine the effect of wetting and redrying on the physical structure of the

cellulose were repeated. Although the work could not be exactly reproduced, its main inference received some support.

CLAIM TO ORIGINAL RESEARCH

1. It has been shown that wetting a dry, highly swollen cellulose with water, followed by direct redrying, decreases the nitrogen content of a technical nitrocellulose (N, 12.0%) prepared from it by 0,15 to 0.6%.

2. Fractionation of such nitrocelluloses from aqueous acetone suggests that the wetting-redrying cycle resulted in technical nitrates of greater chain length but somewhat lower substitution, particularly in the low viscosity fractions.

3. Differences caused by the wetting-redrying cycle were much less marked when the celluloses, and technical nitrates, were nitrated nearly to the trinitrate stage with a phosphorus pentoxide-nitric acid nitration mixture. The cycle was associated with minor fluctuations in the viscosity-fractional distribution plots.

4. Contrary to published reports, the phosphorus pentoxide-nitric acid mixture produced a degraded nitrate when it contained traces of the higher oxides of nitrogen. In one case, nitrates produced from wetted and redried linters by mixtures containing these oxides, did not dissolve normally in butyl acetate.

5. Lead tetraacetate in acetic acid-ethylacetate solution

oxidized twelve different commercial cellulose nitrates to small but variable extents (up to 0.1 mole per glucose residue). Wetting and redrying of linters prior to technical nitration increased the level of oxidation. The cause of the variable behavior toward the reagent was not determined.

6. Decreases in the accessibility of swollen linters caused by the direct desorption of varying amounts of moisture were measured, and were plotted against the percentage of moisture desorbed. Although the shape of the plot did coincide with that reported by an earlier worker, some support was given to the claim that there was a discontinuity in the range of 4 to 8% moisture desorption.

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GENERAL INTRODUCTION

The loss of Swedish wood pulp for the production of nitrocellulose in Britain, during World War II, necessitated the utilization of North American pulps for that purpose. Unfortunately, the nitrocellulose from the latter source was shown by actual test to have irregularities in its ballistic performances, and in its compatibility with nitroglycerine. Although satisfactory for gun propellants, cordites made with North American pulps were less than satisfactory as rocket propellants. An extended research, carried out in Britain and called the "Five Paper Trial" (I), failed to reveal any significant difference between Swedish and American pulps as far as all of the numerous routine methods of quantitative examination were concerned. The explanation for the divergence between the pulps therefore depended upon differences in properties that are not yet precisely defined and were not estimated in the "Five Paper Trial".

Since it is possible that a varying ratio of accessible to the less accessible (crystalline) cellulose in the pulps might influence the course of a standard technical nitration, samples of four of the original Five Papers were examined from this point of view. The results, reported from this laboratory in Part II of the Thesis by R. E. Glegg (2), gave only indefinite support to the idea, since the differences between the four technical nitration papers were very small.

This thesis, which is a sequel to that of Glegg, describes parallel nitrations of dry cotton linters in which

the ratio of accessible to crystalline cellulose was greatly changed by suitable pretreatments. A uniform sample of dewaxed cotton linters was highly swollen in caustic soda, washed free of alkali and dried through solvent exchange. A portion of the resulting swollen cellulose was then nitrated to the extent of I2.2 per cent nitrogen content with a technical sulphuric acid-nitric acid mixture. Another portion was collapsed, by wetting with water followed by direct drying, before being nitrated in exactly the same way. The extent of swelling and collapse, or, in other words, of accessibility, was estimated throughout the work by the thallous ethylate method (IO). The two nitrates were then examined for differences in nitrogen content, chain-length distribution and viscosity. Renitration of the technical nitrates nearly to the trinitrate stage was accomplished with a phosphorus pentoxide-nitric acid mixture, which is considered to cause no decrease in average chain length. These trinitrates were then compared with other samples of nitrocelluloses prepared by the action of the same nitrating agent on the original swollen cellulose and collapsed cellulose samples.

One way in which the different ratios of accessible to crystalline cellulose in pulps might affect the properties of technical nitrates would be by altering the distribution of nitrated and unnitrated free hydroxyl groups along the length of the cellulose macromolecules. Such a change in the distribution of the hydroxyl groups would probably involve an increase or decrease in the number of completely unsubstituted glycol

groups in the 2,3 positions of the anhydro glucose units in the cellulose chain. Attempts were made to follow such changes in a series of technical nitrates by noting the amount of oxidation they underwent when submitted to the action of lead tetraacetate and periodic acid solutions, which are selective agents for cleaving 1,2-glycols.

The results of the foregoing work suggested that, when other factors were unchanged, the course of nitration would be affected by the way in which the pulp was dried prior to nitration. Glegg (2) therefore plotted the extent to which the dry, highly swollen cellulose collapsed, when moistened with water and directly redried, against the percentage of moisture which the swollen cellulose had been allowed to acquire. An attempt was accordingly made to confirm the shape of this plot by noting the amount of accessible cellulose in the samples, before and after each moistening and drying cycle, by the thallous ethylate method.

HISTORICAL INTRODUCTION

Modern theories of the structure of cellulose show that, on the X-ray scale, it consists of a continuous network of crystalline and intercrystalline localities through which the long macromolecular main valence chains of glucose units persist (Fig. I). The crystalline sections are believed to be those regions where portions of several primary valence chains are sufficiently close together and in sufficient alignment to allow crystallization forces to produce a definite lattice, whose outer edges are somewhat irregular. From these "crystallites", the cellulose chains continue into intercrystalline or amorphous sections of more or less disorganized formation, which have no regular crystalline pattern (Fig.2)(3,4). The existence of a mesomorphous state, whose organization is intermediate between that of the amorphous and of the crystalline portions has recently been postulated (5).

As was discussed in detail in the Thesis by Glegg (2), the amorphous portion was originally described as that portion which contributed to the diffuse background in X-ray diffraction patterns. Since many reagents fail to penetrate the crystallites, as is shown by unchanged X-ray diffraction diagrams, the penetration they do accomplish, which measures the fraction of the cellulose directly accessible to them, must occur in the amorphous portion. The "accessibility" of a sample of cellulose depends upon the nature of the reagent used in the measurement, and is not necessarily the same in amount as the "amorphous" fractions, although both would be

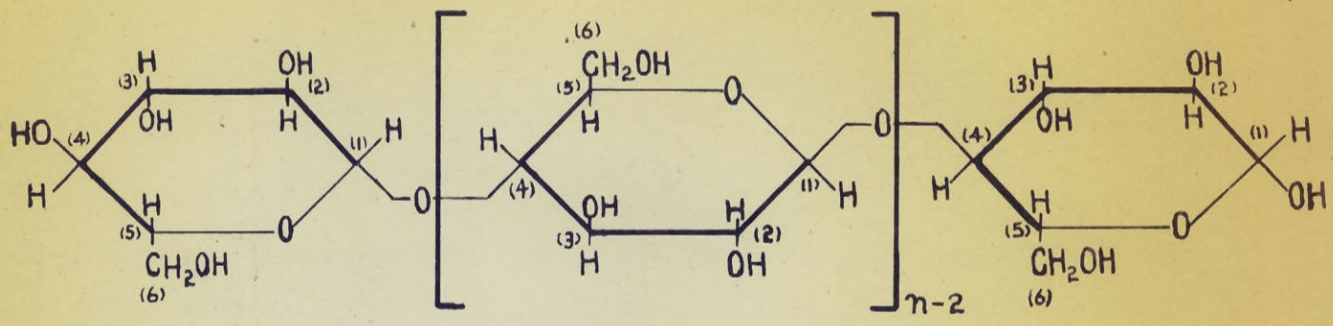

Fig. 1.

Plane projection of cellulose chain of glucose units.

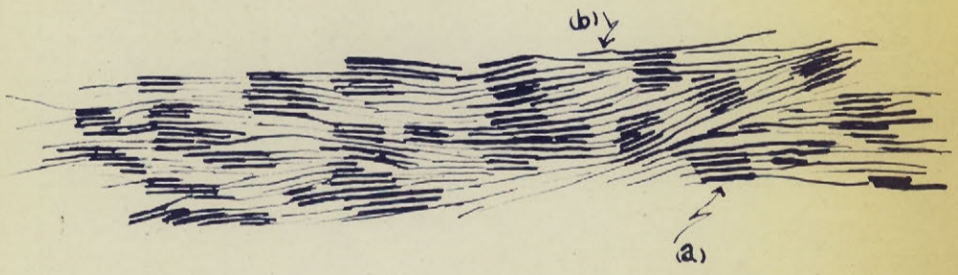

Fig. 2.

Possible fine structure of cellulose fiber, showing (a) crystalline, (b) intercrystalline (accessible) regions.

expected,with a reagent that fails to affect the crystallites, to increase or decrease together.

The proportion of the accessible cellulose (i.e. that part of the cellulose which is easily susceptible to reagents, and in which the hydroxyl groups can most readily undergo chemical reaction) varies from one type of cellulose to another (6,7), and evidence suggests that the bulk, if not all, of the crystalline cellulose is formed during the initial drying of the natural plant, and its extent influenced by the process of plant development and the details of the ripening and drying (8).

When routine fundamental tests for cellulose and its derivatives are considered, it is seen that almost all refer to the chemical structure of cellulose as expressed in Fig.I. Thus, determinations of intrinsic viscosity yield the average degree of polymerization and, when supplemented by fractionation, the chain length distribution. In the case of the partly substituted technical derivatives, some progress has been made in determining the distribution of the substituents between the second, third and sixth positions of the glucose residues(Fig.I), and along the macromolecule (9).

Estimations of α-, β- and γ-cellulose, uronic acid, carboxylic acid, copper number (II) tend to reveal the extent of any oxidative or hydrolytic degradation. In the case of pulps, estimations for naturally occurring non-cellulosic materials, such as those for fats, ash, pentosans, uronic acid and lignin are also normally carried out.

A realization of the importance of the characteristic molecular order and disorder in cellulose fibres, as illustrated by Fig.2, has recently stimulated a search for appropriate methods of its measurement. The initial, rapid hydrolysis and oxidation of various celluloses has been quantitatively measured by Nickerson, and attributed only to the accessible portion (6,7). The thallous ethylate method of Assaf, Haas and Purves (10,58) is thought to give a quantitative measure of the cellulose accessible to the liquid in which the reagent is dissolved. Rapid oxidation by periodic acid (59), and the measurement of the amount of hydrogen deuterium interchange (60,46) may become possible analytical tools. Other means have been employed to indicate the extent of accessible cellulose, such as the absorption of water (61), dielectric constant measurements (26), oil absorption (62), intensity of diffraction radiation in X-ray studies (15,66), integral heats of wetting (63), cobalt chloride adsorption (64) and refractive index measurements (65).

It is, however, almost certain that these, and similar methods, do not always measure the same quality even in a uniform sample of cellulose, and attempts to correlate the methods with each other are few. With the possible exception of the approximate X-ray method, none of them have been used in a routine way by industry, and in consequence, relationships between the amount of the accessible fraction, the chemical reactivity and the physical properties of cellulose are not yet well defined. The problem of discover-

ing such relationships is made more difficult by the necessity of keeping all other attributes of cellulose implied in Fig.I constant throughout the study.

In view of the preceding considerations, careful selection and control in the preparation of cellulosic raw materials has long been essential for the production of a rigorously uniform product. Ball and coworkers (49) have pointed out that the carefully standardized tests used in polymer manufacture give good duplicability between various laboratories as long as the test specimens come from the same source, otherwise such measurements are often found to be widely discordant in spite of precautions in standardizing test procedures. Hawkins, in his discussion of sulphite pulps for boxboard manufacture (50), states that care and regular control tests are necessary for uniform results. Moore and Yorston, in a review on pulping variables, give the same conclusion (51). Steude observes in his study of nitrocellulose (52) that cotton linters for nitration may be non uniform even if supplied from the same district, let alone from various parts of the world; therefore careful selection of material and strictest control are essential for the manufacture of uniform, high grade nitrates. Many other cases may be cited wherein similar viewpoints have been expressed (53, 54, 55, 32, 13). The general impression acquired is that deficiencies in the recognition and measurement of fundamental properties of cellulose still force industry to rely on quality controls of the raw materials empirically calibrated against "use"

tests. It seems probable that some of these deficiencies concern aspects of cellulose summarized by Fig. 2.

The literature cites numerous methods, both physical and chemical, by which the accessible portion of the cellulose can be increased at the expense of that part which is more perfectly organized or is crystalline. The theories of swelling need not be presented here since adequate treatment has been given them in the Thesis submitted by Glegg (2), as well as in excellent texts (67). It is sufficient to make only one addition to Glegg's review of the subject. This involves the concept of the increase of entropy which accompanies the swelling of polymers such as cellulose and rubber (I8). According to Meyer and Ferri's investigation (I9), rubber, upon stretching gives out heat and decreases in entropy. An alignment of the macromolecules of the rubber occurs, resulting in the tendency to form crystalline portions analagous to the crystalline regions in cellulose. In the contraction of rubber the reverse takes place, and the suggestion is made that the tendency to increased entropy supplies the driving force which brings about the contraction, and also the production of disorganized sections in rubber. The extension of this concept to polymers in general, provides another theory which assists in the explanation of the phenomenon of swelling.

Suitable swelling agents, such as solutions of caustic soda(6, I0, I2, I3), of 70 per cent nitric acid and of sulphuric acid (I4) bring about increases in accessibility depending upon the conditions used in swelling as well as upon the history of the cellulose (I2). Grinding dry cellulose in

a ball mill is reported to have transformed the fibers to nearly wholly "amorphous" products, which revert partly to the crystalline stage on treatment with water (I5, I6, I7). An increase in the accessible cellulose can be brought about by the industrial procedure of beating pulps (20, 2I). The relative proportions of the organized and disorganized sections in various polymers have been shown to be sensitive to treatments such as moulding, extrusion, annealing and stretching (22, 23). Even the simple action of combing the cotton fibers is said to cause an increase in the amount of "ordered cellulose" (8). Furthermore, degrees of partial or mixed substitution, or substituents of different chain length can cause permanent local disorder in a polymer (23). Increasing amounts of disorder are attained by the addition of plasticizers to polymers (23).

Thus, one must accept the obvious conclusion that details of the preparation and treatment of cellulose (6, 7, 26) including such actions as the cooking of pulps by alkaline or sulphite methods (25, 3I), the manner and degree of beating pulps, (24, 29, 30), the method of drying cellulose whether from water or by solvent exchange (26, I0, 33), the chemicals used in its purification and bleaching (I3, 24, 25, 26), and even the degree and time of pressing paper sheets,wet or dry,(27, 28, 32) all have an important share in the determination of the fine structure of cellulose.

Perhaps the most prevalent and industrially important effect is that of the intermittent sorption and desorption of moisture, to which all commercial cellulose is subject during mauufacture and storage. Jayme (26) has pointed out that the

degree to which a pulp is dried determines greatly the amount of irreversible "hornification" (or inaccessible cellulose), and consequently affects the water regain capacity. His investigations, which led to this conolusion, involved the desiccation of samples of cellulose to various degrees of dryness by such methods as air-drying and drying under conditions of increased temperatures up to 101°. These dried specimens were immersed in water for periods of one quarter of an hour to one week, and the anount of water retained by the samples was determined by means of dielectric constant measurements. There was a marked decrease in the ability of these dried samples to reabsorb and retain water. This decrease was found to be directly proportional to the intensity (i.e. the temperature) of the drying process. To account for this very apparent characteristic, Jayme suggested that a state of "hornification" occurred within the cellulosic fibers. The ordered regions, or crystallites, (Fig. 3 A), are surrounded by portions of a considerably lower state of organization, (the more accessible sections of the cellulose), in which the chains are arranged so as to form "Lockerstellen", or porous spots, of various sizes (Fig. 3 B). Throughout these larger spaces are found thin layers of hemicellulose materials such as mannans and pentosans (Fig. 3 C - broken line) which are spread out in net-like fashion. During the drying process, a denser arrangement occurs in the region of the polysaccharide chains, through the forces of adhesion and cohesion. A marked constriction of the porous spots thus takes place with the removal of water, involving partial or

total disappearance of the capillaries, comparable to the action of a "slide-fastener", which the solvent action of the water subsequently applied is unable to overcome (Fig.4,A,B,C). At these spots, then, the cellulose fibers are irreversibly "hornified" and inaccessible to water. This brings about a decreased plasticizing ability of the cellulose and a consequent decrease in strength of the papers made from it.

Thus the "hornified" localities may be considered as part of the "amorphous" cellulose, neither crystalline nor accessible. It is quite possible that these sections could affect the degree of reactivity of cellulose towards various reagents. Assaf, Haas and Purves (35) have shown by the thallous ethylate method, that drying cellulose from I00 per cent to,say, 5 per cent moisture content involves more collapse than drying merely from 50 per cent water to 5 per cent. This result is in qualitative agreement,at least, with the observations of Jayme. On the other hand, a cellulose of known percentage accessible surface, when allowed to absorb only small amounts of water (6% to 9%), undergoes further swelling with a consequent increase in accessible surface, the effect being about twenty per cent increase for materials of high available surface, but as much as thirty-fold for those of small degree of disorder (35).

R.E. Glegg (2) recently made an attempt to follow the changes in reactivity, by the thallation technique (I0), of samples of cellulose initially of large accessible surface,

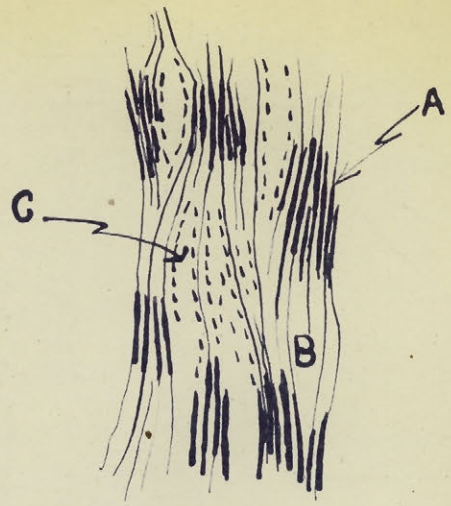

Fig. 3. -Schematic representation of the cellulose fibers before drying, showing (A) crystalline regions, (B) porous spots (Jayme's Lockerstellen) in the more accessible portions, (C) hemicelluloses in the porous spots.

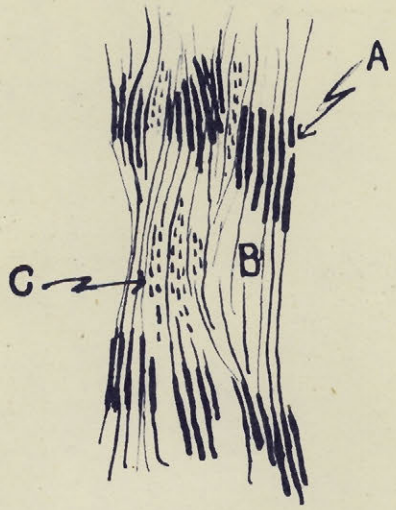

Fig. 4. -Schematic representation of cellulose fibers after drying from water, showing (A) crystalline regions, (B) porous spots, (C) "hornified" sections.

which were allowed to absorb definite amounts of moisture before being dried directly over concentrated sulphuric acid. A summary of the data concerning this work is reproduced in Table I and in Fig. 5. This information points definitely to the fact, as stated by Glegg, that there is a marked decrease in accessibility to thallation (in ether solution) with increase in amount of water absorbed and directly desorbed. Furthermore, the position of one point, C, on the plot (Fig. 5) gives the curve a shape which is of great theoretical interest, some details of which Glegg has developed. According to the interpretation presented in his Thesis, the portion AB, culminating at some point between B and C , represents the removal of about 6 per cent absorbed moisture from the primary hydroxyl groups. Further removal of an amount of water as shown between points B and C, involves very little collapse, and hence, must be withdrawn from sections of the cellulose not involving the secondary hydroxyl groups, since more collapse of the accessible portion would occur. The existence of water, hydrogen bonded to water already attached to the primary hydroxyl groups, (thus forming a multimolecular layer), has been postulated as a probable explanation for this behavior. Further removal of absorbed water to an extent of about 18 per cent, entailed a collapse of an additional 85 per cent of the accessible surface, and was considered to have been taken from the two secondary hydroxyl groups of the accessible cellulose. The values indicated for the amounts

TABLE I

THE DECREASE OF ACCESSIBLE FRACTION CAUSED BY ABSORPTION AND DIRECT DESORPTION OF INCREASING AMOUNTS OF WATER

Cellulose before Absorption		% Water Absorbed & Directly Desorbed	Cellulose after Desorption		% Retention of Accessible Surface	% Accessibility lost
% Methoxyl	% Accessible Surface		% Methoxyl	% Accessible Surface		
23.1	40	0.46	23.3	40	100	0
23.1	40	1.05	22.3	39	98	2
22.3	39	3.80	20.0 (h)	35	90	10
22.3	39	11.60	2.5%(k)	4.5	11	89
21.9 (g)	38	7.78	19.2 (l)	33	87	13
21.9	38	9.73	9.7 (m)	17	45	55

(g) Sample II (k) Sample V (m) Sample X
(h) Sample IV (l) Sample VI

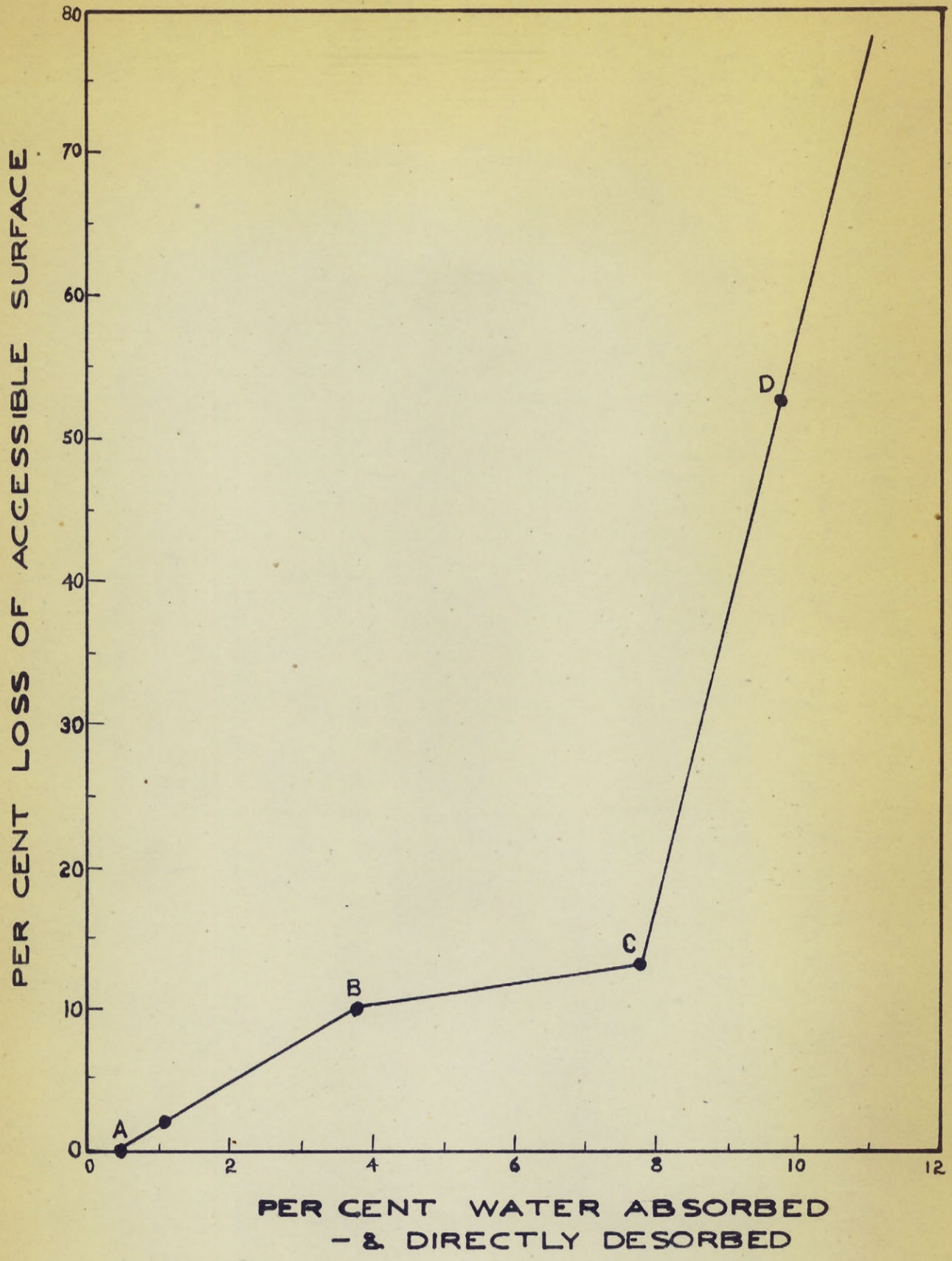

Fig. 5. -Reproduction of Glegg's plot showing the reduction in accessible cellulose brought about by the sorption, then direct desorption, of definite amounts of water by cellulose initially of high accessible surface.

of water absorbed by the primary and the two secondary hydroxyl groups (6%, and an additional I2% respectively) are twice those given by Purves et al in a study of the sorption isotherm involving consideration of the water absorbed by the two types of accessible hydroxyl groups (35). Since the extent of the accessible cellulose in the linters examined by Glegg is twice that found for the materials used by Purves and co-workers, this increase is not conflicting. Considerable support is thus given to the conception that there is a distinct difference in water absorption and in reactivity by the two types of hydroxyl groups. Furthermore, the collapse of the cellulose would thus occur in a stepwise fashion, involving first the secondary positions and then the primary, depending upon the amount of moisture withdrawn.

However, there exists a doubtful factor in this work. The interpretation rests solely upon the legality of the position of one point, C. The argument advanced in favor of the accuracy of this point is that a I00 per cent error in methoxyl determination is necessary to bring it either into line with the remaining points, or cause it to be so far out of position. The error involved in the estimations of accessible surface(by methoxyl analysis) was at the most I0 per cent. The manner of calculation of this "I00 per cent error" is vague, but appears to be based upon a mere doubling of the decrease in accessible surface already measured, But if one considers this decrease in relation to the total amount of

accessible surface (21.9% methoxyl, Table I), it would require an error of about 12.5 per cent to move point C out of line with the other points to where it now is. It is quite probable that such a change in surface may have arisen, for the sample indicated by point C, during the manipulations involved in the sorption and desorption of water.

Hence a confirmation of the sorption-desorption experiments, with particular attention given to the region lying between 0 per cent and 8 per cent Relative Humidity, would be of considerable value.

Investigations during recent years point to the fact that the physical and chemical properties depend, in part, upon the proportions of crystalline and non-crystalline material in a polymer such as cellulose. The first avid absorption of water by dry cellulose exposed to humid surroundings is attributed to the alcoholic groups of the accessible cellulose (35, 21), and accounts for as much as 7 per cent of the absorbed water, as can be seen from a water absorption isotherm (35) and heats of wetting (36). Pure, dry cellulose develops 10-16 calories per gram up to a moisture content of 7 per cent (37). Further absorption occurs, in the main, as capillary condensation, and gives rise to only 1,99 calories per gram of cellulose (26,38). It has long been known that the amount of water sorbed by cellulose varies according to the type of cellulose dealt with (6,7), e.g. whether from wood or from cotton (105), and is affected by pretreatment such as mercerization,

bleaching and beating (6, 7, 24). Support is given to the conception that this water binding capacity is dependent upon the presence of the alcoholic groups in accessible cellulose (35, 105, 21), since progressive substitution of these hydroxyls brings about a corresponding decline in hygroscopicity (26, 21). Regarding the belief that the absorption of water is confined to the amorphous portion of the cellulose, a recent paper suggests that, although the bulk of the water enters the more accessible sections, a small amount is also bound in the crystalline regions (104).

The swelling of cellulose in alkali, followed by removal of the water by direct drying, produces a decrease in accessibility (35) and a parallel decrease in reactivity, whereas removal of the water as an azeotropic mixture by heating with organic solvents such as ethyl acetate, yields a material of greater accessibility. The latter shows an increased reactivity toward acetylating agents, and requires less catalyst to bring about esterification (33). The less perfectly organized part of cellulose is known to acetylate rapidly, and on partial acetylation, this accessible region has been recrystallized and found to consist entirely of cellulose triacetate (34).

The swelling of cellulosic fibers with water plays a great part in determining the degree of fibrillation, upon which depends the physical strength of paper sheets(26, 21). Variation in extent of drying from water causes differences

in the extent of collapse of the accessible portions (35) and this effect is followed by corresponding changes in water binding ability. This characteristic is amply verified by Jayme's study of the irreversible hornification of pulps (26, 47). The change in the ratio of accessible to inaccessible cellulose is probably reflected in the hysteresis exhibited by water sorption isotherms of cellulose (39) in which the absorption curve lies below that of the first desorption.

Moreover, the fine structure of cellulose determines the rate of diffusion of solutions (41), and thus exerts a controlling effect in processes such as xanthation (42), nitration (32, 43) and acetylation (44), with a consequent effect upon the resulting product. Tensile strength, high modulus of elasticity and rigidity are contributed by the crystalline portion, while flexibility, recovery and elongation are brought about by the intercrystalline sections (45, 46). Nickerson and Habrle (5) were able to differentiate between "amorphous, mesomorphous and crystalline" cellulose by their different degrees of resistance to oxidative hydrolysis. Progressive removal of the accessible portion of cellulose by this hydrolysis left a residual linters which had a powdery appearance, suggesting that the small amount of "amorphous" cellulose is important in the structural properties of the fiber (48).

In addition, Staudinger and Sorkin (88) have pointed out a difference between precipitated and unprecipitated cell-

ulose in the solution of their acetates. They observed also that the precipitated cellulose, when dried from water, contained "verhornte massen" (hornified regions) which nitrated with difficulty, a fact which led them to maintain, by solvent exchange, the "loosened state" characteristic of precipitated cellulose.

Thus, in view of this mass of evidence which indicates that the fine structure of cellulose exerts a considerable control upon the physical and chemical properties of the fibers, it appears almost certain that differences in the ratio of accessible to crystalline cellulose would have some effect upon the course of nitration of the cellulose, which effects become apparent in the properties of the nitrates.

The belief that some properties, other than those normally measured by industry, must be of importance in the preparation of nitrocellulose, is definitely upheld by consideration of the results of a thorough investigation of nitrated celluloses carried out under what is termed the "Five Paper Trial" (1). During World War II the supply of Scandinavian sulphite pulps for the manufacture of British cordite was cut off, necessitating the substitution of Canadian and American sulphate and sulphite pulps, chosen to be as nearly similar to prewar supplies as possible. The ballistic performances of the nitrated celluloses from these new sources were satisfactory when they were used as gun propellants, but definitely unsatisfactory when employed as rocket

cordite. Accordingly an extended study of the nitrating papers of the various blends used for the manufacture of cordite, was undertaken in an attempt to uncover the cause of the irregular behavior. Glegg (2) has made a detailed summary of the results of the "Five Paper Trial". It is only necessary here to note that during this careful investigation, although factors due to the differences in techniques of different factories were eliminated by uniformity in processing the papers and in production of the cordite, the usual routine tests (viscosity, copper number, uronic acid, pentosan, lignin and α-cellulose content, as well as fractionation of the nitrocelluloses) showed no striking differences to which might be attributed the undesirable features for their behavior in propellant compositions.

Glegg accordingly studied four of the Five Papers in an attempt to correlate the extent of accessible surface with the properties of the nitrates derived from the papers, as measured by nitrogen estimations, viscosity determinations and fractionation of the nitrates. Table II gives a summary of the pertinent results obtained by Glegg. Only a doubtful qualitative correlation appears between the extent of accessible surface of the papers as estimated by three different methods used in analysis, although A 8 and A 10 are consistently higher than A 11 and Blend 4 in amount of available surface. Differences in accessibility of the four papers as determined

by any one method, are also slight, and considered by Glegg as just beyond experimental error. The differences noted between the pairs A 8, A 10 and A 11, Blend 4 could possibly arise from the fact that the latter are both of North American origin, while A 8 is totally of Scandinavian pulp and A 10 is 50 per cent of Scandinavian and 50 per cent of American pulps. It is equally possible that the differences originated, at least in part, in the preparation and drying of the papers during manufacture, since no uniform control was exercised in this regard. Correlation between the amount of accessible surface and the ballistic properties listed in Table II is also very indefinite. The results obtained, therefore, permit no conclusions regarding the relation of amount of accessible cellulose to the ballistic properties.

The fractionation data on the four papers also fail to show positive differences to which may be attributed the variation in properties of the corresponding cordites. A tentative explanation is proposed to account for the dissimilarity in ballistic properties between A 11 and Blend 4. Though the corrected viscosities show that the chain length distribution for the two is practically identical, and the nitrogen contents are approximately the same, Blend 4 gelatinized more perfectly with nitroglycerine and had a higher burning rate than did A 11. The assumption put forth to explain these differences was that the distribution of the

TABLE II

SUMMARY OF THE DATA COLLECTED BY GLEGG IN A STUDY OF FOUR OF THE FIVE PAPERS

Type of Paper.	Blend 4	A 8	A 10	A 11
Relative Accessible Fraction by;				
1. Thallous Ethylate.	1.0	1.4	1.4	1.0
2. Water Sorption.	2 next	3 next	4 largest	1 smallest
3. Nickerson HCl-$FeCl_3$.	1.0	1.1	1.3	1.0
Cordite Degree of Gelatinization.	1 best	4 worst	4	2
Relative Burning Rate. 550 lb./sq.in.	1.00	1.01	1.05	1.04
Plastic Deformation.	60.7	41.5	38.4	42.0
Tensile Strength. lb./sq.in.	1020	1085	1085	965
Per Cent Nitrogen Technical Nitrate.	12.06	11.96	11.94	11.92

nitro groups along the chains differed in the two cases, an interpretation quite within the realm of possibility but as yet difficult to verify.

It is of interest to note that a viscosity correction for nitro substitution in nitrocelluloses has been applied by Glegg to all nitrates of less than theoretical substitution. This correction arose from the observation that renitration of a technically nitrated cellulose of about 12.2 per cent nitrogen to full substitution, by a mixture which produces no further degradation, resulted in a pronounced increase in viscosity. This increase could be attributed only to increased substitution. This latter statement is confirmed by the observation of Wannow that the viscosity of nitrocelluloses varies with substitution (90), other factors being the same. It is unfortunate that Wannow's original article was not available for consultation.

The nitration of cellulose can be carried out by a variety of methods concerning which excellent summaries are available (68, 69). A stable nitrocellulose of high nitrogen content is attained with mixtures of phosphoric acid, phosphoric anhydride and nitric acid, which bring about no degradation of the cellulose during esterification (70). Phosphoric acid and nitric acid alone also yields high nitrates "without saponification of the ester and destruction of the micelle", but addition of water decreases the nitrogen per

cent and increases degradation (71, 72). The trinitrate of starch has recently been made by employing the pentoxide of nitrogen and sodium fluoride in dry chloroform, and these starch esters, by reason of the anhydrous character of the reagents, are reported to reflect the degree of polymerization of the original materials (73). Nitrogen pentoxide added to nitric acid (74) gives more rapid nitration than does phosphorus pentoxide in the same acid (76), probably because of the greater power of diffusion of the former oxides, but brings about more degradation than is found with the use of the latter(74). The trioxide and tetroxide of nitrogen in nitricacid cause greater degradation than the pentoxide(75). Exposure of cellulose to nitric acid vapors (77, 78) results in an ester of high nitrogen content,but there is a lack in homogeneity, especially in the lower nitrates, unless lengthy reaction times are allowed, or a small amount of water is added (79). Mixtures of glacial acetic acid, acetic anhydride and nitric acid have also been used as nitrating agents (80). The commercial nitration procedures employ a series of mixtures of sulphuric acid, nitric acid and water depending upon the type of nitrate desired, but which produce a more or less degraded product (81, 69).

Two industrial procedures, the mechanical dipping process and the displacement process (113), are worth mentioning for reasons which will later become apparent. In the

mechanical dipper procedure, a quantity of prepared cellulose is immersed in a mixture of nitric acid, sulphuric acid and water, and kept there for a period of thirty minutes under continual agitation. The acid is then removed by centrifugal force and the nitrate, still retaining some of the mixed acid, is drowned in sufficient water to prevent any marked rise in temperature. Washing and stabilization follow. The displacement method involves the treatment of an amount of cellulose, in a container with a false bottom, with a suitable mixture of the same acids. At the end of the esterification time, the spent acid is drained off slowly and replaced at the same time with water.

These two methods, differing in the manner of removal of spent acids, can be adjusted to yield nitrocelluloses of identical nitrogen content, but which are so"vastly different in general properties that they could under no circumstances be interchanged for their respective purposes" (106). It is possible that the difference in mode of removal of the spent acid might give rise to a dissimilar distribution of the nitrate groups caused by different amounts of hydrolysis during the two methods of isolation. In this event, the number of unsubstituted glycol groups in the glucose units (Fig.I) might differ accordingly.

The application to cellulose, of the common technical nitration mixtures must be made under rigorously controlled and

standardized conditions, since slight variations in temperature and time of nitration, composition of mixed acids, ratio of cellulose to acid, all greatly affect the characteristics (degree of polymerization, viscosity, yield, per cent nitrogen) of the nitrocelluloses obtained (69, 81, 82, 83, 32).

In an investigation of fully nitrated cellulose, there is no doubt as to the degree or position of substitution. This is not true, however, concerning those nitrocelluloses whose esterification falls below the theoretical. It would obviously be advantageous to know, in the latter case, the extent to which the replaceable hydroxyl groups (numbers 2,3 and 6, Fig. 1) of the glucose unit have been affected. Two serviceable analytical tools, which have been applied to the estimation of unsubstituted adjacent hydroxyl groups, are lead tetraacetate and periodic acid. Jackson (96) has written an instructive review, with many references, on the subject of glycol cleavage by these oxidants, and also discussed experimental conditions and preparation of materials necessary for the analysis. An investigation of the mechanism involved has been presented by Purves and co-workers (97). Application of this method of analysis has recently been made to cellulose, starch and their derivatives. Jackson and Hudson (98) have determined the amount of periodic acid consumed by starch and cellulose, and studied the products of the oxidation. An evaluation has been made of the number of glycol groups in

partly acetylated celluloses (99) and in cellulose ethers of incomplete substitution (101). Differentiation between, and estimation of,cis trans glycols in simple sugars has also become feasible (100). To this list may be added the estimation of the amount of accessible cellulose by the initial rapid oxidation with periodic acid (59). Within the author's knowledge, no report in the literature deals with the application of this technique to cellulose nitrates.

EXPERIMENTAL

PREPARATION OF CELLULOSE SAMPLES

A quantity of high grade cotton linters, the gift of H. M. Spurlin and the Hercules Powder Co., was dewaxed by extraction in a Sohxlet apparatus for two days with a mixture of ethanol and benzene (1:2). The product was dried in air.

1. A New Swelling Procedure Yielding Accessibility 30 to 40%

A modification of the swelling technique, discovered by Glegg (2) through an omission of a part of the procedure developed by Assaf, Haas and Purves (10), gave twice the amount of accessible cellulose reported by the latter.

Fifteen grams of dewaxed, air-dried cellulose was immersed in 540 ml. of 10% caustic soda solution at 5° (10, 12), and two and one half hours later, the swollen mass, together with the caustic, was poured into an amount of 10% aqueous acetic acid (also previously cooled to 5°) calculated to neutralize the caustic soda used in the swelling. After a period of ten minutes, during which the mixture was stirred at intervals to permit complete diffusion of the acid through the cellulose, the aqueous portion was decanted and the solid pressed free from excess liquid. A second treatment with 1 1/2 liters of 1% acetic acid for ten minutes, rendered the solution slightly acidic and completed the removal of the last

traces of base. This solution was decanted as before, and replaced by 1.5 liters of distilled water, which was thoroughly mixed with the cotton for three or four minutes and then drained away. About six separate washings with 1.5 liter volumes of distilled water was necessary to free the cellulose from salts and acid (litmus test). The excess water was squeezed from the linters by gentle pressure and the wet mass quickly dispersed, and occasionally stirred, in 1 liter of 99% methanol. Fifteen minutes later, the methanol was removed and replaced by a fresh amount, and this process was continued for three additional washings. Two more immersions, for thirty minutes each, in magnesium-dried methanol were followed by four more, one of thirty and three of fifteen minutes each, in one-liter volumes of sodium-dried, thiophene-free benzene, to remove the last traces of alcohol. The supernatant liquids were easily reclaimed and purified. During all the manipulations, care was taken to avoid even superficial drying of the cellulose, since such drying tended to give a non-uniform product.

The swollen linters, wet with benzene, were dried in a desiccator over containers of phosphoric anhydride and paraffin for several days, during which frequent changes of the drying reagent, and repeated evacuation of the desiccator to a pressure of about 25 mm. mercury, were necessary in order to produce a material free from the odor of benzene. The product was then stored in the usual manner (10) in a desiccator for one week, over concentrated sulphuric acid.

2. Old Swelling Procedure Yielding Accessibility 15 to20%

Results of several attempts to swell 10 to 15 gram quantities of cellulose by the method developed by Assaf, Haas and Purves (10) invariably yielded accessibilities corresponding to a methoxyl content of from 9 to 11%.

Fifteen grams of air-dried, dewaxed cellulose was immersed in 540 ml. of a 10% caustic soda solution at 5°. Three hours later the swollen mass was diluted with an equal volume of 2% caustic soda, also at 5°. After an interval of thirty minutes the cotton was recovered by filtration and washed thoroughly and in succession with water, with 1% acetic acid and with distilled water. Slight squeezing quickly removed most of the excess moisture before the wet mass was dispersed in a liter of 99+% methanol. The methanol was removed and replaced by a fresh amount after 15 minutes. A third immersion, this time in magnesium-dried methanol, was followed by two more, each of thirty minutes duration, in one-liter volumes of sodium-dried, thiophene-free benzene. The removal of the benzene and subsequent drying and storage was carried out in exactly the same manner as described in Procedure 1,

3. Collapse to an Accessibility of 0.2 to 0.4%

One half of the completely dried and highly swollen cellulose was soaked with water for twenty minutes, squeezed gently to remove excess liquid, and then dried directly under

vacuum over phosphoric anhydride and then, when thoroughly dry, was kept for a week over concentrated sulphuric acid in the same desiccator with the dried, swollen portion.

ESTIMATION OF ACCESSIBILITY

Accessibility estimations made upon the specimens of prepared cellulose were carried out by employing an ether solution of thallous ethylate and the improved thallation technique of Assaf, Haas and Purves (10). The resulting superficially methylated cellulose, presumably unchanged in the accessible fraction, was then analyzed for methoxyl content by the customary Viebock and Schwappach procedure (108, 109). Duplicate or triplicate analyses were always carried out, and agreed almost invariably to well within ±10%.

The percentage of methoxyl was calculated as 100y/x, where y was the weight of methoxyl found, and x that of the original cellulose. Since trimethyl cellulose, by this method of calculation, has a methoxyl content of 57.4%, the percentage of cellulose exposed to the thallous ethylate in ether was given by(100y/x)(100/57.4). This amount was taken as the per cent accessibility (10).

NITRATIONS WITH SULPHURIC ACID-NITRIC ACID MIXTURES

Technical nitration mixtures were made up according to the tables assembled by Doree (69) to yield a nitrated cellulose of about 12.1 to 12.3 per cent nitrogen. Each batch of nitration mixture was checked by sample nitrations of dewaxed, unswollen cellulose, as well as by analysis of the mixture, and suitable corrections in composition were made, if necessary, to give the desired nitrogen content in the nitrocellulose. The actual nitrations were carried under carefully controlled conditions to ensure duplication of results. One hundred grams of the technical nitration solution was put into a dried, glass-stoppered Erlenmeyer flask of about 200 ml. capacity, and then, after the flask and contents had been brought to 15°, one gram of the dried cellulose was quickly weighed(out to the second decimal place) and immersed in the nitrating fluid. Nitration continued at 15° for thirty minutes, the flask being shaken occasionally to ensure thorough mixing. A thirty-minute reaction time was chosen to conform to that often used in commercial manufacture, and the temperature of 15° was such as to reduce degradation and side reactions (81,69), yet still allow maximum nitration to take place during the half hour. The liquor was removed by filtration with suction through a coarse, sintered-glass funnel of suitable size, the residual nitrocellulose squeezed slightly to remove excess fluid, and then thrown,,piece by piece, with quick stirring, into 250 ml. of a 1:1 mixture (by weight) of ethanol and water

(70) previously cooled to - 15°. The liquid was again filtered from the solid by suction, through a sintered-glass funnel, into another suction flask (to prevent explosion resulting from the addition of ethanol to nitrating solutions) and the solid squeezed from excess liquid. Two more such washings with 100 ml. volumes of cold, aqueous ethanol were followed by four similar immersions in the same ethanol-water mixture at room temperature to ensure complete removal of the free acids (litmus test). The washed cellulose nitrate was subsequently boiled three times in succession in 100 ml. volumes of the 1:1 ethanol-water solution, previously heated to boiling, in order to stabilize the product. Such treatment is reported to remove any bound acid and to yield a thoroughly stable guncotton (70, 68, 110). The hot liquid was removed as before, and the ester then dried over phosphoric anhydride and calcium chloride under vacuum, the drying agent being changed as often as necessary until no further liquifaction of the anhydride occurred. It was then deemed suitably dry for subsequent analyses, and was stored in a desiccator over phosphorus pentoxide. Under these conditions the anhydride removes all but 0.35% of the water even from cellulose, as suggested by Maass and Campbell (111). Heating over the phosphoric anhydride under vacuum at 100° eliminates even this last trace of water, but on cooling the cellulose again regains it from the pentoxide. Since the nitrates of cellulose are considerably less hygroscopic than

cellulose, any slight error due to the water retention of the nitrates is insignificant.

The nitrocelluloses thus obtained were colorless and fibrous, but the texture had a more brittle character than was shown by the original cellulose, suggesting the occurrence of degradation during nitration. The amount of change in texture depended upon the previous preparation of the cellulose (provided, of course, that this standardized technique was carefully followed).

NITRATIONS WITH PHOSPHORIC ANHYDRIDE-NITRIC ACID MIXTURES

Nitration without degradation was accomplished by the use of phosphoric anhydride and concentrated nitric acid (76,70) of at least 99.2% strength, prepared by distillation of a mixture of concentrated sulphuric and concentrated nitric acids (1:1) in an all-glass apparatus, and miscible without turbidity with chloroform (112). A 22% mixture (by weight) of phosphoric anhydride in this nitric acid was made by cooling the acid in a glass-stoppered bottle to -15° and adding the anhydride in small portions with shaking and further cooling till the required amount of pentoxide had been consumed. The preparation covered a period of twenty four to thirty hours, when a liter of nitric acid was involved, depending upon the efficiency of the cooling mechanism. Attempts to hasten the addition brought about evolution of brown fumes, especially at higher temperatures.

The nitration mixture, at first opaque and obviously containing solid anhydride, remained at - 15° for two days, whereupon it became a clear, homogeneous liquid. This change in physical state was found to be most important, for unless it had occurred, a nitration to only about 13% N was possible. The reason for this observation has not been investigated, but it is possible that the solid phosphoric anhydride clings to the cellulose in such a manner as to hinder full nitration. No difficulty in obtaining 13.8 - 13.9% nitrogen was encountered if solution of the phosphorus pentoxide was complete. Furthermore, this nitrating fluid gave identical results on the same cellulose even after having been stored at -15° for a period of two months.

The nitrating liquid, 100 g., was put into a dried, glass-stoppered Erlenmeyer flask, and the flask and contents brought to 15°, whereupon one gram (weighed to the second decimal place) of dried, prepared cellulose was added. The reaction was allowed to continue at 15° for thirty minutes. Berl suggests that reaction is completed in the first five minutes by this powerful mixture (70), but the longer time was allowed so as to be comparable to that used in the technical nitration for the industrial manufacture of guncotton. Removal of the acids, drowning, washing and stabilization, drying and storing of the cellulose nitrate proceeded in exactly the same fashion as in the preparation of the technical nitrates above. A colorless, fibrous material of uniform texture, showing no traces of degradation or tendency towards brittleness, was obtained.

In both the preceding methods, it was easily possible to get reproducible results, as evidence by several nitrations of the same materials.

ANALYSES FOR NITROGEN

1. Semi-micro Kjeldahl

Nitrogen analyses were made by a modification of the Gunning method for the determination of nitrogen (86). The sample of dried cellulose nitrate, 0.1 g., was weighed rapidly on a magnetically damped balance, using a cigarette paper from which the gummed edge had been removed. The nitrocellulose slowly absorbs water from the atmosphere, the resulting increase in weight being much greater and much more rapid for the technical nitrates than for the trinitrate. The sample was then transferred to a 250 ml. Kjeldahl flask and 0.3 g. salicylic acid and 6 ml. concentrated sulphuric acid was added. In earlier determinations, the cigarette paper was allowed to remain in the Kjeldahl flask since its nitrogen content was negligible, but occasional difficulties in obtaining results which checked one another led the author to remove the paper, using it merely as a convenient means of weighing the guncotton samples.

After thirty to sixty minutes of digestion at room temperature, the solids were found to be completely dissolved.

An occasional specimen required a longer time for its complete solution. Sodium thiosulphate, 0.8 g., was then added and the mixture warmed gently over a low flame for about five minutes, whereupon 2.0 g.of powdered potassium sulphate and a tiny pinch of selenium catalyst was inserted. The mixture was then gently heated under a hood, or in a digestion apparatus, until the evolution of gases became less pronounced, and then was heated more strongly till the liquid was clear and colorless. The cooled, viscous liquid was diluted with 100 ml. of distilled water and then made definitely basic by the addition of 45 to 50 ml. of 30% caustic soda solution. A small piece of zinc in the flask prevented bumping while the ammonia, with about 75 ml. of water, was distilled into 30 ml. of 4% boric acid solution containing ten drops of a mixed indicator (114). The ammonia in the boric acid solution was titrated directly with 0.05 N. hydrochloric acid and the per cent nitrogen thus estimated. The 4% boric acid solution was prepared by adding the required amount of solid boric acid to previously boiled, distilled water and after complete solution, was again boiled to eliminate the last traces of carbon dioxide. Any decrease in the volume was made up by the addition of boiled water. It was then stored in a pyrex, glass-stoppered flask for use. The mixed indicator consisted of 10 ml. of a 0.1% solution in ethanol of brom-cresol green added to 2 ml. of a 0.1% solution in ethanol

of methyl red (114, 115). Each solution of boric acid, containthe ammonia, was titrated to the disappearance of the greenish blue color and the first faint appearance of red. A blank of about 0.15 ml. of 0.05 N.hydrochloric acid was applied as a correction for all determinations. Good checks in the duplicate or triplicate analyses were usually obtained in all cases.

2. Micro Kjeldahl

The micro Kjeldahl determination was carried out essentially as described in the preceding section for the semi-micro Kjeldahl estimation, but with the following changes. A 10 mg. sample was weighed carefully on a cigarette paper (without gummed edge) which had previously come to equilibrium with the atmosphere of the balance room, and then put into a micro Kjeldahl flask, whereupon the cigarette paper was removed and reweighed to obtain the size of the sample. Salicylic acid, 0,1 g., was put into the flask and the solids were dissolved with 2 ml. of concentrated sulphuric acid. Sodium thiosulphate, 0.3 g., was added and, after a five-minute period of gentle heating, 0.6 g. of powdered potassium sulphate and a minute amount of selenium were also put into the flask, whereupon digestion proceeded as before. The ammonia, with about 30 to 50 ml. of water, was distilled from the regular micro apparatus into 5 ml. of 4% boric acid solution containing 5 drops of the mixed indicator. The titration, using 0.01 N hydrochloric acid,

required a blank correction of about 0.2 ml. of 0.01 N acid.

Both micro and semi-micro methods were found to give the same results within experimental error when appropriate blank corrections were applied. The size of the blank varied slightly with the nature of the end point, and very little with the reagents employed.

DETERMINATION OF INTRINSIC VISCOSITIES

The viscosities were measured with an Ostwald capillary viscosimeter. From 0.004 to 0.010 g. of the dry cellulose nitrate was weighed out carefully and quickly, to the fifth place, on a magnetically damped balance. About 10 mg. of the technical, nitrate, or 3 to 6 mg. of the undegraded trinitrate, was found to be a satisfactory weight for the determination. With the volume of solvent used, larger quantities required from five to ten dilutions before the Staudinger Intrinsic Viscosity value was reached, especially with the fractions of the nitrocellulose of high degree of polymerization. The nitrate was then added to a weighed amount (25 ml.) of freshly distilled butyl acetate (b.p. 125-127° at 760 mm.) in a glass-stoppered container. A glass tube, closed at one end, with a ground glass joint at the other end, dimensions approximately 1" by 8", and capacity about 40-50 ml., was found to be suitable. Mechanical shaking was continued till a perfectly homogeneous liquid was obtained. The

time for solution varied, depending upon the degradation of the sample, but as a rule the samples were shaken gently overnight. A few tiny, insoluble, threadlike bodies were observed in all solutions, the quantity being somewhat greater for the technical nitrates, even after prolonged agitation. These bodies were allowed to settle before measurements were made, and were found to have no effect on the times of flow. A 5 ml. aliquot of this solution was pipetted into a clean, dry, Ostwald viscosimeter, which was then suspended in a water bath at 25° (within $\pm$ 0.1°). After an interval of five minutes, during which time the apparatus reached the temperature of the bath, the small bulb in the instrument was filled with solution by gently exerting pressure on the surface of the liquid in the other arm of the viscosimeter by means of a rubber bulb. This technique minimized evaporation, which inevitably accompanies suction. Times of flow, 80 to 140 secs., were measured with a stopwatch reading to one fifth of a second, and relative viscosities were taken in these dilute solutions as proportional to the time of flow. The quotient of the specific viscosity, η_{sp} or $\eta_{rel} - 1$, by the per cent concentration by weight of the solution was then calculated. The remainder of the original solution was weighed and then diluted with 5 ml. of butyl acetate, and, after a few moments' shaking to allow thorough miximg, weighed again. From these weights, the amount of the solvent and the amount of residual nitrocellulose could be cal-

culated (by aliquots) and the concentration of the cellulose nitrate, in the diluted solution, estimated. Viscosity measurements were repeated on this solution and $\frac{\eta_{sp}}{c\%}$ again calculated. Dilution was continued in the above manner until the numerical value of $\frac{\eta_{sp}}{c\%}$ became constant, and was thereupon considered to be equal to the Intrinsic Viscosity, $[\eta]$. With the quantities of nitrates quoted above, one to three dilutions were usually sufficient to obtain this constant value. Duplicate or triplicate determinations were always made to verify observations. All butyl acetate residues were recovered by fractional distillation.

The Intrinsic Viscosities, obtained as directed in the preceding paragraphs, were taken to be proportional to the degree of polymerization and were used as such. They are, however, easily converted to numerical values representing the degree of polymerization by resorting to the Staudinger equation,

$$\lim_{c \to 0} \left[\frac{\eta_{sp}}{C_{\text{sub moles}}} \right] = K_m M$$

where

$C_{\text{sub moles}}$ = Concentration in sub moles per liter.

K_m = A constant.

M = Molecular weight of the macromolecule.

Since the Concentration in sub moles, expressed as a per cent = $\frac{\text{Weight of a sub mole}}{1000} \times 100\%$

$$\text{therefore } \frac{\text{Concentration \%}}{\frac{\text{Submolar weight} \times 100}{1000}} = \text{Concentration in submoles.}$$

where Concentration % = Concentration in grams per 100 ml.

Therefore the Staudinger Equation can be written as

$$\lim_{c \to 0} \left[\frac{\eta_{sp}}{c_{\text{sub moles}}} \right] = \lim_{c \to 0} \left[\frac{\eta_{sp}}{c\% / \frac{\text{Submolar weight} \times 100}{1000}} \right] = K_m M.$$

$$\text{or} \quad \lim_{c \to 0} \left[\frac{\eta_{sp}}{c\%} \right] = \frac{K_m M \times 10}{\text{Submolar wt.}}$$

But the Molecular Weight (M) = D.P. x Submolar weight.

where D.P. is the Degree of Polymerization.

$$\text{Therefore, } \lim_{c \to 0} \left[\frac{\eta_{sp}}{c\%} \right] = 10 K_m \text{ D.P.} = [\eta] \qquad (a)$$

According to the work of Kraemer (92, 94), evaluation of the constant, K_m , gives the relation

$$\text{D.P.} = 270 [\eta]$$

FRACTIONATION OF CELLULOSE NITRATES

The details of the fractionation of nitrocellulose followed those given by Gladding (87, 144). Acetone was purified by heating under reflux with the addition of successive small amounts of potassium permanganate until a reasonable time of reflux no longer discharged the pink color. The acetone was thereupon distilled from sodium carbonate, and kept in a glass-stoppered bottle. By mechanical shaking, 2 to 3.5 g. of nitrocellulose was dissolved in about 500 ml. of the purified acetone (144). Fine, undissolved, threadlike particles invariably remained suspended in the solution, and were removed by filtration through glass wool. In order to ascertain the exact concentration, two samples (25 to 30 ml. each) of the slightly viscous solution were accurately weighed into all-glass containers and subsequently diluted with 150 ml. of distilled water. The addition of 1.5 g. of sodium chloride aided in the precipitation of any colloidal suspension. Vigorous shaking of the solution and container for a period of five minutes hastened the coagulation of the fine particles. The mixture was then allowed to stand for one hour, after which time the precipitate was transferred quantitatively to a Gooch filter with paper base, and washed eight times with small portions of distilled water. The precipitate was never allowed to suck dry and thus mat heavily. Dispersion of the precipitate in 150 ml. of distilled water for an interval of two hours then followed. The thoroughly-washed

nitrocellulose was filtered free from liquid through a previously dried and weighed Gooch crucible (with paper base), washed with a small amount of water and dried under vacuum over phosphorus pentoxide for a day (or until the surface of the anhydride, freshly replaced, showed no liquifaction). The material was then weighed and the concentration of the original solution calculated.

About 275 to 300 g. of the nitrocellulose solution was weighed, to the second decimal place, in a 500 ml. wide-mouthed Erlenmeyer flask, which was subsequently partially immersed in a water bath at 25° (± 0.1°) and then fitted with a stirring mechanism. After a five-minute interval, to permit the temperature of the liquid to reach equilibrium, water from a burette was added dropwise, with continued ,rapid stirring, until the first faint cloudiness appeared. Usually, 25 to 30 ml. of water was necessary before any change in the physical state of the liquid was apparent. Extreme care had to be taken in the observation of this point, especially in the precipitation of the first two or three fractions, otherwise these were found to contain too great a percentage of the nitrocellulose. The policy was to carry out the addition of water, during the precipitation of these initial fractions, to the point where only a barely perceptible haziness occurred; while in subsequent fractions, the intensity of the cloudiness was allowed to become progressively more pronounced, especially toward the conclusion of the operation. This precaution

permitted a more even distribution of the quantity of nitrocellulose over the number of fractions obtained. It was found that if the precipitate was too heavy at any particular time, the addition of a small amount of acetone caused partial or total dissolution, with no apparent ill effects. Too rapid an addition of water induced localized precipitation which required a long time to redissolve. Rapid stirring was essential in the solution of these isolated "globules" of cellulose nitrate, as well as for a quick distribution of the water to bring about uniform, gradual and general formation of the solid.

When the appropriate amount of water had been added, the solution was stirred for twenty minutes at 25° (± 0.1°) to attain equilibrium between the phases. A tendency was noted toward increased precipitation during the period of stirring, particularly in the case of the first few fractions, and this occurrance led to larger weights for these fractions than was anticipated. Hence it was important to add a somewhat smaller volume of water to obtain each of these fractions, and to regulate the stirring mechanism in such a way as to minimize evaporation.

The solid was now separated from the liquid by means of a centrifuge, twenty minutes being allowed to complete the sedimentation. The supernatant liquid was returned to the wide-mouthed Erlenmeyer flask, and a second precipitation was carried out as before. The fraction already obtained was

dissolved in acetone and precipitated with 150 ml. of water plus 1.5 g. of sodium chloride, and given further treatment identical to that devised for the determination of concentration. From seven to twelve fractions were obtained from each sample of the nitrate used. After some experience, and with ordinary apparatus, a careful investigator can satisfactorily fractionate, in the manner indicated, as small an amount as 0.8 grams of the nitrate.

CALCULATION OF NITROGEN AND VISCOSITY INTEGRAL DISTRIBUTION FUNCTIONS (Tables III,IV,V,VI; Figs. 7,8,9)

The per cent nitrogen, as well as the viscosity values, found for each fraction of the nitrates examined, was related to the various fractions(expressed as a per cent of the total weight of cellulose nitrate) by an Integral Weight Distribution plot (140) in such a way that any point on the curve represents the total percentage of nitrocellulose with nitrogen values lying between unity and the per cent under consideration. Thus, any two adjacent points, x and y, lying upon the curve, indicate the percentage (by difference) of the total material having a substitution lying between the nitrogen values represented by these two points. The numerical values of the Integral Distribution Function (Ip), were obtained for the viscosity and per cent nitrogen values of the fractions, arranged in descending order of Intrinsic Viscosities, in the following manner.

To one half of the weight percentage of each fraction was added the sum of the weight percentages of all the fractions appearing above it in the table.

CORRECTION OF VISCOSITIES FOR VARIABLE NITRATE CONTENT

Since a variation in degree of substitution causes a corresponding change in the Intrinsic Viscosity, other factors being equal, (70) a correction was applied to all nitrates of less than theoretical substitution in order to bring them to the comparable trinitrate basis. The method of its calculation was identical to that devised by Glegg (147). The uncorrected values of the Intrinsic Viscosities, divided by the correction factor obtained from Fig. 6, yielded the viscosities corrected for variation in substitution. These corrected viscosities are assembled in Tables V and VI. The correction was found to be greater for the nitrated collapsed cellulose than for the nitrated swollen cellulose; hence the correction plots are not the same for the two types of cellulose (Fig. 6), and somewhat different from that obtained by Glegg(147).

Tables VII, VIII and IX contain summaries of the data on the swelling, collapsing, nitration and viscosity determination of four samples of cellulose (A,B,C and C), each of a definite amount of accessible cellulose, before fractionation of their nitrates.

TABLE III

INTEGRAL DISTRIBUTION FUNCTIONS, INTRINSIC VISCOSITIES AND NITROGEN CONTENTS OF THE FRACTIONATED NITROCELLULOSE

Cellulose Sample "B".

Treatment 1. Swollen by Assaf's method(a)
2. Nitrated with P_2O_5-HNO_3 .

Accessible Surface 18.7% (b)

Fraction	Wt.g.	Wt. %	I(P)	Av. [η]	Av. % N
(1)	(2)	(3)	(4)	(5)	(6)
I	1.2804	57.9	28.95	21.9	13.92
II	0.4106	18.57	67.19	15.6	13.92
III	0.1859	8.40	80.67	10.84	13.80
IV	0.0941	4.25	87.00	8.34	13.75
V	0.0850	3.85	91.05	7.02	13.78
VI	0.0789	3.57	94.78	5.35	13.73
VII	0.0760	3.44	98.28	2.72	13.76
Unfractionated sample precipitated from acetone				16.70	13.80

% Recovery 100.3(c)

$$\frac{\Sigma \text{ Wt. x \%N}}{\Sigma \text{ Wt.}} = 13.84\% \qquad \frac{\Sigma \text{ Wt. x } [\eta]}{\Sigma \text{ Wt.}} = 17.30$$

(a) See ref. (10)
(b) Obtained from the product of the % Methoxyl and 100/57.4
(c) A small amount of glass inadvertently fell into fraction V.

(Cont'd. p. 51)

TABLE III

(cont'd)

Cellulose Sample "B"

Treatment 1. Swollen by Assaf's method, then collapsed by drying from water.
2. Nitrated with P_2O_5-HNO_3.

Accessible Surface 0.26%.

Fraction	Wt. g.	Wt. %	I(P)	Av.[η]	Av.%N
(1)	(2)	(3)	(4)	(5)	(6)
III	1.1431	47.70	23.85	24.3	13.87
I	0.0572	2.38	48.89	21.7	13.69
II	0.1119	4.67	52.42	21.1	13.82
IV	0.7157	29.83	69.67	14.5	13.96
V	0.1167	4.86	87.07	11.6	13.75
VI	0.0974	4.07	91.48	10.6	13.82
VII	0.0736	3.07	95.05	9.20	13.45
VIII	0.0463	1.93	97.48	7.52	13.49
IX	0.0375	1.56	99.22	3.59	13.19
Unfractionated sample precipitated from acetone				19.38	13.66

% Recovery 99.9

$$\frac{\Sigma \text{ Wt. x \% N}}{\Sigma \text{ Wt.}} = 13.86\% \qquad \frac{\Sigma \text{ Wt. x } [\eta]}{\Sigma \text{ Wt.}} = 18.90$$

(Cont'd p.52)

TABLE III

(cont'd)

Cellulose Sample "B"

Treatment 1. Swollen by Assaf's method.
2. Nitrated by HNO_3-H_2SO_4-H_2O.

Accessible Surface 18.7%

Fraction	Wt. g.	Wt. %	I(P)	Av. $[\eta]$	Av. % N
(1)	(2)	(3)	(4)	(5)	(6)
I	0.1063	4.98	2.49	12.94	12.37
II	0.3035	14.21	12.09	11.75	12.42
III	0.6726	31.48	34.96	9.57	12.34
IV	0.1517	7.11	54.23	7.73	12.22
V	0.2034	9.53	62.55	7.02	12.07
VI	0.1349	6.32	70.47	6.67	12.07
VII	0.1742	8.17	77.72	5.91	12.16
VIII	0.1216	5.68	84.64	5.24	12.03
IX	0.0840	3.94	89.44	4.49	11.95
X	0.0896	4.19	91.43	3.57	11.78
XI	0.0934	4.38	97.81	2.08	11.54
Unfractionated sample precipitated from acetone				8.36	12.01

% Recovery 98.1

$$\frac{\Sigma \text{ Wt. x \% N}}{\Sigma \text{ Wt.}} = 11.75\% \qquad \frac{\Sigma \text{Wt. x } [\eta]}{\Sigma \text{ Wt.}} = 8.24$$

(Cont'd. p.53)

TABLE III

(cont'd)

Cellulose Sample "B"

Treatment 1. Swollen by Assaf's method, then collapsed by drying from water.
2. Nitrated by HNO_3-H_2SO_4-H_2O.

Accessible Surface 0.26%

Fraction	Wt. g.	Wt. %	I(P)	Av.[η]	Av.% N
(1)	(2)	(3)	(4)	(5)	(6)
I	0.1946	8.63	4.23	13.55	12.31
II	0.2038	9.04	11.15	11.60	12.27
III	0.2047	9.09	22.22	10.23	12.32
IV	0.2658	11.79	32.66	9.22	12.39
V	0.2140	9.50	43.30	8.73	12.12
VI	0.4391	15.37	55.75	7.85	12.07
VII	0.2321	10 30	68.59	6.86	11.73
VIII	0.1904	8.45	77.97	6.16	11.70
IX	0.1755	7.78	82.22	5.13	11.53
X	0.1109	4.92	92.46	4.01	11.28
XI	0.1144	5.08	97.46	2.26	11.22
Unfractionated sample precipitated from acetone				8.10	11.91

% Recovery 98.6

$$\frac{\Sigma \text{ Wt. x \% N}}{\Sigma \text{ Wt.}} = 11.98\% \qquad \frac{\Sigma \text{Wt. x } [\eta]}{\Sigma \text{Wt.}} = 8.22$$

(Cont'd.p. 54)

TABLE III

(cont'd)

Cellulose Sample "B"

Treatment
1. Swollen by Assaf's method.
2. Nitrated by HNO_3-H_2SO_4-H_2O.
3. Renitrated by P_2O_5-HNO_3.

Accessible Surface 18.7%

Fraction	Wt. g.	Wt. %	I(P)	Av.[η]	Av.% N
(1)	(2)	(3)	(4)	(5)	(6)
I	0.2257	17.13	8.57	17.49	13.95
II	0.1336	10.14	22.20	15.40	13.90
III	0.0785	5.96	30.25	15.40	13.78
IV	0.0877	6.66	36.56	13.45	13.63
V	0.0896	6.81	43.30	12.69	13.63
VI	0.0958	7.28	50.34	11.82	13 60
VII	0.0781	5.93	56.95	10.84	13.82
VIII	0.1656	12.58	66.20	9.25	13.87
IX	0.0483	3.71	74.35	8.79	13.66
XI	0.0362	2.75	77.58	6.38	13.64
X	0.1828	13.88	85.89	6.00	13.92
XII	0.0946	7.18	96.41	3.29	13.39(a)
Unfractionated sample precipitated from acetone				11.62	13.90

% Recovery 96.8

$$\frac{\Sigma \text{ Wt. x \% N}}{\Sigma \text{ Wt.}} = 13.78\% \qquad \frac{\Sigma \text{ Wt. x } [\eta]}{\Sigma \text{ Wt.}} = 11.48$$

(a) Doubtful value since small size of sample permitted only one analysis.

(Cont'd. p. 55)

TABLE III

(cont'd)

Cellulose Sample "B"

Treatment
1. Swollen by Assaf's method, then collapsed by drying from water.
2. Nitrated by HNO_3-H_2SO_4-H_2O.
3. Renitrated by P_2O_5-HNO_3.

Accessible surface 0.26%

Fraction	Wt.g.	Wt. %	I(P)	Av.[η]	Av.% N
(1)	(2)	(3)	(4)	(5)	(6)
I	0.5531	33.99	17.00	21.73	13.68
II	0.2166	13.31	40.65	16.38	13.79
III	0.1182	7.26	50.93	14.30	13.81
IV	0.2031	12 48	60.80	11.41	13.73
V	0.0928	5.71	69.90	9.93	13.62
VI	0.1360	8.34	76.92	8.42	13.76
VII	0.0582	3.57	82.88	7.29	13.58
VIII	0.0754	4.63	86.98	6.09	13.58
IX	0.0658	4.05	91.33	4.21	13.20(a)
X	0.0779	4.78	95.74	3.21	13.48
XI	0.0305	1.87	99.07	1.36	10.07(b)
Unfractionated sample precipitated from acetone				14.10	13.83

% Recovery 97.8

$$\frac{\Sigma \text{ Wt. x \% N}}{\Sigma \text{ Wt.}} = 13.62\% \qquad \frac{\Sigma \text{ Wt. x } [\eta]}{\Sigma \text{ Wt.}} = 14.15$$

(a) Doubtful value since this is the average of four determinations which deviate quite widely.
(b) Doubtful value since small size of sample permitted only one determination.

TABLE IV

INTEGRAL DISTRIBUTION FUNCTIONS

INTRINSIC VISCOSITIES AND NITROGEN CONTENTS

OF THE FRACTIONATED NITROCELLULOSE

(Data collected from the fractionation of a second portion of the P_2O_5-HNO_3 nitrated collapsed cellulose, in an attempt to verify the information assembled in Table III, p.51, and the shape of the plot in Fig.7)

Cellulose Sample "B"

Treatment 1. Swollen by Assaf's method, then collapsed by drying from water.
. Nitrated by P_2O_5-HNO_3.

Accessible Surface 0.26% (a) (Compare Table III, p.51)

Fraction	Wt.g.	Wt. %	I(P)	Av.[η]	Av.% N
(1)	(2)	(3)	(4)	(5)	(6)
I	0.1245	22.00	11.00	28.11	13.92
II	0.0505	8.93	26.47	25.90	13.71
III	0.0548	9.69	35.78	22.13	13.90
IV	0.0588	10.39	45.82	19.11	13.88
V	0.0392	6.93	54.48	17.70	13.92
VI	0.0770	13.61	64.75	14.79	14.00
VII	0.1603	28.37	85.74	9.70	13.82
Unfractionated sample precipitated from acetone				18.08	13.82

% Recovery 96.1

$$\frac{\Sigma \text{Wt. x \% N}}{\Sigma \text{Wt.}} = 13.88\% \qquad \frac{\Sigma \text{Wt. x } [\eta]}{\Sigma \text{ Wt.}} = 18.61$$

(a) Obtained from the product of the % methoxyl and 100/57.4.

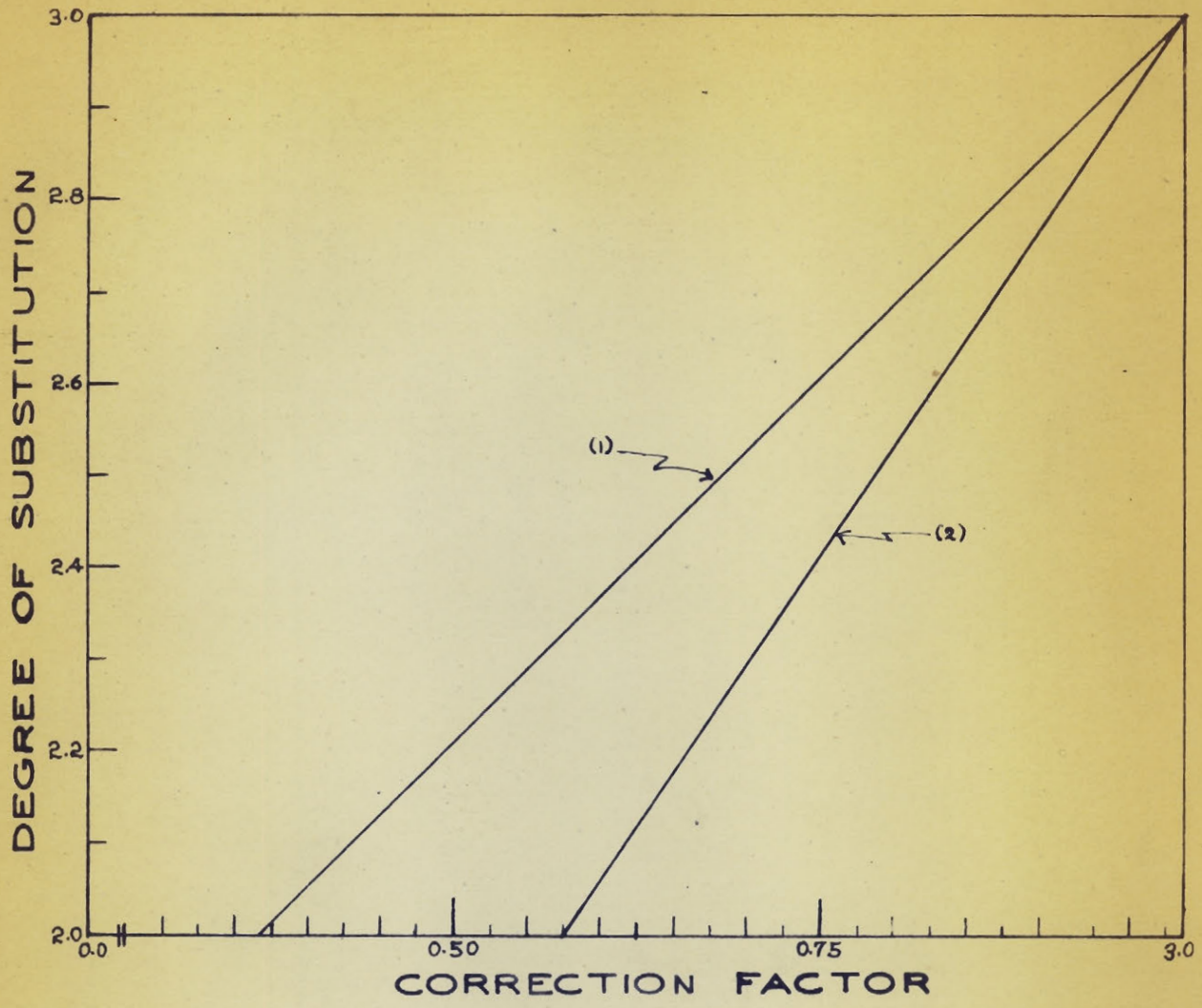

Fig. 6 - Plot of viscosity corrections applied for degree of substitution of the alcoholic groups in nitrocelluloses.

(1) Correction curve for nitrated collapsed cellulose of methoxyl content 0.15%

(2) Correction curve for nitrated swollen cellulose of methoxyl content of 10.72%

TABLE V

CORRECTION TO THE TRINITRATE BASIS FOR NITROGEN SUBSTITUTION OF THE FRACTIONATED NITROCELLULOSES IN TABLE III

(Cellulose Sample "B")

Type of Prepared Cellulose	Fraction	Av. % N	Degree of Substitution	Wt. %	$[\eta]$ uncorr.	Corr. Factor	Corr. $[\eta]$	I(P)
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
Swollen by Assaf's Method. Nitrated by HNO_3-P_2O_5.	I	13.92	2.92	57.9	21.9	0.97	22.59	28.95
	II	13.92	2.92	18.57	15.6	0.97	16.08	67.19
	III	13.80	2.87	8.40	10.84	0.94	11.54	80.67
	IV	13.75	2.85	4.25	8.34	0.93	8.97	87.00
	V	13.78	2.86	3.85	7.02	0.94	7.52	91.05
	VI	13.73	2.85	3.57	5.35	0.93	5.75	94.84
	VII	13.76	2.86	3.44	2.72	0.94	2.91	98.29
Swollen by Assaf's Method, Collapsed by drying from water. Nitrated by HNO_3-P_2O_5.	III	13.87	2.89	47.70	24.3	0.92	26.38	23.85
	I	13.69	2.83	2.38	21.7	0.87	24.95	48.89
	II	13.82	2.88	4.67	21.1	0.92	22.94	52.42
	IV	13.96	2.93	29.83	14.5	0.95	15.27	69.67
	V	13.75	2.85	4.86	11.6	0.90	12.92	87.01
	VI	13.82	2.88	4.07	10.6	0.92	11.52	91.48
	VII	13.45	2.74	3.07	9.20	0.83	11.07	995.05
	VIII	13.49	2.76	1.93	7.52	0.84	8.95	97.55
	IX	13.19	2.65	1.56	3.59	0.77	4.67	99.29

(Cont'd. p. 59)

TABLE V

(Cont'd)

Type of Prepared Cellulose	Fraction	Av. % N	Degree of Substitution	Wt. %	[η] uncorr.	Corr. Factor	Corr. [η]	I(P)
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
Swollen by	I	12.37	2.37	4.98	12.94	0.74	17.49	2.49
Assaf's	II	12.42	2.40	14.21	11.75	0.75	15.67	12.09
Method.	III	12.34	2.37	31.48	9.57	0.74	12.89	34.93
Nitrated	IV	12.22	2.33	7.11	7.73	0.72	10.73	54.23
by	V	12.07	2.28	9.53	7.07	0.70	10.06	62.55
HNO_3-H_2SO_4-	VI	12.07	2.28	6.32	6.67	0.70	9.53	70.47
	VII	12.16	2.31	8.17	5.91	0.71	8.33	77.72
H_2O.	VIII	12.03	2.27	5.68	5.24	0.69	7.59	84.64
	IX	11.95	2.25	3.94	4.59	0.68	6.74	89.44
	X	11.78	2.19	4.19	3.57	0.66	5.41	01.43
	XI	11.54	2.12	4.38	2.08	0.63	3.31	97.81
Swollen by	I	12.31	2.36	8.63	13.55	0.59	22.96	4.32
Assaf's	II	12.27	2.34	9.04	11.60	0.58	20.00	13.15
Method.	III	12.32	2.36	9.09	10.23	0.59	17.37	22.27
Collapsed	IV	12.39	2.38	11.79	9.22	0.60	(V)15.86 (a)	31.51
by drying	V	12.12	2.30	9.50	8.73	0.55	(IV)15.26	42.16
from water.	VI	12.07	2.28	15.39	7.85	0.54	14.52	55.75
Nitrated	VII	11.73	2.18	10.30	6.86	0.48	14.29	68.59
by	VIII	11.70	2.17	8.45	6.16	0.47	13.11	77.79
HNO_3-H_2SO_4-	IX	11.53	2.12	7.78	5.13	0.44	11.67	86.08
	X	11.28	2.05	4.92	4.01	0.40	10.02	92.43
H_2O.	XI	11.22	2.04	5.08	2.26	0.39	5.79	97.43

(a) Application of the correction has reversed the order of fractions IV and V, in magnitude of [η] and thus affected I(P)

(Cont'd. p. 60)

TABLE V

(Cont'd)

Type of Prepared Cellulose	Fraction	Av. % N	Degree of Subsitituion	Wt. %	[η] uncorr.	Corr. Factor	Corr. [η]	I(P)
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
Swollen by	I	13.95	2.93	17.13	17.49	0.97	18.02	8.57
Assaf's	III	13.78	2.86	5.96	15.40	0.94	16.38	20.11
Method.	II	13.90	2.91	10.14	15.40	0.96	16.02	28.16
Nitrated by	IV	13.63	2.81	6.66	13.45	0.92	14.62	36.56
HNO_3-H_2SO_4-	V	13.63	2.81	6.81	12.69	0.92	13.79	43.30
H_2O.	VI	13.60	2.79	7.28	11.82	0.91	12.99	50.34
Renitrated	VII	13.82	2.88	5.93	10.84	0.95	11.48	56.95
by	VIII	13.87	2.89	12.58	9.25	0.95	9.74	66.20
HNO_3-P_2O_5.	IX	13.66	2.82	3.71	8.75	0.92	9.54	74.35
	XI	13.64	2.81	2.75	6.38	0.92	6.83	77.58
	X	13.92	2.92	13.88	6.00	0.97	6.22	85.89
	XII	13.69	2.72	7.18	3.29	0.88	3.74	96.42
Swollen by	I	13.68	2.82	33.99	21.73	0.87	24.96	17.00
Assaf's	II	13.79	2.87	13.31	16.38	0.91	18.00	40.65
Method.	III	13.81	2.88	7.26	14.30	0.92	15.57	50.93
Collapsed	IV	13.73	2.85	12.48	11.41	0.90	12.69	60.80
by drying	V	13.62	2.81	5.71	9.93	0.87	11.36	69.90
from water.	VI	13.76	2.86	8.34	8.42	0.91	9.30	76 92
Nitrated by	VII	13.58	2.79	3.57	7.29	0.86	8.48	82.88
HNO_3-H_2SO_4-	VIII	13.58	2.79	4.63	6.09	0.86	7.08	86.98
H_2O.	IX	13.20	2.65	4.05	4.21	0.77	5.47	91.33
Renitrated	X	13.48	2.75	4.78	3.21	0.83	3.87	95.75
BY	XI	10.07	1.72	1.87	1.36	0.36	3.74	99.07
P_2O_5-HNO_3.								

TABLE VI

CORRECTION TO THE TRINITRATE BASIS, FOR NITROGEN SUBSTITUTION OF THE FRACTIONATED NITROCELLULOSES IN TABLE IV

(Cellulose Sample "B")

Type of Prepared Cellulose	Fraction	Av. % N	Degree of Substitution	Wt. %	$[\eta]$ uncorr.	Corr. Factor	Corr. $[\eta]$	I(P)
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
Swollen by	I	13.92	2.92	22.00	28.11	0.97	28.90	11.00
Assaf's	II	13.71	2.84	8.93	25.90	0.93	27.80	26.47
Method.	III	13.90	2.91	9.69	22.13	0.97	22.95	35.78
Collapsed	IV	13.88	2.90	10.39	19.11	0.96	19.92	45.82
by drying	V	13.92	2.92	6.93	17.70	0.97	18.26	54.48
from water.	VI	14.00	2.95	13.61	14.79	0.98	15.09	64.75
Nitrated by P_2O_5-HNO_3.	VII	13.82	2.88	28.37	9.70	0.95	10.21	85.74

TABLE VII

SURFACE ESTIMATIONS, NITROGEN CONTENTS AND VISCOSITIES OF THE NITROCELLULOSES OF CELLULOSE SAMPLE "A"

Type of Prepared Cellulose	Accessible Surface %	Nitrated by	Appearance of the Nitrocellulose	% N	Av. % N	Substitution	Submolar Wt.[a]	[η]	Av. [η]
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
Swollen by Assaf's Method.[b]	26.3	HNO_3-H_2O-H_2SO_4	Colorless, fibrous. Some change in texture to brittleness.	12.02 12.06	12.04	2.27	264	4.46 4.50	4.48
Swollen by Assaf's Method. Collapsed by drying from water.	0.23	HNO_3-H_2O-H_2SO_4	Colorless, fibrous. More brittle than swollen sample above.	11.41 11.42	11.42	2.09	256	1.73 7.40 2.54 4.39	Doubtful
Swollen by Assaf's Method.	26.3	HNO_3-P_2O_5	Colorless, fibrous. No change in texture.	13.63 13.55 13.75	13.64	2.82	289	6.51 6.53	6.52
Swollen by Assaf's Method. Collapsed by drying from water.	0.23	HNO_3-P_2O_5	Colorless, fibrous. No change in texture.	13.50 13.61 13.71	13.61	2.80	288	11.08 9.53 7.93	Doubtful

Unswollen cellulose (dried as were samples above) nitrated by H_2SO_4-HNO_3-H_2O gave 12.2% N.
Unswollen cellulose (dried as were samples above) nitrated by HNO_3-P_2O_5 gave 13.95% N.

(A) Calculated from the % N by the relation, $\%N = (1400x)/(162+45x)$, where x is the degree of substitution, 162 is the weight per unsubstituted glucose unit, and 45 is the net weight contributed to the glucose unit by each nitro group.

(b) See ref. (10).

TABLE VIII

SURFACE ESTIMATIONS, NITROGEN CONTENTS AND VISCOSITIES OF THE NITROCELLULOSES OF CELLULOSE SAMPLE "B"

Type of Prepared Cellulose	Accessible Surface %	Nitrated by	% Yield	Appearance of the Nitrocellulose	Av. % N.	Substitution	Sub-molar Wt.[a]	Av. [η]
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
Swollen by Assaf's Method.[b]	18.7	HNO_3-H_2O-H_2SO_4	98.5	Colorless, fibrous, of somewhat brittle character.	12.19	2.32	266	9.24
Swollen by Assaf's Method. Collapsed by drying from water.	0.26	HNO_3-H_2O-H_2SO_4	97.8	Colorless, fibrous, of somewhat brittle character.	11.84	2.21	262	9.58
Swollen by Assaf's Method.	18.7	HNO_3-P_2O_5	99.1	Colorless, fibrous. No change in texture.	13.80	2.87	291	20.1

(a) See Table VII, p. 62, footnote (a).
(b) See ref. (10).

(Cont'd. p. 64)

OXIDATIONS WITH LEAD TETRAACETATE

Pure, dry ethyl acetate was prepared according to the directions given by Fieser (116) in which commercial ethyl acetate was washed with an equal volume of 5% aqueous sodium carbonate, then with the same quantity of saturated calcium chloride solution. It was dried overnight with anhydrous potassium carbonate, then for three hours with phosphoric anhydride, from which it was then decanted and fractionally distilled twice under anhydrous conditions.

A good grade of lead tetraacetate was made by the procedure of Hockett and McClenahan (118,cf. also 119,120). A mixture of 530 ml. of purified glacial acetic acid and 115 ml. of acetic anhydride was heated to 75° in a 1-liter, 3-necked, round-bottom flask, fitted with a thermometer and a mechanical stirrer. Dry red lead, 150 g., was added in small portions, each successive addition being made only when the color of the oxide previously added had vanished. At the end of the reaction, wherein the temperature had been maintained below 90°, the faintly red solution, now practically free of unreacted lead oxide, was allowed to cool in the stoppered flask, whereupon the remaining traces of color disappeared, and the lead tetraacetate crystallized out in long, colorless needles. The salt could, if desired, be kept unchanged in this solution for an indefinite period. The

acetate was then separated from the liquid by filtration with gentle suction, washed with glacial acetic acid, and dried under vacuum over containers of phosphorus pentoxide and potassium hydroxide. Storage was over the same desiccants. The pentoxide darkened considerably, but permitted the preservation of the dried tetraacetate in an undecomposed, colorless state for a lengthy period. Any color, caused by contact of the salt with water vapor in the air, might be removed by solution of the solid in hot glacial acetic acid, decolorization with Norite if necessary, and then recrystallization. About 60 to 70 g. of the pure material was obtained.

Four liters of acetic acid was freed from aldehydes by heating for two hours under reflux with 10 g. chromic anhydride, after which time an additional 6 g. of chromic anhydride was inserted. Gentle boiling was continued for another hour, whereupon the acid was fractionated from any impurities in an all-glass apparatus (99, 122). Acetic anhydride was purified by careful fractionation of the stock material.

The strength of the acetic acid solution of the lead tetraacetate was determined by pipetting 20 ml. of the liquid into 30 ml. of a sodium acetate buffer (consisting of 20 g. potassium iodide plus 250 g. sodium acetate per liter) and titrating the liberated iodine to a starch end point with 0.02N sodium thiosulphate (121, 99).

About 0.5 g. of the prepared nitrocellulose, previously dried for twenty four hours under vacuum over phosphoric anhyd-

ride, was put into a 200 ml. volumetric flask. The solid was covered with 125 ml. of purified, anhydrous ethyl acetate, and slowly dissolved by agitation on a mechanical shaker, whereupon 40 to 50 ml. of 0.1 N glacial acetic acid solution of lead tetra-acetate was added, followed by enough anhydrous ethyl acetate to bring the total volume to the 200 ml. mark. Oxidation was carried out at 25° (± 0.1°), and followed by the potassium iodide-sodium thiosulphate method of Dimroth and Schweitzer (121). At suitable intervals, 15 ml. aliquots were pipetted into 30 ml. of potassium iodide- sodium acetate solution (99) contained in a 250 ml. Erlenmeyer flask, and 10 ml. of pure ethyl acetate was added to prevent precipitation of the nitrocellulose. Water, 75 ml., and starch solution, 3 ml., followed, and titration of the liberated iodine proceeded with 0.02 N sodium thiosulphate. The titration was slow, and required considerable agitation of the flask to allow all the iodine in the ethyl acetate layer to come into intimate contact with the thiosulphate in the water layer. Near the end point, after the addition of each drop, the flask had to be shaken for a time, since the darkening due to the starch indicator reappeared very slowly. A colorless liquid denoted the completion of the titration. Oxidation in two blank determinations was carried out at the same time. Consumption of oxidant was expressed as the difference in titrations between the blanks and the sample.

Tables X and XI, also Figs. 10 and 11, give the

results of oxidations for twelve technical nitrocelluloses, made by the displacement or mechanical process, whose properties are discussed later. Table XIV and Fig. 14 give similar results for swollen and collapsed linters. Part of the work was duplicated on samples reprecipitated from acetone and intensively dried, first under vacuum over phosphorus pentoxide for forty eight hours, then under vacuum over phosphorus anhydride at 50° for seventy two hours. Table XII and Fig. 12 give the results of oxidations of the precipitated technical nitrocelluloses dried with the pentoxide for forty eight hours, while Table XIII and Fig. 13 show similar oxidations of the same cellulose nitrates after they had been subjected to the more intensive drying at 50°.

OXIDATIONS WITH PERIODIC ACID

Sodium arsenite solution was prepared by adding 5.94 g. (0.03 moles) of arsenic trioxide and 10 g. of solid sodium hydroxide to 50 ml. of distilled water. After solution was complete, the liquid was neutralized with enough molar sulphuric acid to make it just acid to methyl orange. Solid sodium bicarbonate, 20 g., was then added and the volume made up to two liters, to give approximately a strength of 0.05 N in arsenite. The preparation was shaken thoroughly, and allowed to stand a day before use (since immediate use was found to yield extreme variations in titrations) (123, 124). The standardization was

TABLE XIV

OXIDATIONS OF TECHNICAL NITROCELLULOSES FROM SWOLLEN AND COLLAPSED LINTERS WITH 0.025 MOLAR LEAD TETRAACETATE

Oxidation Time	Consumption of Oxidant in Moles x 10^{-2} by Nitrocellulose Sample	
Hours	A. Accessible surface ....31.5% Nitrogen ....12.01% Substitution ..2.27	B. Accessible surface ..... 0.26% Nitrogen .....11.80% Substitution ..2.20
(1)	(2)	(3)
3.0	4.3	2.7
16.5	4.1	3.6
44.5	8.7 (a)	6.5 (a)
94.5	5.2	3.1
152.0	5.1	6.5
219.5	5.4	9.1
269.5	5.7	9.0
328.5	7.6	13.5
400.5	9.7	13.5

(a) Evidently in error, perhaps due to erratic behavior of the blank.

be calculated. A plot of the per cent uptake of water against the relative humidity (Fig. 15) gave a smooth adsorption isotherm comparable with those obtained by Purves et al (35).

Each dried sample was analyzed in triplicate for percentage accessible cellulose by the thallous ethylate method (10), and the per cent loss of accessible cellulose (based upon the original amount of accessibility) was plotted against the per cent moisture desorbed. Table XV and Fig. 16 show the results of the experiments carried out in the manner indicated above.

A second sorption-desorption experiment was carried out in exactly the same way as described in the preceding paragraphs in order to confirm the data already obtained. The results of this second determination are given in Table XVI and Figs. 17 and 18.

TABLE XV

RELATIONSHIP OF THE DECREASE IN ACCESSIBLE CELLULOSE TO THE REMOVAL OF DEFINITE AMOUNTS OF WATER BY DIRECT DRYING

Sample Number	Density of[a] Sulphuric Acid at 25°	Relative Humidity % at 25°	Weight of dry Sample	Weight of Water Desorbed	% Water Desorbed (on dry Wt.)	Average %[b] Methoxyl (after drying)	% Loss in[c] Accessibility
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
A	1.2675	64.2	0.33751	0.03384	10.02	1.31	93.14
I	1.3008	57.1	0.46033	0.04065	8.83	2.14	88.7
B	1.3147	53.5	0.36167	0.02913	8.06	2.49	86.9
C	1.3569	43.9	0.41195	0.02624	6.38	4.52	76.2
D	1.3772	39.8	0.42488	0.02480	5.84	6.74	64.6
J	1.3990	35.8	0.41068	0.02152	5.23	7.78	59.2
E	1.4268	30.0	0.45248	0.02012	4.43	9.17	51.8
F	1.4525	25.7	0.46938	0.02024	4.30	9.51	50.1
G	1.4953	17.5	0.53683	0.01789	3.34	10.72	43.1
H	1.5434	10.0	0.40307	0.01078	2.68	10.06	47.4
Swollen linters 0.0						19.02	0.0
Collapsed linters....(Soaked with water)						0.13	99.3

(a) See ref. (125).
(b) By thallous ethylate method. See ref. (10).
(c) Based on accessibility of original dry, swollen linters.

TABLE XVI

RELATIONSHIP OF THE DECREASE IN ACCESSIBLE CELLULOSE TO THE REMOVAL OF DEFINITE AMOUNTS OF WATER BY DIRECT DRYING[a]

Sample Number	Density of[b] Sulphuric Acid at 25°	Relative Humidity% at 25°	Weight of dry Sample	Weight of Water Desorbed	% Water Desorbed (on dry Wt.)	Average %[c] Methoxyl (after drying)	% Loss in[d] Accessibility
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
A	1.2675	64.2	0.61307	0.06014	9.80	0.83	95.4
I	1.3008	57.1	0.72290	0.06212	8.60	1.71	90.3
B	1.3147	53.5	0.60422	0.4849	8.03	2.10	88.2
C	1.3569	43.9	0.58756	0.03821	6.51	3.33	81.3
D	1.3772	39.8	0.64638	0.03746	5.80	4.65	73.8
J	1.3990	35.8	0.68735	0.03576	5.20	5.02	71.7
E	1.4268	30.0	0.66515	0.02985	4.48	8.70	50.8
F	1.4525	25.7	0.66403	0.02596	3.91	7.63	56.8
G	1.4953	17.5	0.67946	0.02051	3.02	11.57	34.6
H	1.5434	10.0	0.62583	0.01394	2.23	11.44	35.3
K	1.5880	6.4	0.60414	0.01108	1.83	11.65	34.1
Swollen linters		0.0	.....			17.67	0.0
Collapsed linters....(Soaked with water)						0.15	99.3

(a) Duplicate experiment to check data in Table XVI.
(b) See ref. (125).
(c) By thallous ethylate method. See ref. (10).
(d) Based on accessibility of original dry, swollen linters.

DISCUSSION OF RESULTS

The bulk of the experiments were carried out with four samples of the same dewaxed cotton linters, which were separately subjected to similar treatments involving swelling with caustic solution, drying through solvent exchange followed by intensive drying *in vacuo* at room temperature over phosphoric anhydride, and finally storing over concentrated sulphuric acid. Accessible fractions were then measured by the thallous ethylate method. As mentioned in the Experimental Section (pp. 30-32), the way in which the caustic soda was neutralized markedly influenced the final accessibility when other techniques were standardized. Linter samples A, B and D were swollen and dried as already described, but sample C was obtained from Mr. Glegg (2), who had conducted the swelling by his modification of the earlier technique (10), and transferred the swollen sample through anhydrous methanol into anhydrous benzene in the usual way. After remaining in the benzene for a year, the standard drying procedure was completed and the accessibility found to be high. Half of each of the four swollen samples were collapsed by direct drying from water. Each pair of the swollen and collapsed samples therefore had the same chain-length distribution. As far as is known, each pair was dried with the same degree of intensity, and the members differed in accessibility only.

Portions of each pair were then nitrated with the same

technical nitric acid-sulphuric acid mixture, three batches of which were freshly made up, and preserved at -15°, one for Sample A, another for Sample B and the third for Samples C and D. A similar procedure was adopted for the phosphorus pentoxide nitrating mixture, and every detail of the nitration and stabilization was standardized. The only known difference occurred with Sample A, the nitration mixtures for which were made up with fuming nitric acid whose color indicated the presence of oxides of nitrogen. Although redistilled immediately before use, the acid was faintly colored by the oxides of nitrogen present in the distillate. The acid for all other nitrations was obtained by distillation of equal weights of concentrated sulphuric acid and concentrated nitric acid (112). It is known that higher oxides of nitrogen cause degradation during nitration (74, 75), and nitrates from Sample A were presumably more degraded than those from Samples B, C and D.

It is clear from Tables VII, VIII and IX that a decrease in accessibility from the range 18 to 33% to about 0.25% was associated with decreases in the nitrogen contents of the technical nitrates A, B, C and D of (12.04-11.42) or 0.6%, 0.35%, 0.15% and 0.3% respectively. Since the Kjeldahl duplicate or triplicate analyses did not diverge fron their mean by more than ± 0.1% N, and were usually within ± 0.05% N, all but one (Sample C) of the above differences fell well outside analytical error. Whether or not proportionality exists between the amount of decrease in accessible cellulose and the decrease

in the extent of nitration with the technical nitrating mixture, cannot be ascertained from the data. Although the accessibilities of the swollen samples A, B, C and D were apparently decreased by factors of 110, 70, 140 and 80 respectively, only the order of magnitude of the decrease is significant, since the thallous ethylate method did not measure the accessibility of collapsed samples with sufficient accuracy. Furthermore, accessibilities measured by such a non-swelling method would be less than the fraction directly available to nitrating mixtures which are swelling agents.

It is also evident from Tables VII, VIII and IX, that decrease in accessibility from 33% to about 0.25% exerted no effect upon the degree of nitration obtained by nitrating mixtures of phosphoric anhydride and nitric acid. Both the collapsed and swollen specimens A,B, C and D were nitrated to the same extent, within the limits of experimental error, by this reagent. Renitration of the technical nitrates of Sample B by the phosphoric anhydride-nitric acid solution also obliterated their original difference in nitrogen content(Table VIII, column 6).

In the course of control experiments, samples of the dewaxed, but unswollen, linters were dried through solvent exchange and nitrated with the same mixtures employed in the work with A, B, C and D. The phosphorus pentoxide-nitric acid mixtures yielded nitrates with 13.95, 13.9, 13.76% N respectively, or 0.3, 0.1 and 0.1% N higher than the parallel work with the

swollen samples (C and D being counted as one). In similar fashion , the unswollen linters yielded technical nitrates with 12.2, 12.2, and 12.26% N, or increases of 0.15, 0.0, 0.1 and 0.15% N over the nitrogen contents of the technical nitrates of A, B, C and D respectively. All these changes, except the first (0.3%) are on the borderline of experimental error, but all except one (0.0%) tend to show that nitration proceeded to a somewhat higher level, other conditions being the same, with the unswollen than with the highly swollen linters. It is possible, therefore, that these changes may be significant. Berl also (71), by the use of a mixture of phosphoric acid, nitric acid and phosphorus pentoxide upon ramie, cotton, rayon and regenerated cellulose, obtained nitrogen values ranging from 13.3 to 13.9 %. Although no standardization of method was definitely claimed by Berl, the range of nitrogen content observed seems rather wide for such a powerful reagent.

Intrinsic viscosities were calculated throughout the research from specific viscosities determined in butyl acetate solutions successively diluted until the value was directly proportional to the concentration. The individual viscosity values quoted in Table VII (column 9) for the nitrates of the swollen linters A gave good checks, but both the phosphorus pentoxide-nitric acid and technical nitrates from the collapsed samples yielded solutions that were obviously"grained"in appearance. These solutions gave viscosity values that were

too erratic to be worth averaging. The data obtained on nitrates from the collapsed Sample B (Table VIII, column 9), giving good duplicate or triplicate checks in the viscosity determinations and good solutions in butyl acetate, were free from the above irregularity. Since the only definitely known difference between the series of nitrates of A and B is the quality of the nitric acid used in the nitrating mixtures, it is at first sight reasonable to attribute the irregular behavior of the collapsed Sample A to increased amount of oxidation by oxides of nitrogen during the preparations. Such oxidation undoubtedly did occur in Sample A, because the intrinsic viscosity of the phosphoric anhydride-nitric acid nitrate from the swollen portion, $[\eta]$, 6.5, was only one-third that of the corresponding preparation from Sample B, $[\eta]$, 20.1 (Table VIII); good solutions being obtained in both cases. It is, however, difficult to understand why oxidation during the phosphorus pentoxid-nitric acid and the technical nitrations of the collapsed Sample A would give "grained" products when a similar oxidation of the swollen portion A failed to do so. There may, however, have been undetermined variables in the swelling, drying, collapsing and drying procedure used to produce the collapsed samples A and B that brought about the differences. It also follows from the above comparisons that phosphorus pentoxide-nitric acid mixtures may produce degraded nitrates if the acid used contains oxides of nitrogen. The claim that

this nitrating mixture produces no degradation (71) must therefore be accepted with this reservation.

Reference to Table VIII also shows that the intrinsic viscosities of the phosphoric anhydride-nitric acid and technical nitrates from the collapsed cellulose B were 6% and 4%, respectively, higher than the corresponding values from the swollen sample. Renitration of the technical nitrates by the phosphorus pentoxide-nitric acid method reversed this relationship,but the difference in the figures (14.9 and 14.6) was well within the experimental error of the viscosity determinations. If it be assumed in this particular case that the phosphoric anhydride-nitric acid nitration did not alter the degree of polymerization of the cellulose, then as a first approximation, the ratios of the intrinsic viscosities of the phosphoric anhydride-nitric acid nitrates ([η],20.1 and 21.1) to those of the renitrated technical nitrates ([η], 14.9 and 14.6) compare the average chain length occasioned by the technical nitration, with that of the original cellulose. The results, 74% for the swollen and 68% for the collapsed samples, may agree within experimental error.

In order to study any differences in chain length distribution brought about by the collapse of the accessible fraction, the nitrates of Sample B (the technical nitrates, phosphorus pentoxide-nitric acid nitrates and the renitrated technical nitrates) were fractionated by precipitation with

water from a dilute solution of acetone (p. 45). Each fraction was again reprecipitated from acetone, thoroughly washed with water, and thoroughly dried so as to yield a pure sample of the cellulose nitrate. The results of the viscosity measurements on each fraction of the six nitrates are expressed in Table III and in Fig. 7, in which the intrinsic viscosity of the individual fractions is plotted against the Integral Weight Distribution Function. The manner of calculation of the Integral Weight Distribution Function has been explained on page 48 of the Experimental Section. Any point on the plot, Fig. 7, represents the total percentage of nitrocellulose having values for the intrinsic viscosities lying between unity and that represented by the particular point. For all except two of the six nitrocelluloses, the fractions precipitated in order of decreasing viscosity. The two exceptions were the phosphorus pentoxide-nitric acid nitrated swollen sample (Table III, p. 50) and the technically nitrated swollen sample renitrated by the phosphoric anhydride-nitric acid mixture (Table III, p. 54), and with them the order of precipitation was not followed.

Examination of Fig. 7 shows that the fractions of the nitrocelluloses obtained from the collapsed cellulose by its nitration with the phosphorus pentoxide-nitric acid reagent (plot 3), and by nitration with the technical mixture followed by renitration with the phosphorus pentoxide-nitric acid solution (plot 5), have a distinctly higher viscosity than those obtained similarly from the highly swollen linters (plots 4 and 6).

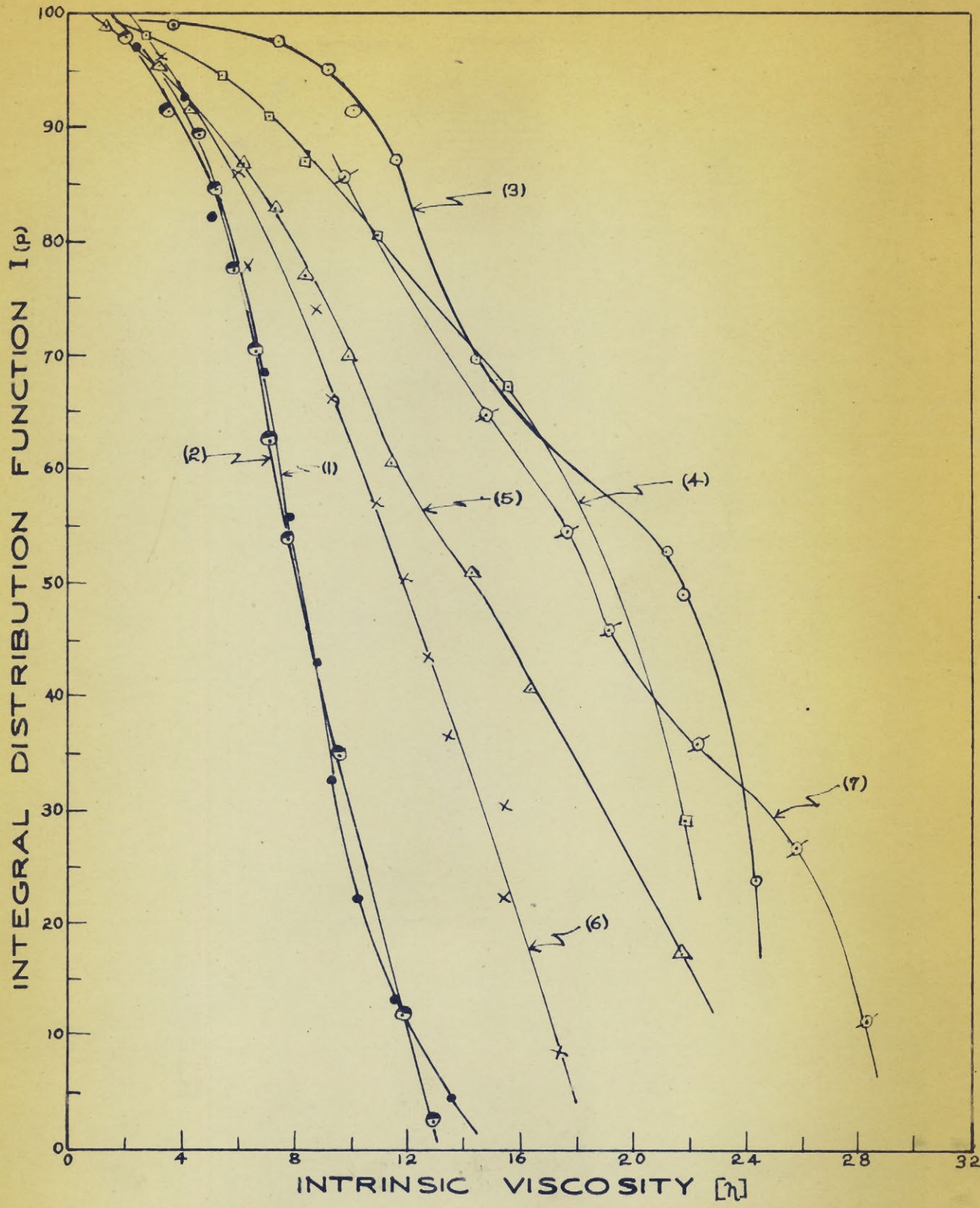

Fig. 7.-Integral Weight Distribution Function, I(P), vs Intrinsic Viscosity of fractionated nitrates of celluloses of different accessible fractions. Viscosities uncorrected for nitro substitution.
(1) & (2), Collapsed and Swollen cellulose, resp., technically nitrated.
(3) & (4), Collapsed and Swollen cellulose, resp., Nitrated by HNO_3-P_2O_5.
(5) & (6), Collapsed and Swollen cellulose, resp., technically nitrated, renitrated by HNO_3-P_2O_5. (7), Repetition of No.(3).

This trend bears out the differences exhibited by the unfractionated nitrates after, but not before, precipitation from acetone (Table III) wherein the viscosities of the collapsed phosphoric anhydride-nitric acid nitrated, and the renitrated, celluloses are 16% and 21% respectively higher than are those of the corresponding nitrates of the swollen cellulose.

The irregularity of plot 3 (Fig. 7) for the collapsed sample nitrated by phosphorus pentoxide-nitric acid, in contrast with the regular shape of the remaining five curves, suggested that some error had occurred during the manipulations involved in the fractionation. Accordingly, the remainder of the sample nitrated by this non-degrading mixture was fractionated in exactly the same manner as before, and the results are recorded in Table IV and Fig. 7,plot 7. This second fractionation exhibits the same type of irregularity. However, almost the whole curve is shifted somewhat toward the region of lower viscosity, indicating a definite drop in degree of polymerization. This drop was possibly caused by slow degradation of the nitrocellulose during storage,for the five months interval between the two "duplicate" fractionations. After this time, a 7% decrease in $[\eta]$ was observed (Table III, p. 51, and Table IV). This degradation, involving the nitrate obtained by the action of phosphorus pentoxide and nitric acid on the collapsed cellulose, revealed the possibility that the lower viscosities of the nitrated swollen specimens might be attributed to a similar slow degradation.

Thus, if the nitrates of the collapsed cellulose had been fractionated and analyzed for nitrogen and viscosity in all cases before those obtained from the swollen cellulose, the relative decrease might be accounted for without recourse to any effect caused by decrease in accessible surface. As it happened, nitrations and analyses of the nitrates were carried out in no systematic way in point of time. The technically nitrated and renitrated products from the swollen cellulose were both prepared in September and then examined in November1945 and January 1946 respectively, or after the corresponding investigations of products from the collapsed cellulose (prepared in September and examined in October and January). Although this time order is consistent, on the degradation hypothesis, with the lower viscosities of the swollen series , the reverse is true for the nitrates directly prepared with the phosphorus pentoxide-nitric acid mixture. In this case the nitrate from the swollen linters, of lower viscosity, was prepared and examined (September) before that from the collapsed product (prepared in September and examined in October).

Direct observations of stability during storage over phosphorus pentoxide were made with several of the nitrates. The intrinsic viscosities of fractions I and II of plot 6(Fig. 7), for example, were 21.7 and 21.1 when first measured, and after storage for five months, values of 21.2 and 21.3 respectively,were recorded. The nitrate yielding plot 6, however, had an original intrinsic viscosity of 19.4, reduced to 18.1 after storage for four and a half months and then reprecipitation from acetone. From the data

it is evident that the cellulose nitrates, purified by precipitation from acetone, did not exhibit a degradation on standing, whereas the one that was left in an unpurified state suffered a very slow degradation with time. It can therefore be inferred that the degradation of cellulose nitrates during storage depends upon the state of purity of the products, a conclusion in agreement with that obtained by Staudinger and Sorkin (88). It was also concluded that, with the possible exception of plot 7 (Fig. 7), the forms of the other plots in Fig. 7 were not appreciably altered by degradation during the period between preparation and examination.

Referring again to Fig. 7, the plots of the two technical nitrates from the collapsed and swollen cellulose coincide extremely closely (plots 1 and 2). In view of the fact that there was a considerable difference in nitrogen content between the two specimens (Table VIII, column 6, and Table III, pp. 52-53, column 6), and that renitration by phosphoric anhydride and nitric acid (presumably without further degradation) to nearly the theoretical per cent nitrogen destroyed the coincidence of the I(P) plots (Fig. 7, plots 5 and 6), it was quite conceivable that, since both degree of substitution (90) and chain length determine the numerical value of the intrinsic viscosity, a compensating effect had occurred in the viscosities of the technical nitrates. Portions of lower polymerization might have been nitrated to a higher degree than some of the longer chains, resulting by chance in the same value for $[\eta]$. The mode of substitution in the glucose unit might also exert some influence on

the value of the intrinsic viscosity. Thus, a dinitrate having substituents on carbon atoms 2 and 3, might give a value for $[\eta]$ different from that obtained if positions 3 and 6 were esterified (Fig.1), even if both dinitrates had equivalent chain lengths.

The nitrogen values of the various fractions obtained from the fractionation (Table III) are plotted, in Fig. 8, against the same Integral Weight Distribution Function as used for the viscosities (Fig. 7), and the ordinates of the two figures are superimposable. A marked difference is to be noticed in nitrogen content between the low viscosity fractions of the technically nitrated swollen and collapsed celluloses (Fig. 8, plots 1 and 2). It appears, therefore, that the major portion of the difference in nitrogen content between these two unfractionated technical nitrates, as observed in Tables VII, VIII and IX, occurs in the shorter chain length fractions. The fairly gradual alterations in the slopes of plots 1, 2 and 4 suggests that the error in the nitrogen estimations was not large. If this was true, the peculiar , wavy nature of plots 3, 5 and 6 may be of significance.

Since the degree of substitution is a factor affecting the viscosity of nitrocelluloses (90), a correction was applied to the viscosities of fractions whose nitrogen content was less than that of cellulose trinitrate (N, 14.14%). This empirical correction factor, as mentioned on page 49 of the Experimental Section, was thought to reduce the viscosity of the nitrocelluloses to the trinitrate basis. Tables V and VI record the corrections obtained

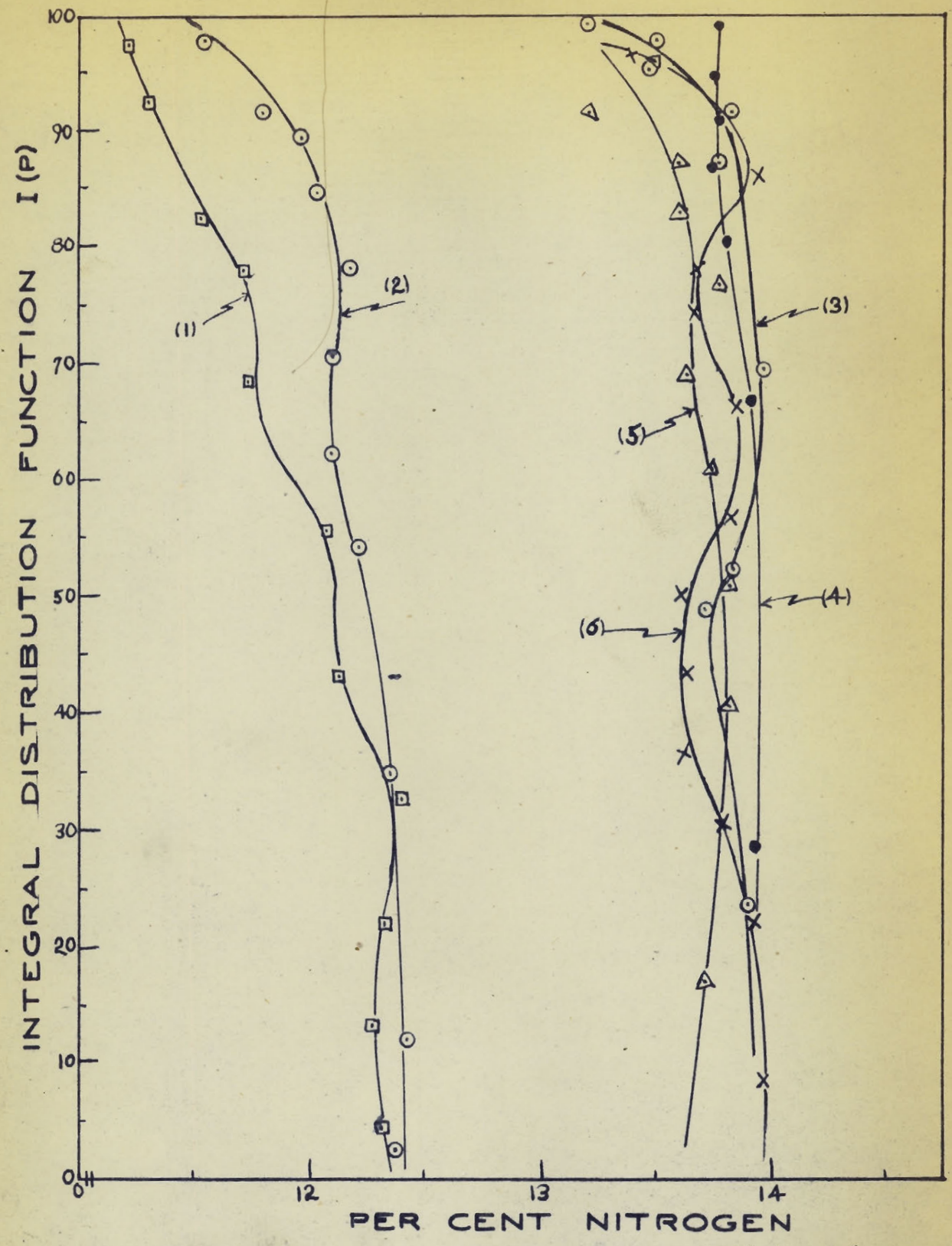

Fig. 8. -Integral Weight Distribution Function, I(P), vs %Nitrogen Content, for fractionated nitrates of celluloses of different accessible fractions. (1) & (2), Collapsed and Swollen cellulose, resp. technically nitrated. (3) & (4), Collapsed and Swollen cellulose, resp. nitrated by HNO_3-P_2O_5. (5) & (6), Collapsed and swollen cellulose, resp, technically nitrated, renitrated by HNO_3-P_2O_5.

from Fig. 6 for the individual fractions, and Fig. 9 illustrates the I(P) plots which were obtained by this correction. No great changes in the plots for the various nitrates were occasioned, except in the case of the technical nitrates, in which the correction for substitution brought out the same type of dissimilarity between the viscosities of the nitrates from collapsed and swollen cellulose (plots 1 and 2, Fig. 9) as was noted in the case of the phosphoric anhydride-nitric acid and renitrated nitrates (plots 3,4 and 5,6, Figs. 7 and 9)

Since the viscosity I(P) plots of the technical nitrates are now transformed to the trinitrate basis, as is the case for the technically nitrated materials renitrated with phosphoric anhydride and nitric acid, the two pairs of plots should really coincide, because the chain length distribution (1 and 5, 2 and 6, Fig. 9) in each pair is presumably the same. This is substantially the case for the products from the swollen cellulose (plots 2 and6) but a wide divergence is apparent between the pair of plots derived from the collapsed cellulose (plots 1 and 5). The lack of coincidence, and the probable inaccuracy of the position of the corrected curve of the technical nitrate, may be due to the large correction from substitution 2.2 to 3.0 which was necessary. It is possible that the correction factor did not produce entirely true results, since it is assumed to be reasonably accurate only over short ranges of substitution (2). Whatever the correct explanation may be, it appears that the technical nitrate from the swollen cellulose had a somewhat higher nitrogen content and a somewhat shorter chain

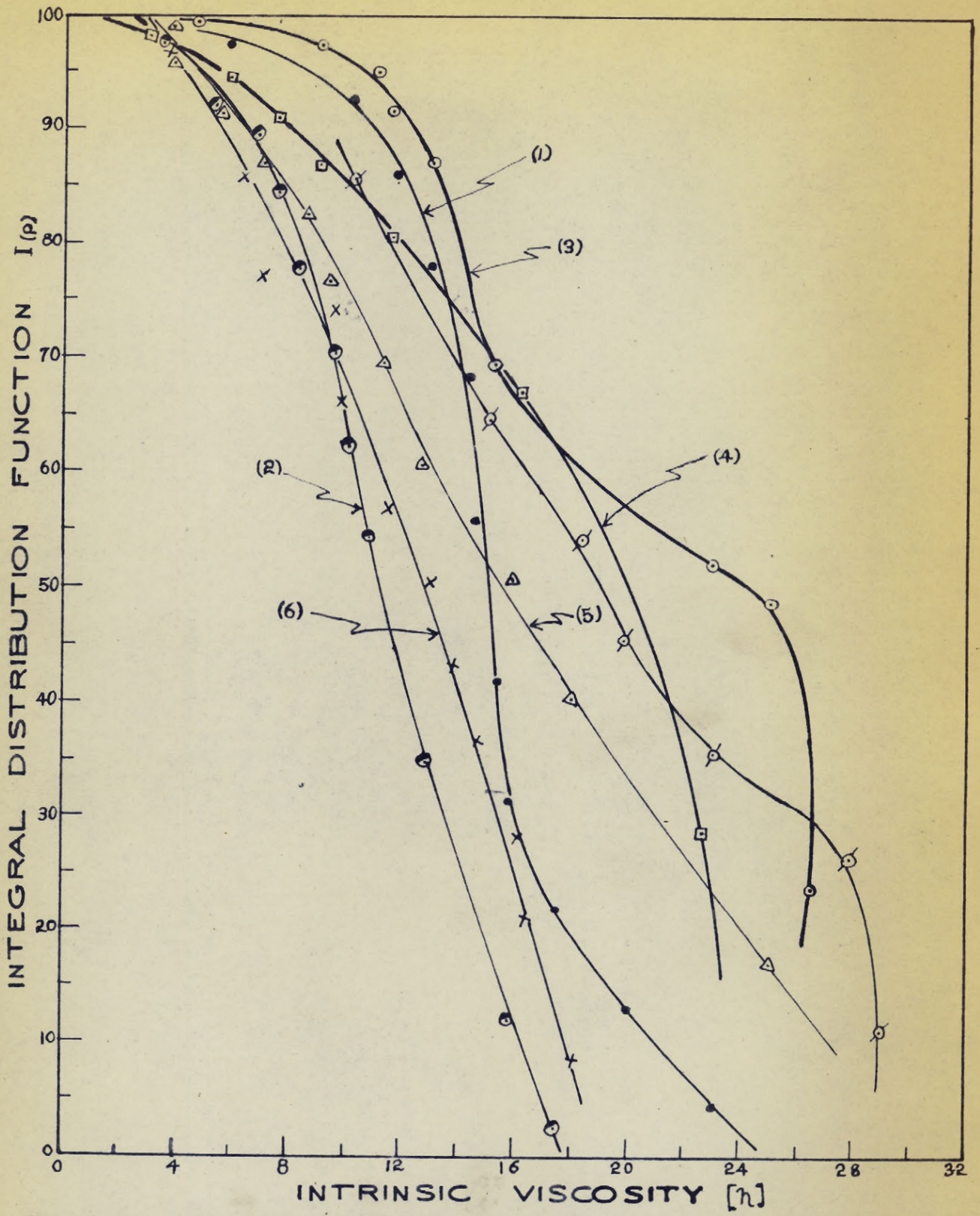

Fig. 9 - Integral Weight Distribution Function I(P), vs Intrinsic Viscosity of fractionated nitrates of celluloses of different accessible fractions. Viscosities corrected for nitro substitution.
(1) & (2), Collapsed and Swollen cellulose, resp., technically nitrated.
(3) & (4), Collapsed and Swollen cellulose, resp., nitrated by HNO_3-P_2O_5.
(5) & (6), Collapsed and Swollen cellulose, resp., technically nitrated, renitrated by HNO_3-P_2O_5. (7) Repetition of No. (3).

at all points in the I()P plot than the product from the collapsed sample. It is also interesting to note that the corrected viscosity plots 2, 4 and 6, Fig. 9, derived from the swollen cellulose altered their shape in a gradual and regular way, whereas in those from the collapsed sample 1,3 and 6, the changes were more abrupt.

In connection with the application of these viscosity corrections for substitution, a similar increase in viscosity for each 0.1 unit of substitution might be expected for both the collapsed and swollen nitrated celluloses. But actually, increase was greater for the former than for the latter, and necessitated the construction of two separate correction factor plots (Fig. 6). The correction factor plot obtained by Glegg (2) differs somewhat from those obtained for the nitrocelluloses under consideration, although it approximates to that obtained for the collapsed nitrated cellulose. This approximation may be connected with the fact that the papers which he examined had a relatively low accessible surface, or were partially collapsed. It therefore appears that mere increase in substitution alone is not the only factor which determines the magnitude of the intrinsic viscosity (cf.plots 1 and 5, Fig. 9), apart from the chain length. As suggested previously, the distribution of substitution along the macromolecule (Fig. 1) may influence the result and thus show an effect upon the viscosity. If this speculation is true, it might be that a certain combination of hydroxyl groups in the collapsed cellulose was preferentially mitrated, as compared with another combination in the swollen cellulose. Such a result would be possible only with a steric hindrance

or directed nitration, otherwise random esterification should occur. Some evidence of such steric hindrance has been noted in this laboratory by Lemieux during experiments on the further nitration of a cellulose mononitrate substituted largely in the sixth position (133). If such directed nitration occurred, and was different for the collapsed and the swollen cellulose, the two technical nitrates might possibly differ in the number of 2,3 unsubstituted glycol groups in the glucose units (Fig.1). To check this possibility, oxidations of various technical nitrates with lead tetraacetate and periodic acid were attempted. Tables X,XI, XII and XIII, and Figs. 10 to 13 inclusive show the results of lead tetraacetate oxidations in ethyl acetate of twelve commercial nitrocelluloses, obtained from Mr. Fensom (102), Table XVII summarizes all data received from Mr. Fensom as well as that obtained in this laboratory for the twelve nitrocelluloses. Table XIV and Fig. 14 express the results of similar oxidations carried out upon the technical nitrates of swollen and collapsed cellulose of accessible fractions of 31.5% and 0.25% respectively, as measured by the thallous ethylate technique. Oxidations upon most of the twelve technical nitrates were performed twice. Table XI and Fig. 11 give the results of oxidation with a higher concentration (0.025 molar) of lead tetraacetate than was employed in the oxidation whose data are given in Table X and Fig. 10 (0.020 molar).

The difficulty involved in the oxidations of these nitrocelluloses was to find a suitable solvent which would retain, in solution, nitrocelluloses of various degrees of substitution, be compatible with the solvent containing the oxidant, and yet not be itself readily oxidized. The action of such oxidants

upon alcohol has been reduced by including ethyl acetate (96), and since the ester readily dissolves nitrocelluloses, and is miscible with a large amount of the acetic acid-lead tetraacetate reagent, it was selected as a suitable solvent. In a trial oxidation carried out upon an ethyl acetate solution of methyl-α-glucopyranoside-6-nitrate, and with the concentrations used, exactly the theoretical two moles of tetraacetate per mole of the glucoside was consumed in a period of two hundred hours. The ethyl acetate slowly reduced some tetraacetate, but this effect was corrected by a blank oxidation. For periodate oxidations, the common solvent,"cellosolve" (the monoethyl ether of ethylene glycol) was found to be most promising, since it readily dissolves nitrates, and retains them in solution even after the addition of a considerable amount of aqueous periodic acid.

It was found that if the concentration of the reactants was low, no evidence of oxidation was noticeable, even with the methyl-glucoside-6-nitrate. This result is of course quite reasonable, since the reaction is bimolecular (135). Therefore, care was observed to keep the concentration of both reactants at a sufficiently high level to permit oxidation, yet below the point of precipitation of the nitrocellulose. Thus,the second series of oxidations (duplicates), shown in Table XI and Fig. 11, was carried out with a higher concentration both to accelerate the rather lengthy oxidation process and to establish the validity of the oxidation upon the nitrocelluloses.

To discover whether the reagent would hydrolyze or otherwise attack positions protected by nitrate groups, a simultaneous experiment was performed upon a trinitrate obtained with the phosphorus pentoxide-nitric acid mixture. No consumption of oxidant could be detected, even after a period of three hundred and fifty to four hundred hours.

Examination of the oxidation plots depicted in Figs. 10 and 11, reveals that all the nitrocelluloses except numbers V, IX and X attained a maximum consumption of lead tetraacetate, as indicated by the zero slope of the curves, after perhaps two hundred hours. Several of the oxidations were continued over a period of four hundred hours, with no sudden rise in the position of the plot. Rather, a slight decrease in the amount of lead tetraacetate consumed occurred with some samples after an extended time; no doubt because of slow decomposition of either the solvent, or more probably the nitrate. The second oxidation of number VII (Table XI, Fig. 11b), and the first of number X(Table XI,Fig.11 c), show this peculiarity, but in the case of number VII (Fig. 11 b) the plateau persisted for some time before a negative slope occurred, a result supported by the duplicate oxidation shown in number VII,Fig.10 a. Number X, on the other hand, showed continual consumption of oxidant in the duplicates represented in Fig.11 d,(Table 11), therefore the decrease in slope exhibited by this one oxidation shown in Fig. 11 c was considered to be due to error. It is noticeable that the increase in concentration of the oxidant for the second oxidation

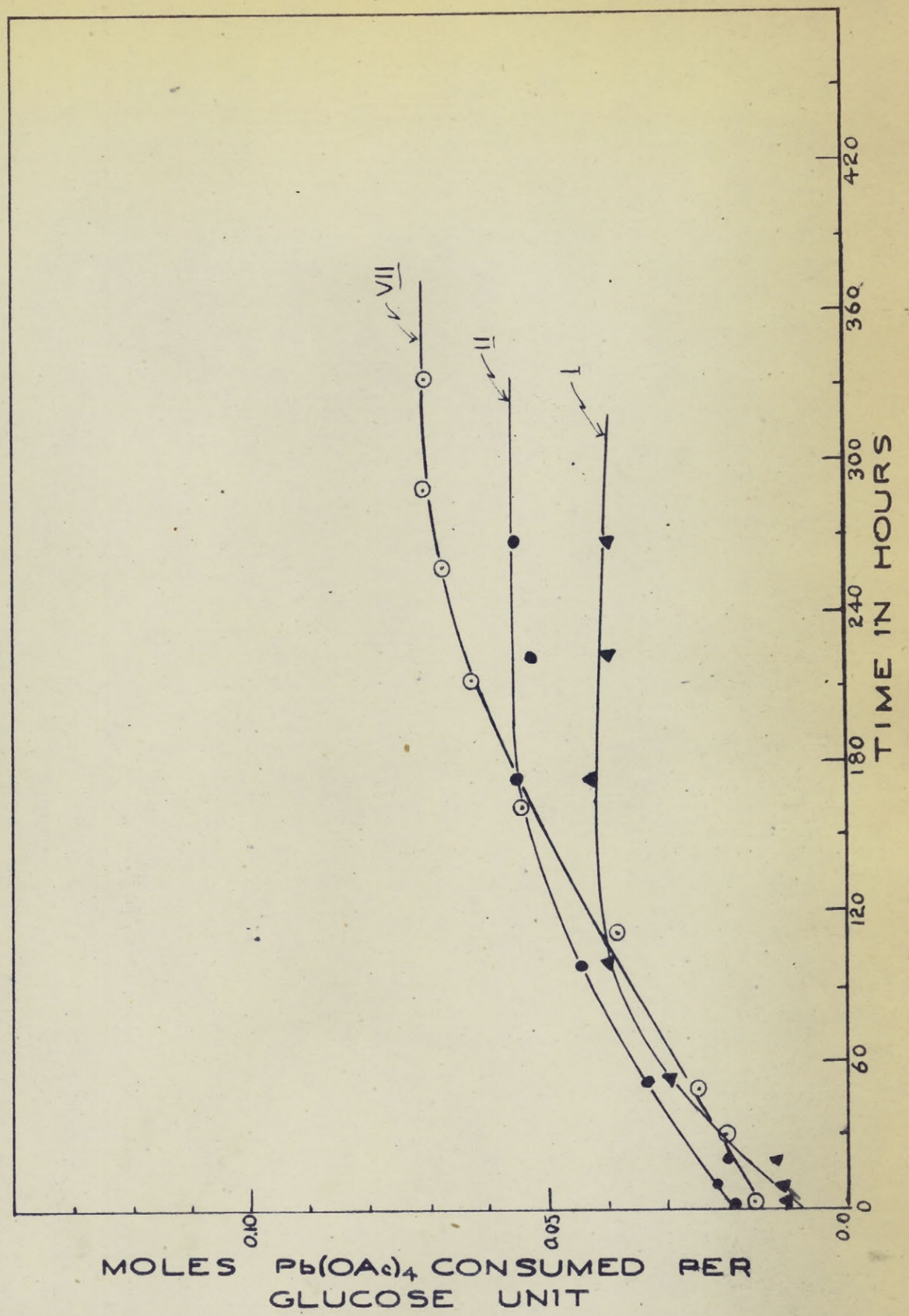

Fig. 10a. -Lead tetraacetate oxidations of commercial nitrocelluloses finely ground and dried under vacuum over P_2O_5 for 24 hours. Oxidations carried out at 25° in ethyl acetate. Concentration of oxidant was 0.02molar, and of nitrate 0.01 molar.
Table XVII shows history of nitrates.

(Cont'd on p.104)

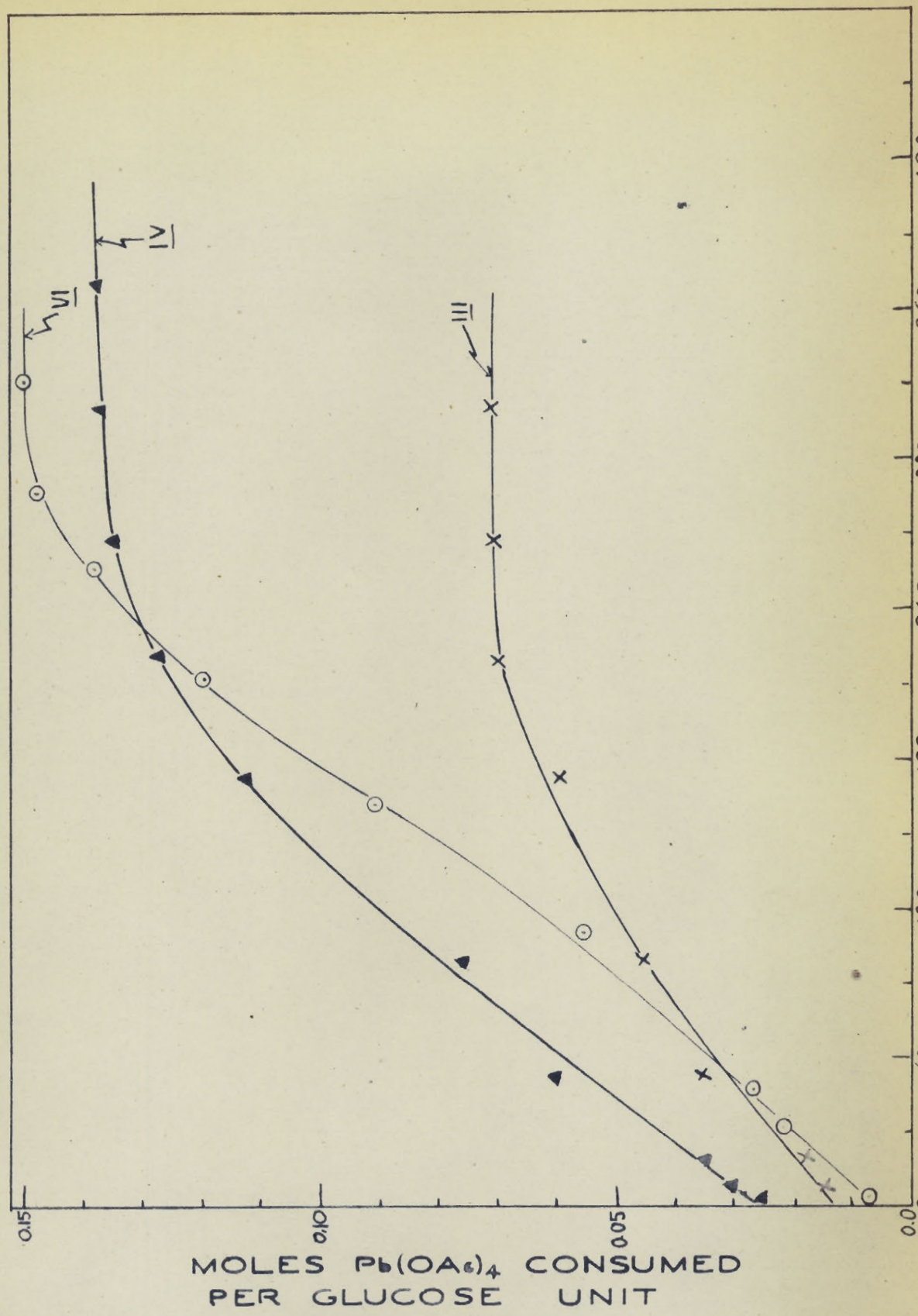

Fig. 10b. (Continued from p. 103)

(Cont'd p. 105)

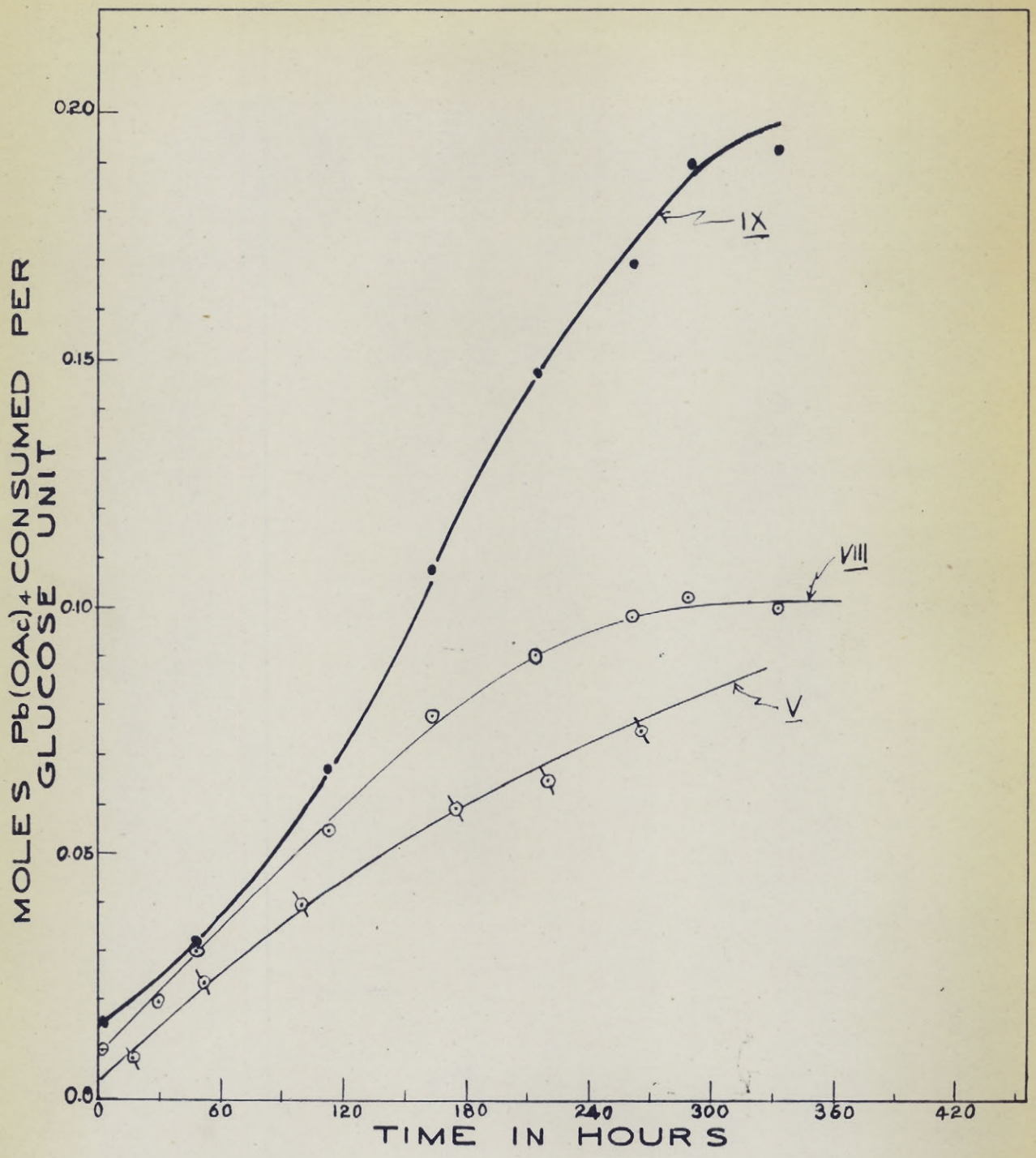

Fig. 10c. (Continued from p. 104)

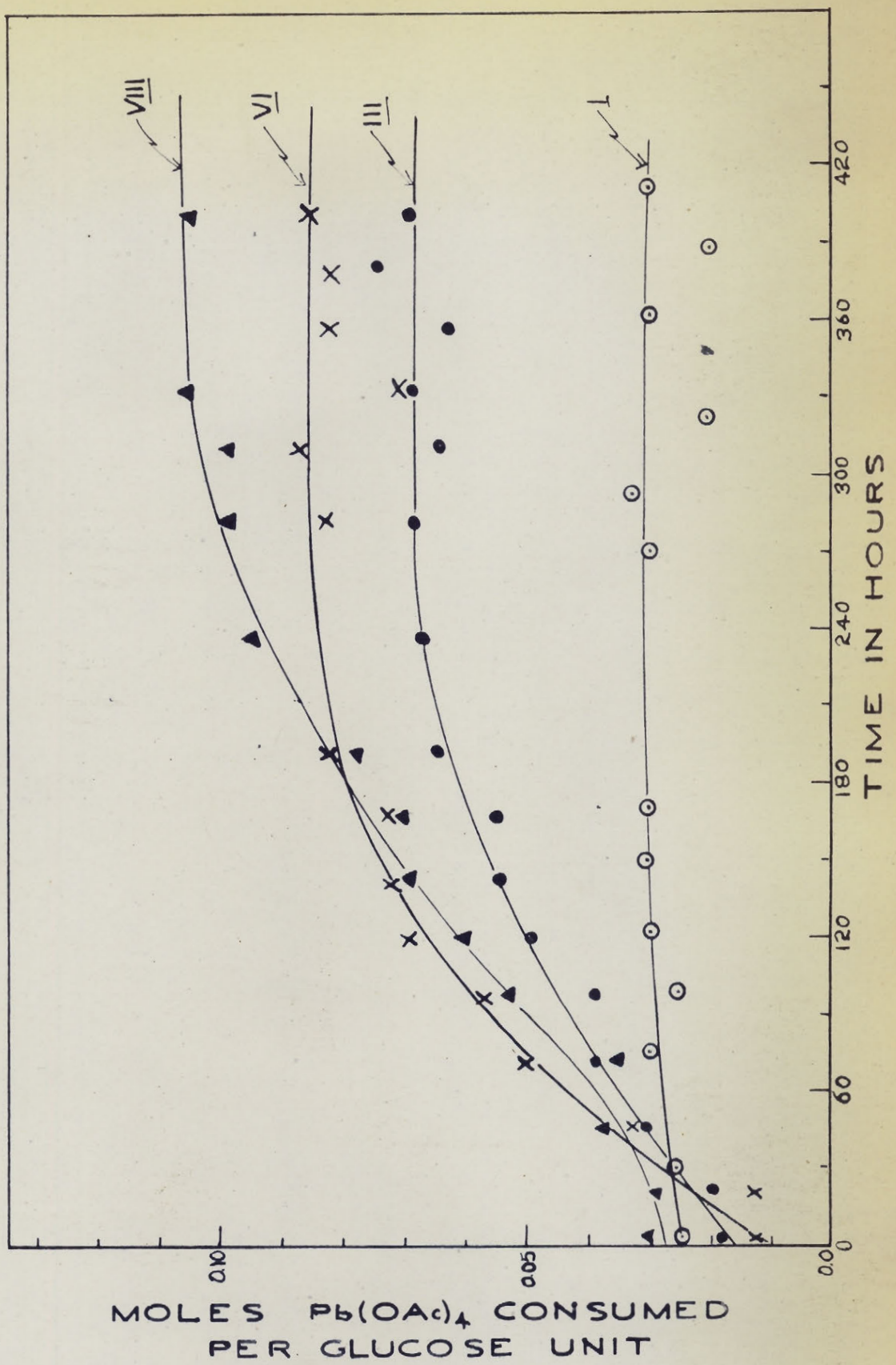

Fig. 11a. Lead tetraacetate oxidations of commercial nitrates at 25° in ethyl acetate. Concentration of oxidant, 0.025 molar, of nitrate, 0.01 molar.

(Cont'd p. 107)

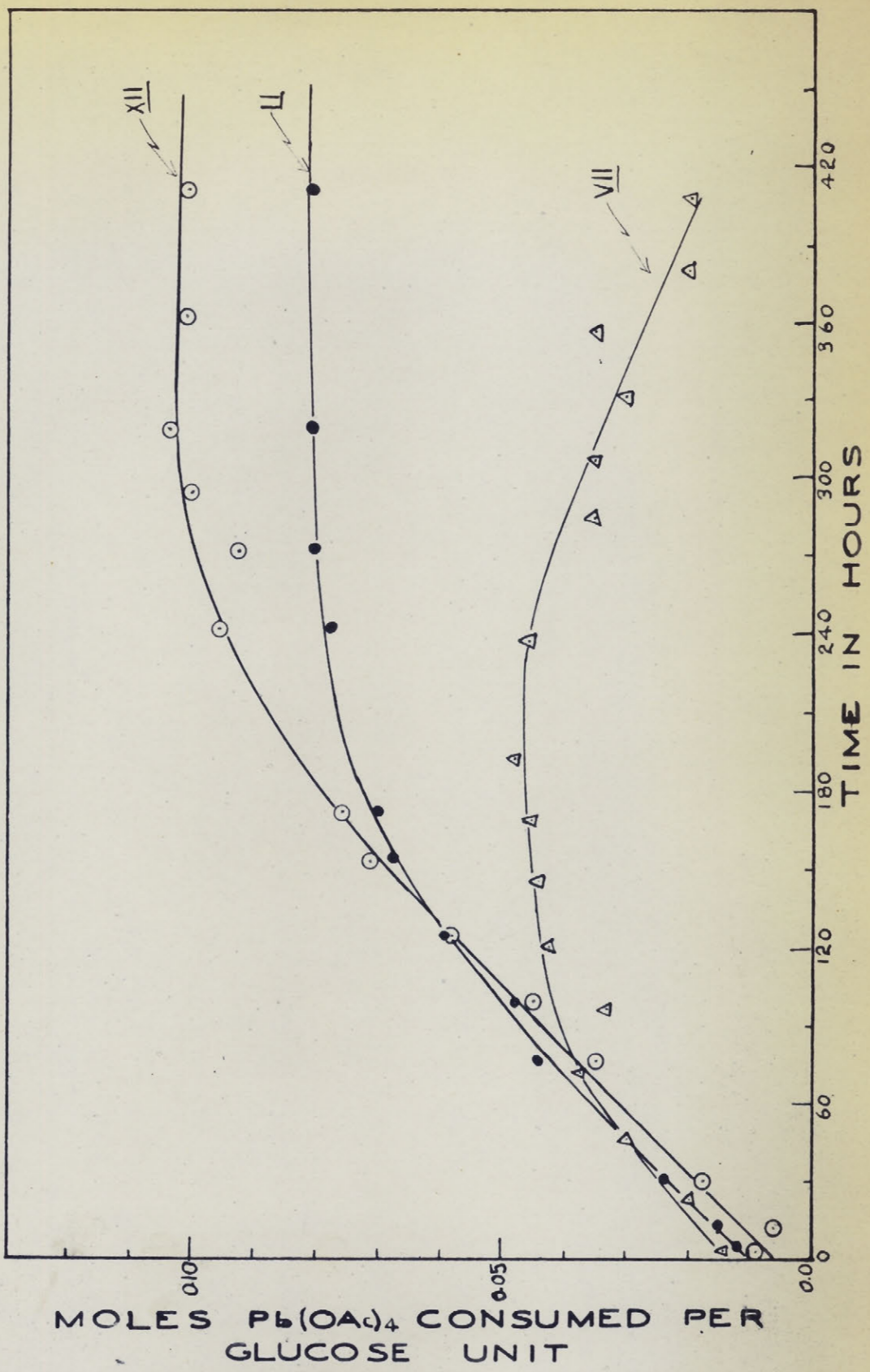

Fig. 11b. (Continued from p. 106)

(Continued p. 108)

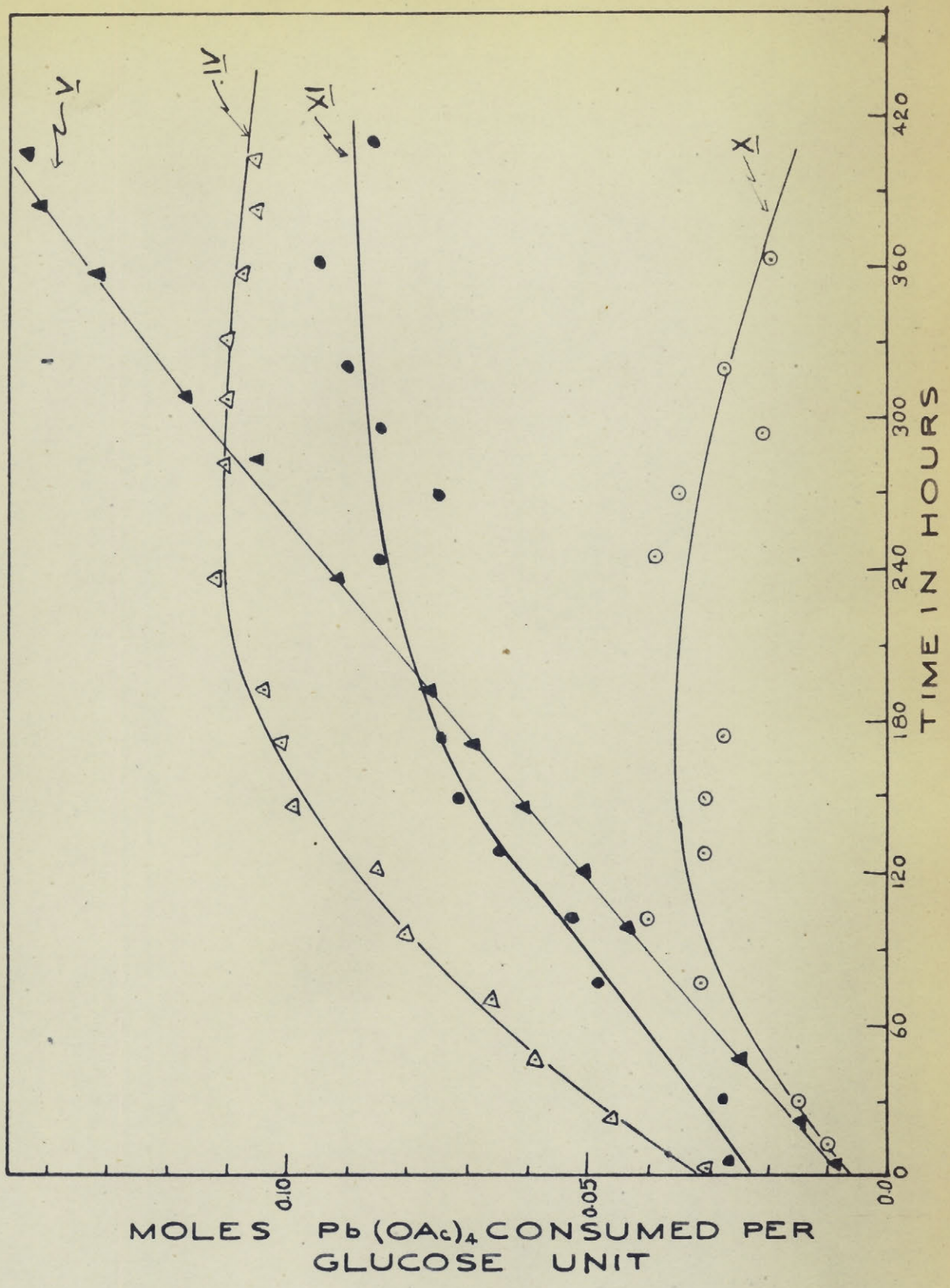

Fig. 11c. (Continued from p. 107)

(Cont'd p. 109)

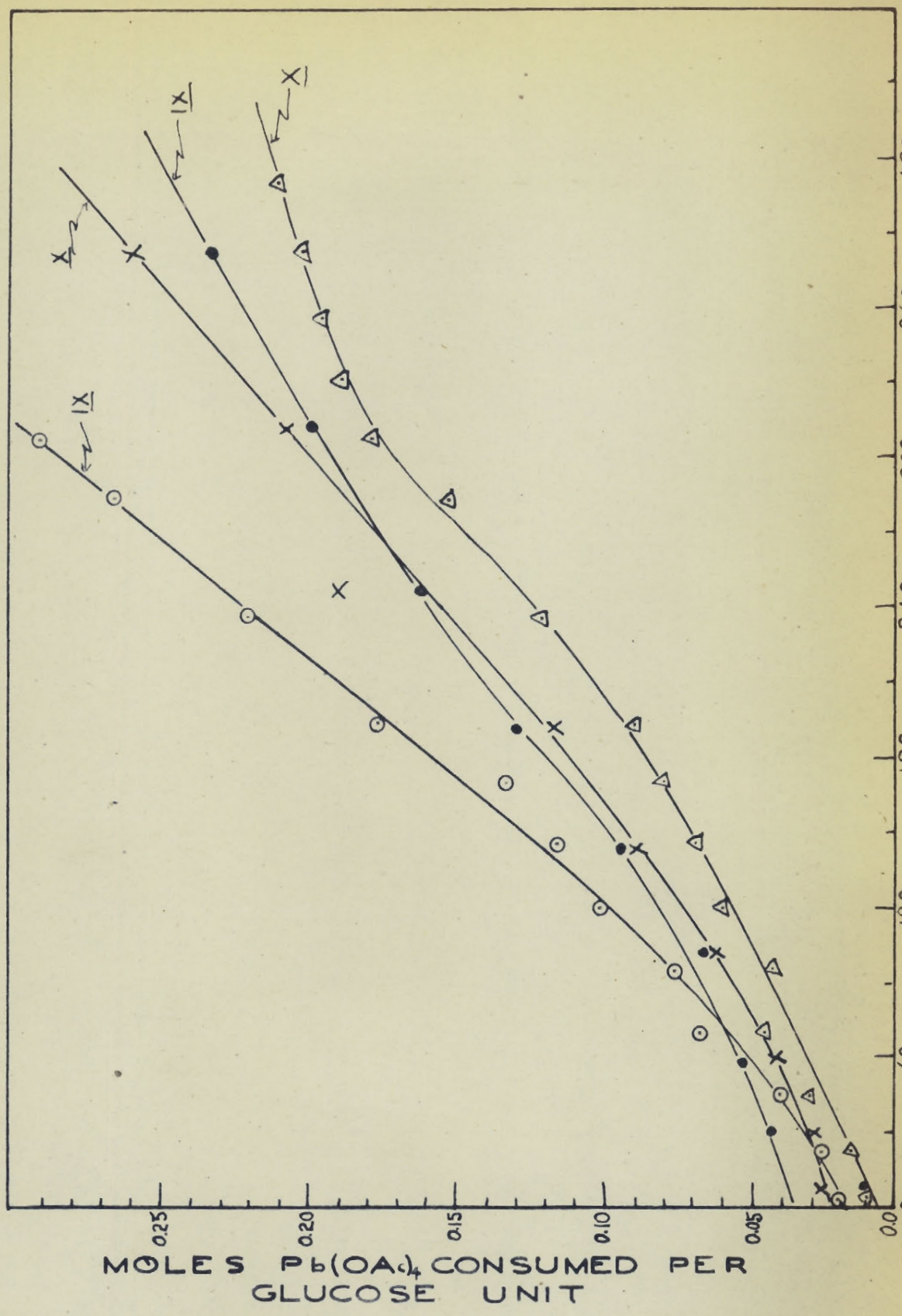

Fig. 11d. (Continued from p. 108)

(Fig. 11), did not greatly hasten the oxidation (e.g. numbers II,III, VIII) but did reveal the true characteristics of such doubtful nitrates as numbers IX and X. In the first oxidation (Fig. 10 b) number IX appeared to reach a constant value, whereas two further repetitions at the higher concentration of tetraacetate (Fig. 11 d) revealed no maximum, and showed approximately a uniform slope throughout. This anomaly would suggest that these two guncottons,IX,X, were more readily decomposed, and hence more unstable than the remaining nitrocelluloses. It is significant to note that specimen IX,and also X, were made by the displacement process of nitration, which may entail a certain amount of hydrolysis during the removal of the acids from the cotton fibers. Sample XII is also a displacement product,and though it showed no unlimited oxidation, it did consume a considerable quantity of tetraacetate (Fig.11 b). Number V, a mechanically nitrated guncotton, also displayed continued consumption of oxidant, but much less than exhibited by IX and X (Fig. 11 c and d).

It is to be noted that most of the duplicates did not show closely similar degrees of oxidation, although they did check each other to within 0.02 moles of oxidant. This is a rather large error, considering the small total consumption of reagent, and that the maximum oxidation was equal to about 0.1 moles of the acetate. Table XVII, column 10 contains the figures representing the first and second oxidations. From these, it is apparent that the estimation as conducted was in error about $\pm$ 20%, a condition

TABLE XVII

HISTORY AND ANALYSES OF TWELVE COMMERCIAL NITRO-CELLULOSES

No.	Type of Guncotton	Batch or Lot Number	Nitration Process	Raw Material	% N uncorr.	Vis-(a) cosity	Sub-stit-ution	sub-molar Wt.	Moles $Pb(OAc)_4$ per Glucose Unit	
									1st Oxid	2nd Oxid
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	
I	Pyro N/C	719	Mechanical	F linters	12.63	26 (6)	2.46	273	0.02	0.00
II	High N% Guncotton	2A	"	B linters	13.42	6 (6)	2.73	285	0.040	0.065
III	Blasting Soluble N/C	III	Ardeer	cotton cops	11.99	88 (4)	2.25	264	0.050	0.050
IV	Industrial N/C, HX 8-13	1477	Mechanical	B linters	11.96	9 (40)	2.25	263	0.055	0.040
V	Industrial N/C, HM 15-20	3172	"	"	12.15	20 (10)	2.31	266	slow oxidation	
VI	Industrial N/C, LL 55	9433	"	"	11.36	65 (20)	2.07	255	0.02	0.055
VII	Industrial N/C, HH 5-15	4577	"	A linters	12.23	8 (3)	2.34	267	0.055	0.035
VIII	Industrial N/C, 120-170	2496	"	B linters	12.02	74 (20)	2.26	264	0.090	0.075
IX	Low Soluble N/C	ex magazine 50	Displacement	"	10.89	29 (6)	1.94	249	slow oxidation	
X	Guncotton	ex magazine 477	"	cotton waste	13.11	26 (6)	2.62	280	"	"
XI	Industrial N/C, LX, 30-50	8645	Mechanical	B linters	12.03	39 (40)	2.27	264	0.45(b)	
XII	Propulsive Soluble N/C	426	Displacement	G linters	12.24	16 (10)	2.34	267	0.09(b)	

(a) Poises in solution of x gms in 100 ml. acetone (95) at 20° C. The value of x is given in brackets.

(b) Only one oxidation performed.

which is not surprising, since the titration differences were small (1 to 3 ml.) and errors arose in pipetting and titration, particularly when the concentration of the reagents was increased. However, despite these large discrepancies, a definite limited oxidation was indicated and was shown to vary from one specimen of cellulose nitrate to another.

Very little oxidation occurred during the first forty or fifty hours, yet the extension of any curve to the axis (Figs. 10 and 11) points to an immediate destruction of a certain amount of oxidant. The cause is attributed to the fact that the delivery of the pipette varied slightly with the viscosity of the cellulose nitrate solution, which in turn was determined by the concentration and by the nature of the nitrate. Hence in the calculation of the extent of oxidation (Table XVII, column 10), this initial value at the ordinate was subtracted from that obtained by extrapolation of the flat portion of the curve. Further refinement of the technique might bring more accurate results.

It is quite within reason to attribute the consumption of oxidant to the presence of adventitious impurities. If such were the case, the preceding analyses would by entirely valueless. (It was learned, some time after the following purifation and examination had been completed, that the twelve nitrates were entirely free from any impurities(138)). To investigate this possibility, the twelve,dried guncotton samples were dissolved

in acetone, filtered through glass wool, and then precipitated by allowing a fine stream of the acetone solution to flow into distilled water. The products were dried under vacuum over phosphoric anhydride for forty eight hours, whereupon oxidations were again performed on each sample, according to the procedure described. The surprising result (Table XII,Fig. 12) was that all except numbers VII and VIII showed a continued consumption of lead tetraacetate, so large that a different scale had to be chosen for the ordinates. The two exceptions, VII and VIII, retained oxidation rate plots comparable with those observed before (Figs. 10, 11) "purification".

The difference in behavior before and after "purification" must be associated with the acetone precipitation. It is known that compound formation occurs between cellulose nitrates and acetone (136). Moreover, the harder masses, formed during precipitation, are suspected of occluding a certain amount of solvent. These"purified"materials were,therefore, again vigorously dried for seventy-two hours at 50° under vacuum over phosphoric anhydride. Table XIII and Fig. 13, with ordinates still on the same scale as was employed for Fig. 12, show that considerable improvement was obtained, though by no means as much as expected. Evidently , certain nitrocelluloses have a much greater affinity for acetone than have others, a result in itself not surprising since the degree of substitution varies from one type to another, and it is suspected that the mode of

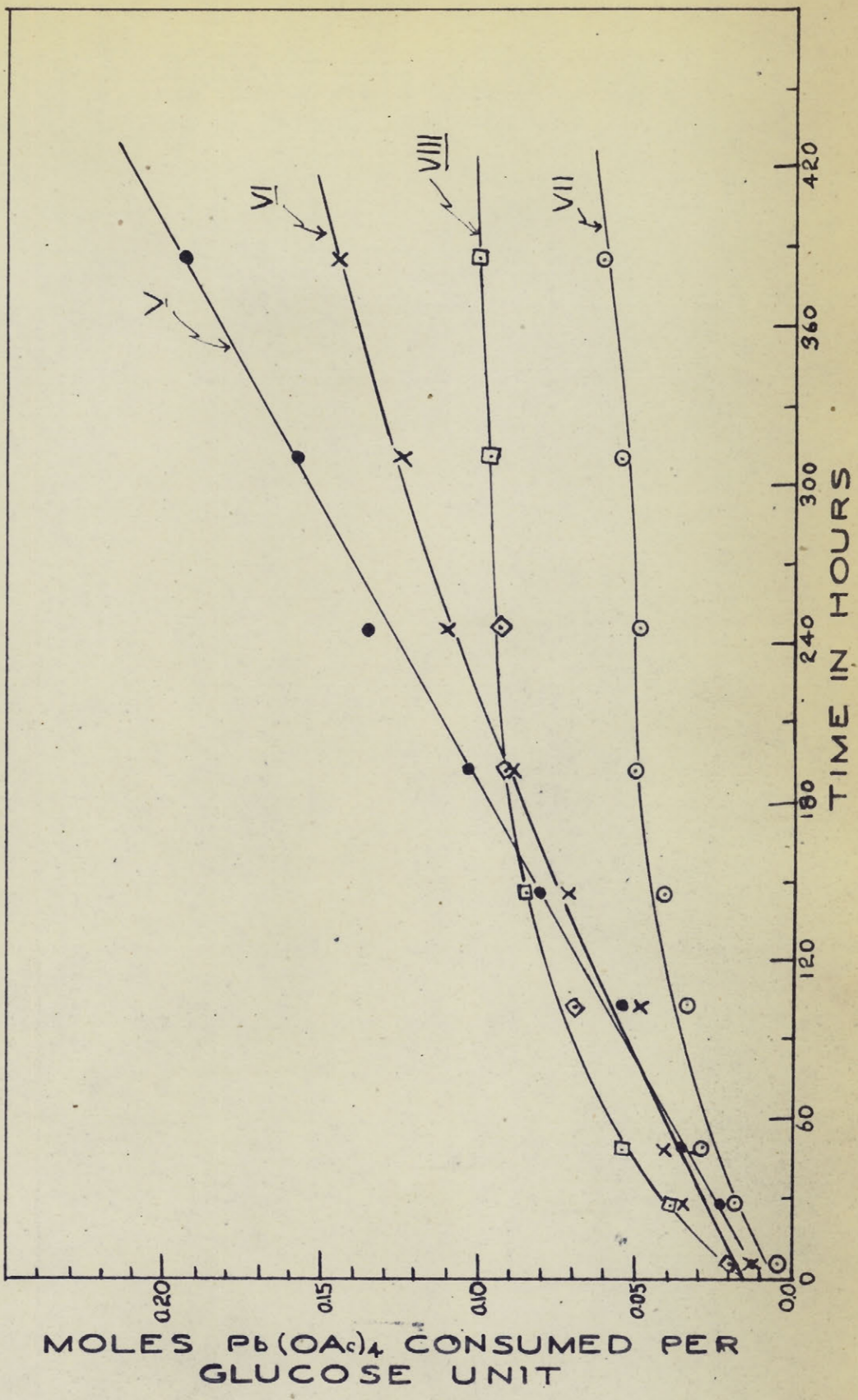

Fig. 12a. Lead tetraacetate oxidations of commercial nitrates after "purification" by preciitation from acetone. Concentration of oxidant, 0.025 molar, of nitrate, 0.01 molar.

(Cont'd p. 115)

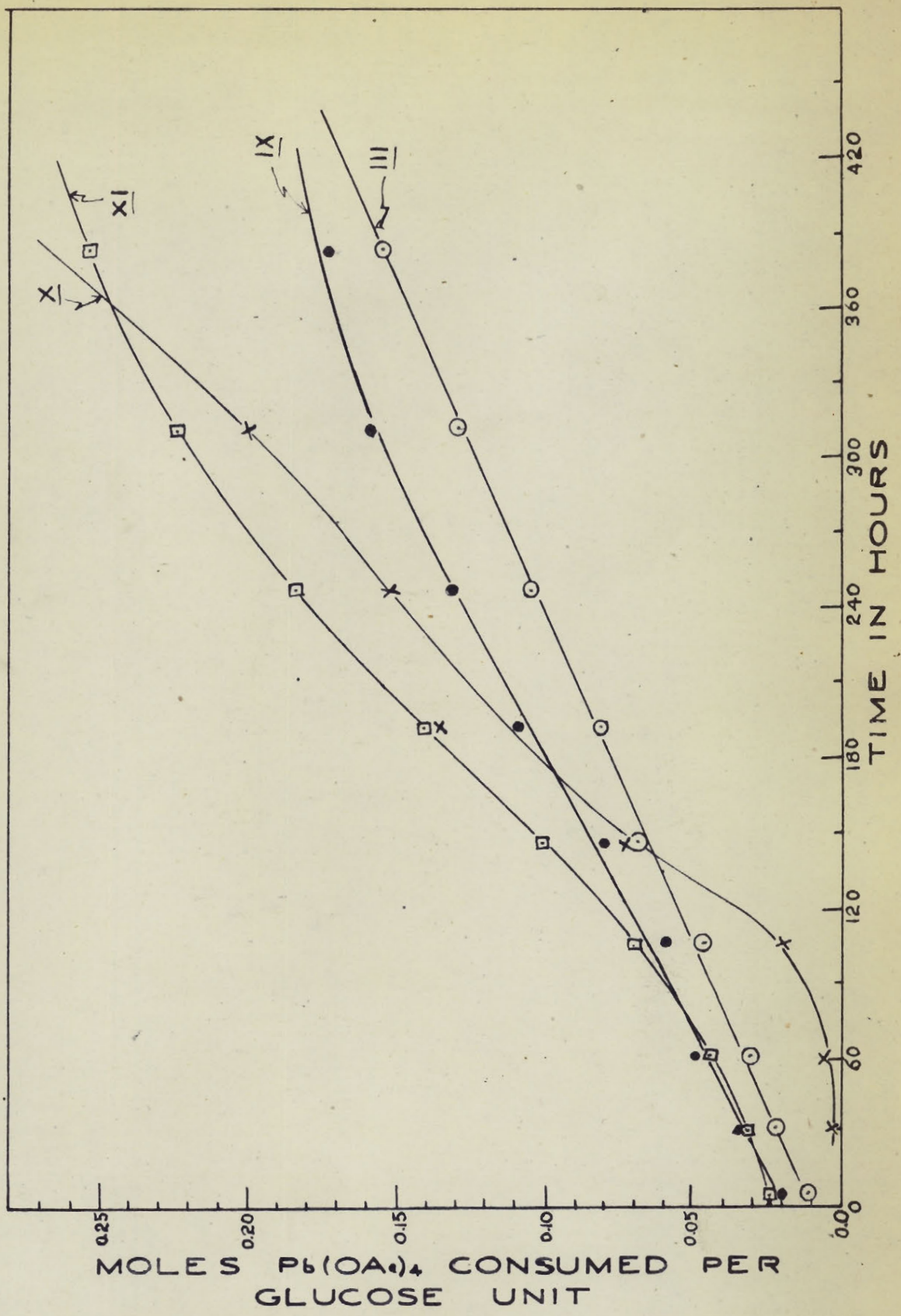

Fig. 12b. (Continued from p. 114)

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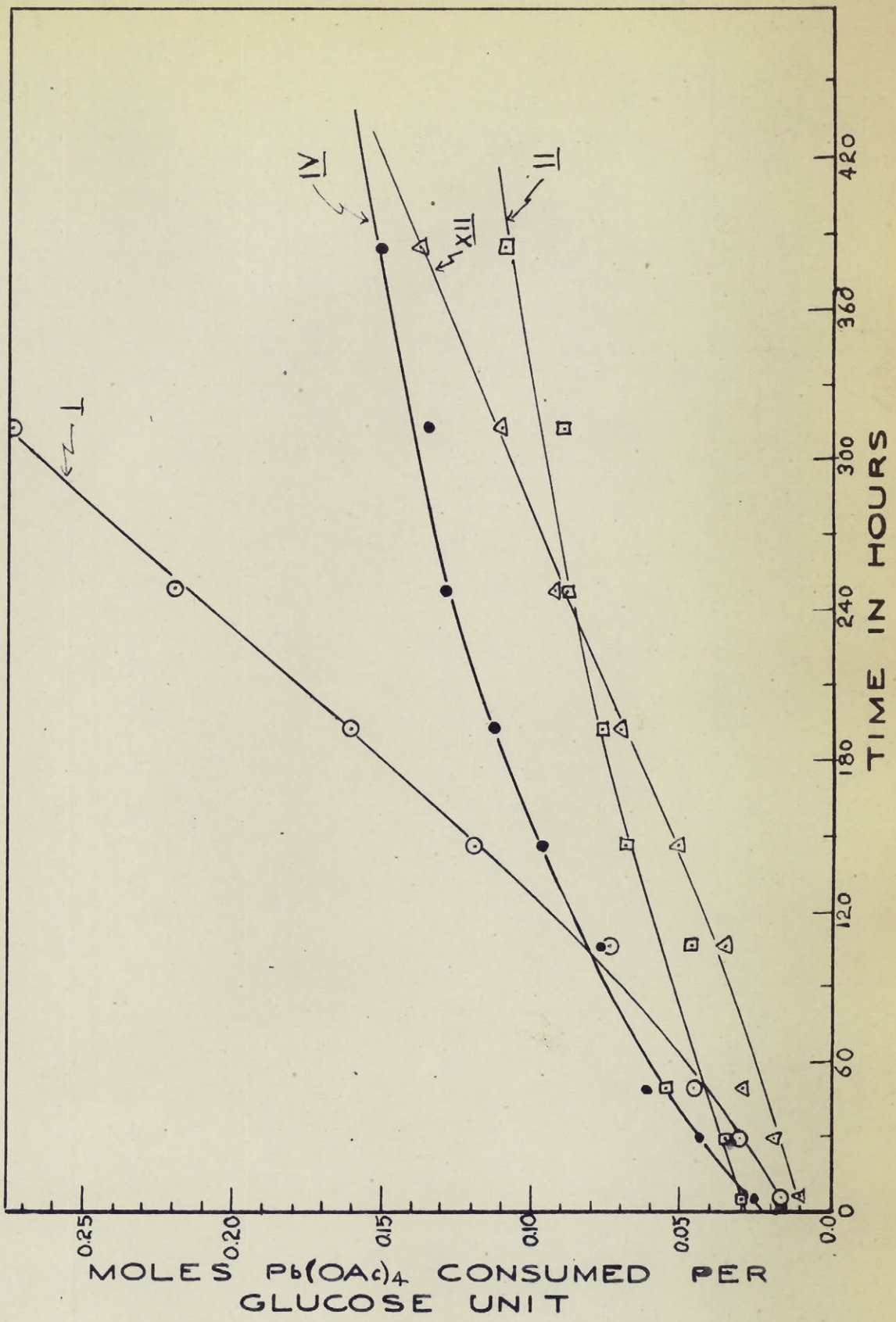

Fig. 12c. (Continued from p. 115)

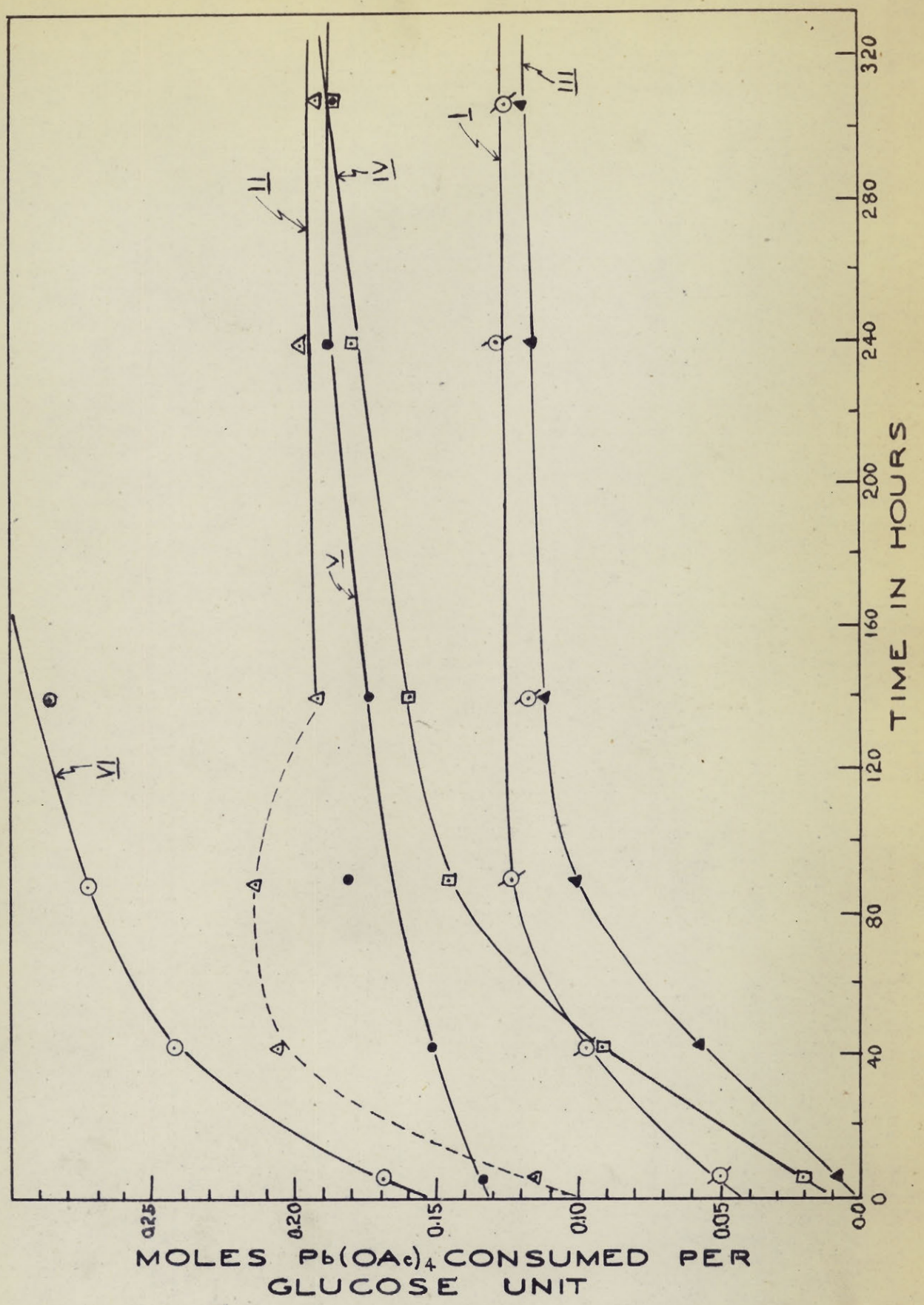

Fig. 13a. Lead tetraacetate oxidations of commercial nitrates, in the same concentrations as before, showing the effect of rigorous drying at 50° under vacuum over P_2O_5.

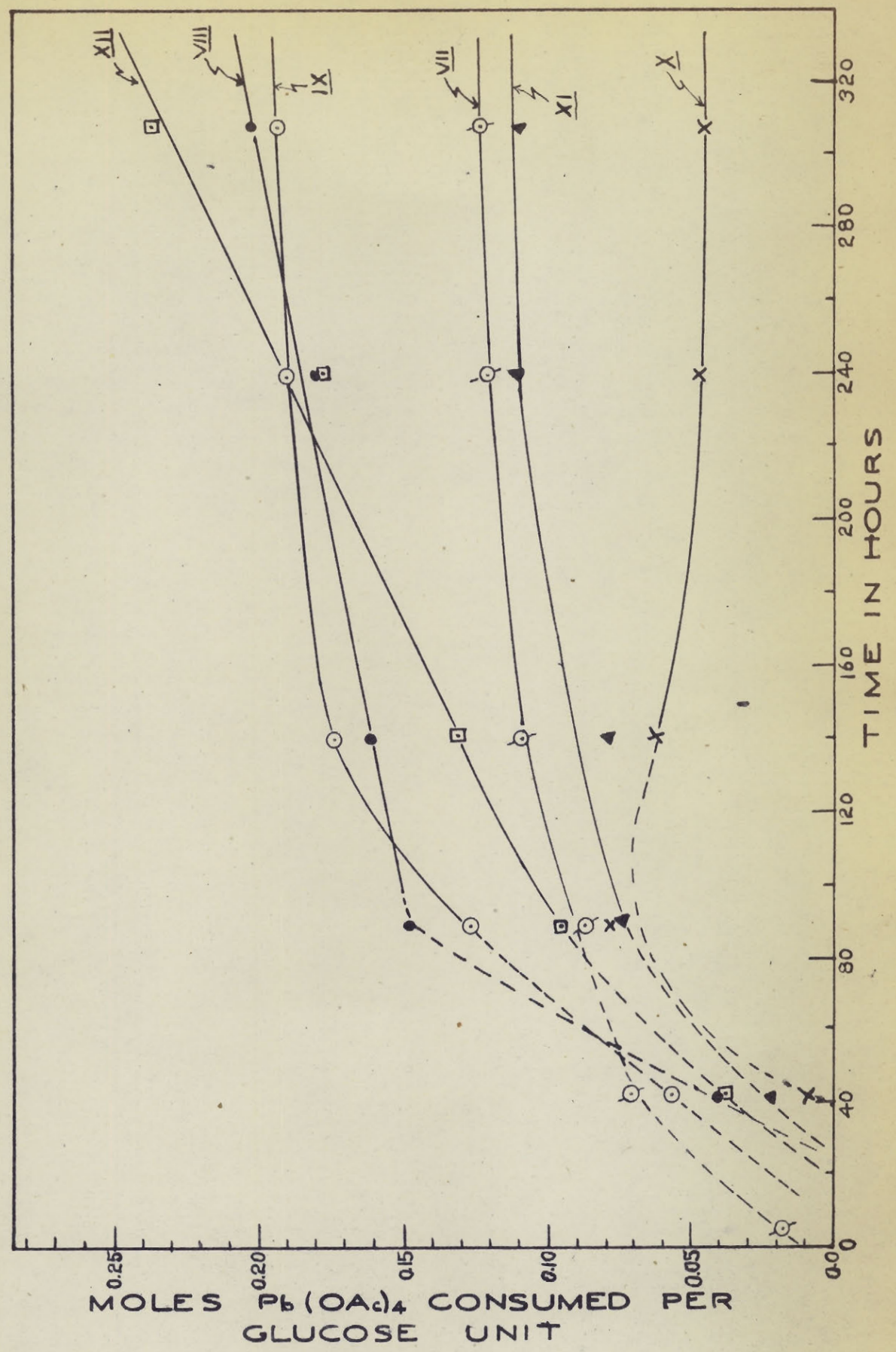

Fig. 13b. (Cont'd from p. 117).

substitution does likewise. No attempt at further dessication of these "purified" nitrocelluloses was made, though it is probable that if the materials were finely divided and again vigorously dried, the improvement in behavior towards the oxidant would increase. Since tenaciously adsorbed acetone apparently reduced the tetraacetate, the data in Tables XII and XIII, and in Figs. 12 and 13, were not valid, and those for the original nitrocelluloses (Figs. 10 and 11, Tables X and XI) were more likely to be correct.

An attempt was made to verify the results realized with the lead tetraacetate, by cross-checking with periodate oxidations. During the course of the oxidations, in aqueous cellosolve, of methyl-α-glucoside-6-nitrate, it was found that in the titration manipulations, both the standard arsenite solution, and the periodic acid were consumed by the cellosolve, the consumption of either increasing with vigorous stirring and also with exposure of the solvent to light. This peculiarity of oxidation and reduction pointed to peroxide formation, the presence of which was definitely verified by the liberation of iodine from acidified potassium iodide solution. The presence of aldehydes, resulting from cleavage of the peroxides, was also detected. However, removal of these impurities by careful fraction, and subsequently storing of the cellosolve under nitrogen in the absence of light, gave a solvent whose characteristics were greatly improved. No arsenite loss was detected

even after keeping the cellosolve for a week under these conditions. But even with this purified material , repeated attempts to oxidize the glucoside invariably gave a type of plot which rose to about 1.75 moles consumption of periodate (theoretical,2 moles), and then rapidly showed and apparent decrease in oxidant consumption,of practically 100%. Increase of the concentration of the periodate only hastened the advent of this "peak" in the curve. Oxidation of one of the samples of nitrocellulose, known to absorb a certain quantity of lead tetraacetate, exhibited the same characteristic. Therefore, the homogeneous periodate oxidations of these nitrates in cellosolve was abandoned, not without some reluctance, since this solvent had the surprising characteristic of greatly retarding the normally fast periodate reaction. The duration of the oxidation in the unsuccessful experiments noted above was from thirty to one hundred hours, depending upon the concentration of the reactants. Its successful use would have supplied an additional means for the study of water-soluble cis and trans glycols.

Heterogeneous oxidations, in aqueous periodate, of several of the twelve nitrocelluloses, known to reduce lead tetraacetate, were also unsuccessful, no periodate being consumed.

Since the tetraacetate oxidation procedure had shown positive results with the twelve commercial nitrocelluloses, it was employed with two technical nitrocelluloses, one from a cellulose of 32% accessibility,and containing 12.01% nitrogen,

the other from the same cellulose, collapsed to an accessibility of 0.26%, and having a per cent nitrogen equal to 11.80. The same technical acid mixture was used in the nitration of both celluloses.

Table XIV and Fig. 14 contain the results of these oxidations. The consumption of oxidant was greater for the "collapsed" nitrated cellulose than for the "swollen" material. Also, the course of oxidation of the former was somewhat more irregular than that of the latter, which observation may be due to either experimental error or to the nature of the cellulose nitrate. The sudden rise shown by both curves from three hundred hours onward suggests that either the nitrate molecule may have undergone change, or that the solvent was affected. However, by comparison with the plots shown in Figs. 10 and 11, wherein the oxidation was completed in about three hundred hours, the change in shape of the plots in Fig. 14, after the elapse of the same period of time, may be insignificant. A repetition of the experiment is obviously necessary. The most that can be said about these two nitrocelluloses, from oxidation results, is that the "collapsed" sample probably possessed more glycol groups (simultaneously unsubstituted positions 2 and 3, (Fig. 1)) than the nitrate from the swollen cellulose, or that the former was more unstable,in some other fashion, to the oxidant. If the former deduction is correct, then the collapsed cellulose offers resistance to nitration of positions 2 and 3 in

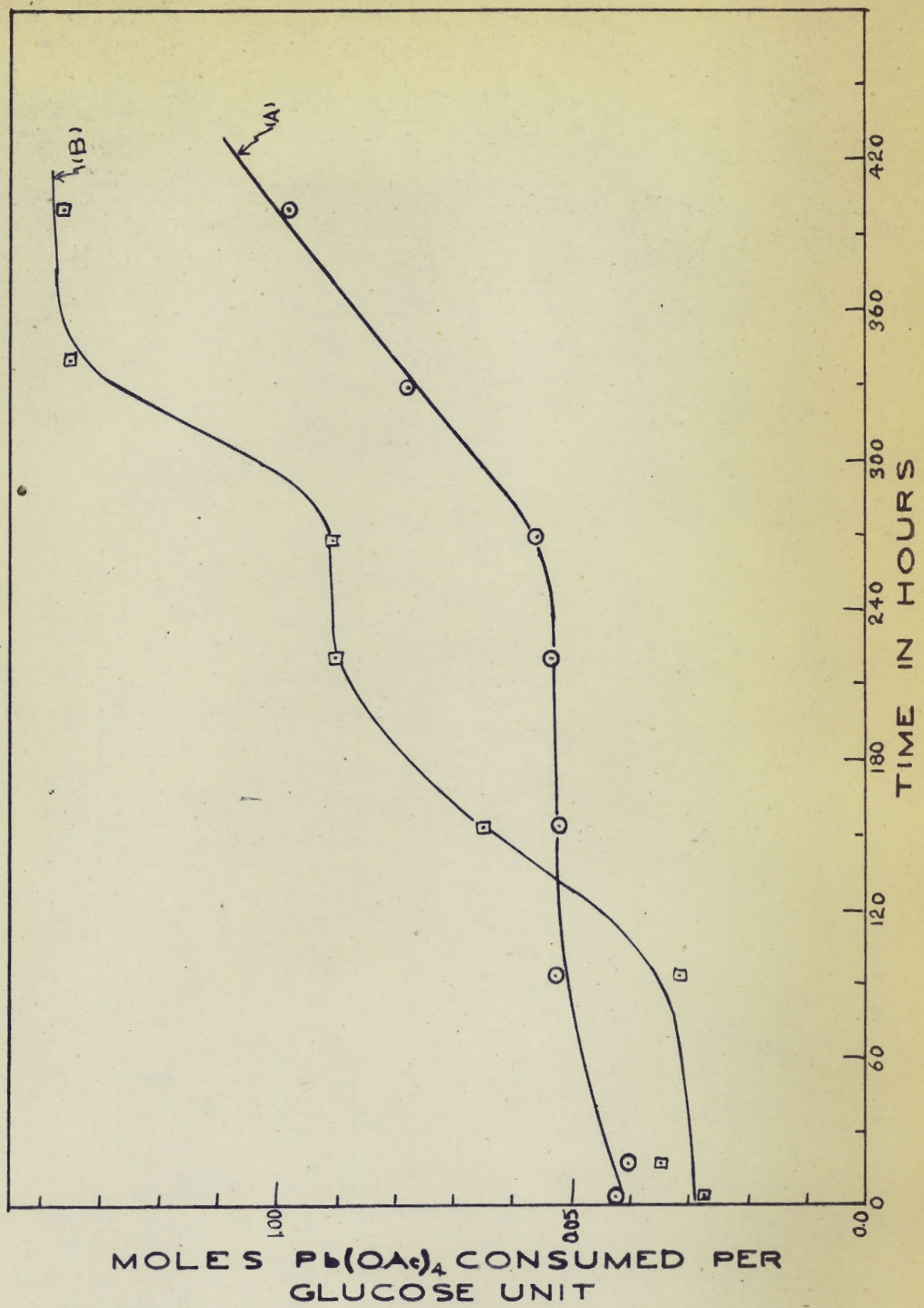

Fig. 14. - Lead tetraacetate oxidations of technical nitrates from celluloses of widely differing accessible fractions. Concentration of oxidant, 0.025 molar, of nitrate, 0.01 molar

the glucose unit to a greater extent than is exhibited by the swollen cellulose. This difference amounts to about 0.05 glycol units, 0.10 hydroxyl groups in positions 2 and 3, which, approximately, is the difference in degree of substitution observed between the two nitrates-2.27 for the swollen and 2.20 for the collapsed (Table XIV). The approximate agreement, however, may well be fortuitous.

The importance of removing the last trace of water from highly swollen cellulose by solvent exchange (10) before drying, cannot be overemphasized, if the increased accessibility is to be maintained. The effect upon the decrease of accessible cellulose of removal, by desiccation with concentrated sulphuric acid or phosphorus pentoxide, of small amounts of water still remaining in the material, is clearly demonstrated by the results of partial sorption and then total desorption of water shown in Table XV and Figs. 15 and 16. A gradual reduction of the amount of accessible cellulose, in a highly swollen specimen, occurs with removal of the increasing quantities of water sorbed by the cellulose. This agrees with the general results obtained from similar work carried out by Glegg (103) (Fig. 5, Table I).

However, the purpose of this repetition of Glegg's work was not to verify the existence of this decrease, but to clarify the shape of the curve obtained by plotting the decrease

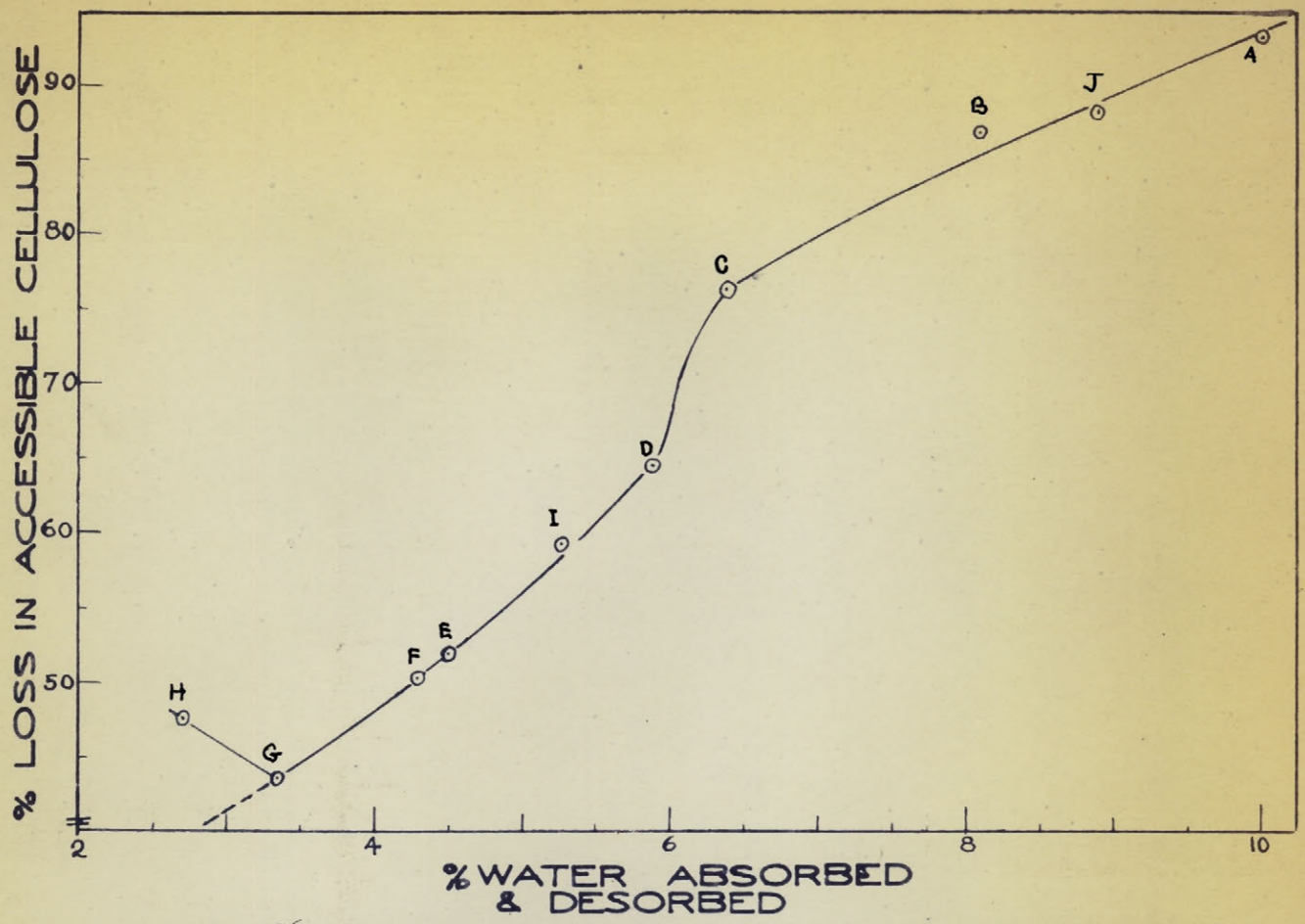

Fig. 16 - Decrease in accessible cellulose with removal of water, sorbed in increasing amounts by cellulose of high accessible surface.

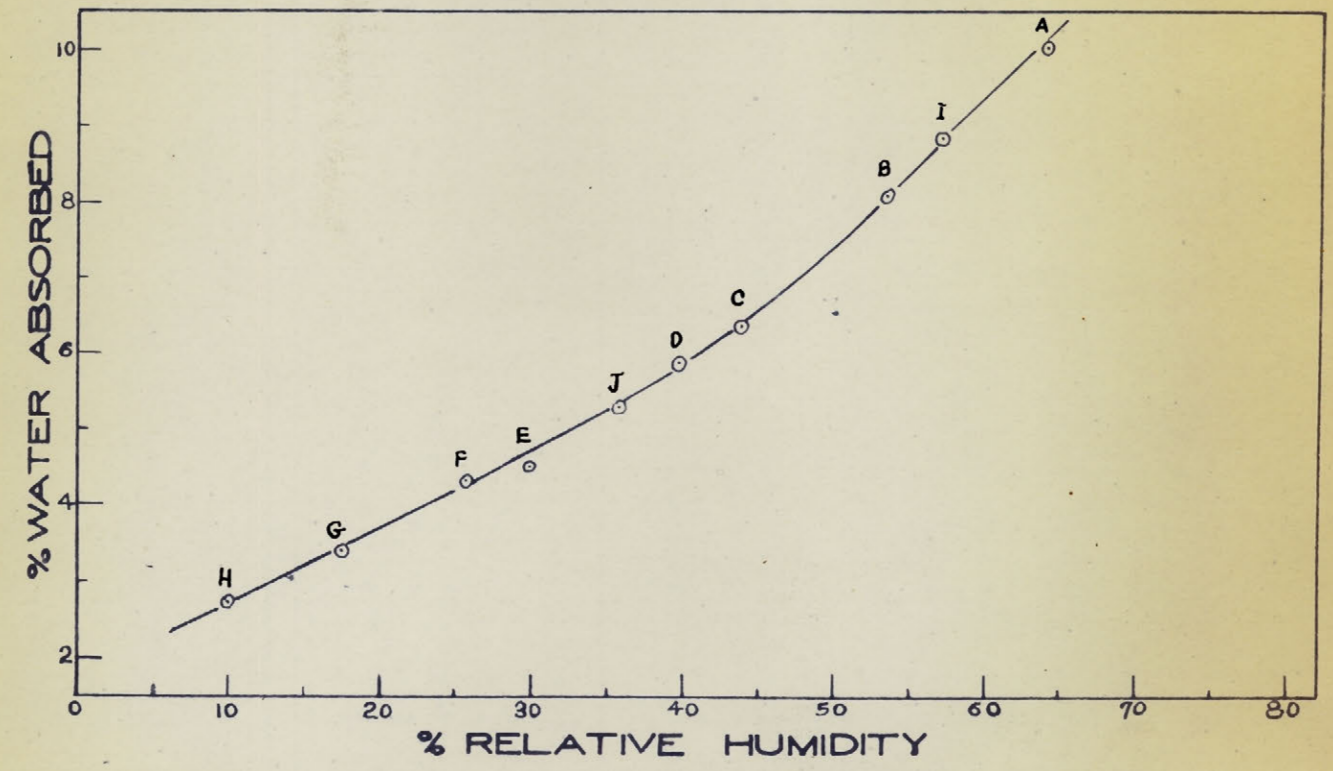

Fig. 15 - Cellulose water-absorption isotherm, determined at 25°

against the per cent of water sorbed and directly desorbed. One point,C, in Fig. 5, is either grossly in error, or has great significance in portraying the manner in which the accessibility of the cellulosic hydroxyl groups changes with desiccation. If it is in error, then the error must have occurred during the desorption or thallation procedure, rather than in the duplicate methoxyl determinations, since the latter checked well.

Repetition of the experiment, as was described in the Experimental Section,(p.77), yielded a smooth, typical sorption curve, shown in Fig. 15, (35), but the plot showing the loss in accessible surface revealed no inflections (Fig. 16) correspond- to those found by Glegg (Fig. 5). A slight break occurred in this curve between points C and D, at about 6% water sorption, but had doubtful significance. Point H, which should have shown less loss of accessible surface than point G, is somewhat out of place, probably because of some experimental error.

An interesting observation is that the per cent loss of accessible cellulose is much greater in Fig. 16 than is shown by Glegg's data (Fig. 5), even though the accessibilities of the swollen celluloses used in the experiments of both Glegg and the author were approximately the same. The cause of this dissimilarity may be attributed to the differences in the degree to which the samples were dried. The specimens depicted in Fig. 5 were dried over concentrated sulphuric acid, while those portrayed in Fig. 16 were given an additional treatment with phosphoric anhydride under vacuum, to remove any moisture which the sulph-

uric acid had been unable to withdraw.

A second repetition of the experiment, with desiccation carried out only with concentrated sulphuric acid, showed a plot similar to that obtained in the first repetition (Fig. 18). Here, points F or E are also misplaced quite beyond reasonable experimental error. But points G,H and K lie on an approximately straight line, and show about the same loss of accessible cellulose within the range of 1 to 3 per cent adsorption of water. However, sudden unexplainable deviations do occur, and slight sorption of water during manipulation becomes significant with cellulose of high accessibility, and causes greater collapse than expected. It is therefore difficult to attach great importance to these points.

Although the present results fail to confirm the shape of Glegg's plot, they tend to strengthen rather than diminish the possibility that some sort of discontinuity exists when 4 to 8% of moisture is desorbed. Adequate information must await a special research with more refined methods.

The above observations are most likely connected with an effect demonstrated in the sorption and desorption isotherms of cellulose (129,35), wherein the amount of water sorbed, after initial desorption, is lower than that present during the desorption cycle at any particular relative humidity. Urquart (128) has explained this peculiarity by the theory of hydrogen bonds.

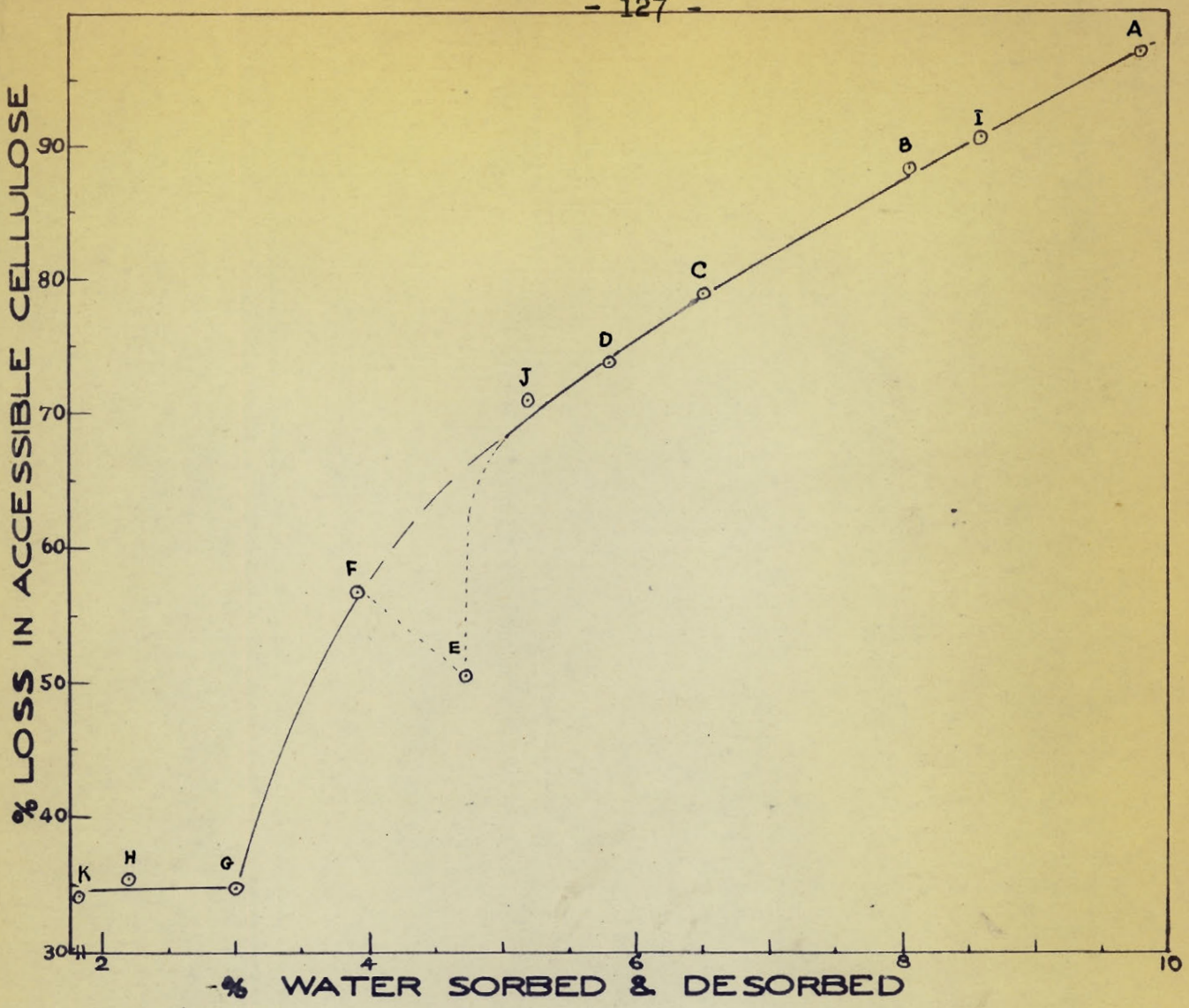

Fig. 18. Repeated sorption-desorption plot, showing loss of accessibility.

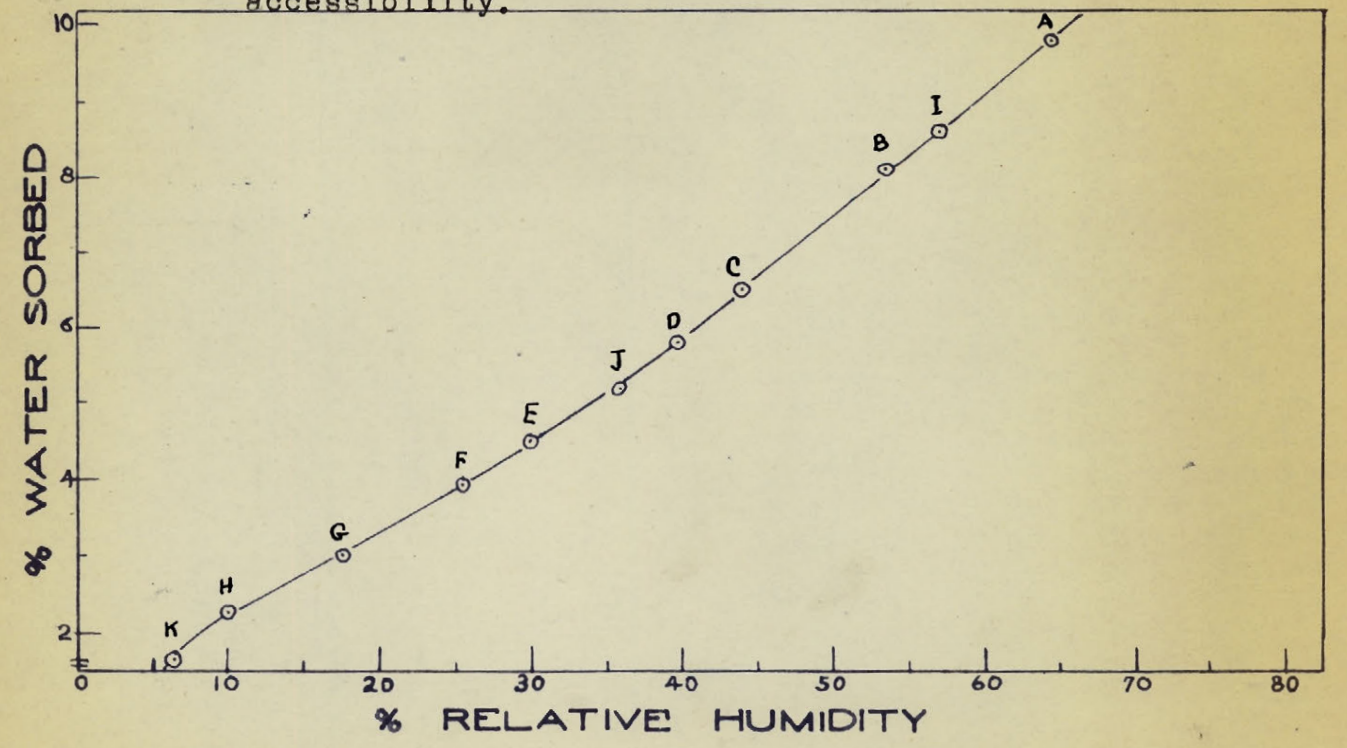

Fig. 17. Repeated water sorption isotherm at 25°.

According to this interpretation, during the removal of water, certain of the formerly water-accessible hydroxyl groups in the cellulose become so firmly bound to each other, that the solvent action of water can no longer loosen the bonds. An interesting characteristic of this hysteresis, as observed by Seborg (129), is the regularity with which successive sorptions and desorptions follow the first adsorption curve, and the constancy of the "Hysteresis Constant" (ratio of adsorption equilibrium moisture content to the desorption equilibrium moisture content), over a relative humidity range of 12 to 88 per cent, a relationship which is remarkably alike for various types of cellulosic materials. A chance coupling and uncoupling of the hydroxyl groups, seems somewhat doubtful. A definite "pattern" seems to be followed, which may possibly dictate the amount and location of the irreversible change resulting from the various degrees of drying and collapse.

Jayme, in a discussion of the "reactivity of cellulose" (26), has suggested that an "irreversible hornification" occurs in cellulose, caused by the removal of its moisture, and its extent depends, (as was stated on p. 11), directly upon the degree to which the pulp is dried. Evidently, certain parts of the previously accessible regions have been effectively closed to the reentrance of the water molecule, probably by a very strong mutual attraction of neighboring portions of the inner surface. Such localities might be of a vitreous rather than a crystalline nature. Jayme's "hornification" theory appears to offer a

qualitative and tentative explanation for some of the major results in this thesis. If "hornification" occurred during the wetting and redrying of the highly swollen linters, and the technical nitrating mixture failed to penetrate the "hornified" portions, a somewhat lower degree of nitration would be expected, as was found, for the product from the collapsed linters. The persistance of submicroscopic, "hornified" particles, holding a small number of nitrated molecules together, would tend to increase the apparent intrinsic viscosity in solution and thereby tend to offset the lowering of the viscosity occasioned by the lower average degree of substitution. These nitrates might well give less uniform viscosity distribution plots when fractionated and, even, in an extreme case, visible evidence of "granularity" when in solution. When oxidized with lead tetraacetate, unsubstituted, or lightly substituted "hornified" portions might consume more of the oxidant and thereby account for the results of the experiments with the technical nitrates from the swollen and collapsed linters.

In spite of careful control of nitration mixes, and of the measureable properties of the celluloses, the industrial nitration of successive batches of the raw materials occasionally encounters, for no obvious reason, slight deviations in the degree of substitution, the solubility, compatibility or stability of the product. It may be that the explanation of these anomalies is to be found in the presence of variable amounts of "hornified"

cellulose produced by variation in the moisture history and the drying of the cellulose.

SUMMARY

The amount of accessible cellulose in dewaxed cotton linters was increased to 18 to 33% by swelling in caustic soda. After thorough drying, one half of the product was wetted with water and directly redried at ordinary temperature, thereby reducing the accessibility to about 0.25%. Accessibility was measured throughout the research by the thallous ethylate method, which causes no swelling of cellulose.

With all conditions carefully standardized, portions of the dry swollen and the dry collapsed linters were nitrated nearly to the trinitrate stage with a phosphorus pentoxide-nitric acid nitration mixture. Other portions of the same linters were nitrated with a technical sulphuric acid-nitric acid mixture approximately to 12.0% nitrogen content. Part of each of these technical nitrates was then renitrated nearly to trinitrate by phosphorus pentoxide-nitric acid. All known factors, save degree of accessibility of the cellulose before nitration, thus having been kept unchanged, the six nitrocelluloses were examined.

In four independent experiments, the nitrogen contents of the "trinitrate" directly prepared from the swollen and collapsed celluloses probably agreed within the error of the estimation, but those of the technical nitrates from the collapsed celluloses were lower by 0.6,0.4, 0.3, and 0.15% nitrogen than

the corresponding derivatives from swollen cellulose. Renitration to the trinitrate stage almost obliterated this difference, which is thought to be significant. Parallel nitrations with the original, unswollen linters gave products of uniformly higher nitrogen content, although the increase was within the probable error.

In the main experiment, the intrinsic viscosities, measured in butyl acetate, both of the "trinitrate" and the technical nitrate made from the collapsed linters were 6% and 4% respectively, higher than similar preparations from the swollen cellulose. The difference in the case of the "trinitrates" increased when the products were precipitated from acetone. Fractionation of each of the six nitrates from dilute acetone solution by the gradual addition of water, made it possible to plot the Integral Weight Distribution Function of the fractions against intrinsic viscosities and nitrogen contents. Technical nitrates from the swollen and collapsed linters gave almost superimposable viscosity plots, but the plots of nitrogen content were somewhat higher in the former case, particularly in the low viscosity range. Two empirical factors, one for the swollen and one for the collapsed linters series, were used in an effort to correct the Integral Weight Distribution Function-viscosity plot to a trinitrate basis and so eliminate the effect of variable nitrate substitution on intrinsic viscosity. The tentative conclusion was that, other factors being the same,

swollen linters were more degraded, but were nitrated to a slightly higher level, than collapsed linters by the technical nitration mixture, the difference being more marked in the low viscosity fractions. The viscosity-distribution plots from the collapsed showed more irregularities than those from the swollen linters. In the course of the work, it was observed that a phosphorus pentoxide-nitric acid nitration mixture containing traces of higher oxides of nitrogen yielded trinitrate from swollen linters whose viscosity was reduced by two-thirds. The same sample of nitric acid, made up in a technical mixture, yielded a technical nitrate whose solution in butyl acetate was "grained", although a definite connection between the granularity and oxidative degredation by oxides of nitrogen was not established.

A series of technical nitrates of various substitution, and free from stabilizers, were oxidized, in ethyl acetate solution,by lead tetraacetate in glacial acetic acid, in an attempt to discover significant differences among them. Eight out of nine specimens made by the mechanical process consumed 0.02 to 0.10 moles of the tetraacetate in conditions when two out of three specimens made by the displacement process had a variable and different behavior. A technical nitrate made from collapsed linters reduced more of the oxidant than an otherwise identical nitrate made from swollen linters. The interpretation of these differences is still uncertain, although the lead tetraacetate may have been

exercising its usual selective action on unsubstituted glycol groups in the technical nitrates. In this event, the results would tend to show that the distribution of nitrate groups in the cellulose macromolecule of the different specimens was variable.

Separate samples of dry, highly swollen linters were permitted to absorb increasing amounts of water, and then were directly redried. The decrease in accessibility was plotted against the percentage of water added and removed. Although the shape of the plot did not coincide with an earlier one obtained by another worker, it did support the claim that there was an abrupt discontinuity when drying was from between four and eight per cent moisture content.

All of the results supported the hypothesis that the previous moisture history of the cellulose is an important factor in determining its behavior during nitration.

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