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CELLULOSE NITRATE - ACETATE MIXED ESTERS

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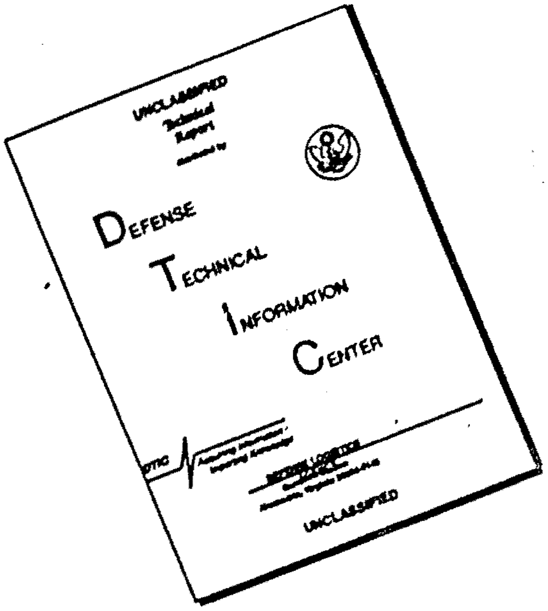

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CELLULOSE NITRATE-ACETATE MIXED ESTERS

by

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Feltman Research Laboratories
Picatinny Arsenal
Dover, N. J.

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ABSTRACT

A preliminary investigation of the preparation and properties of cellulose nitrate-acetate mixed esters was conducted. These mixed esters can be prepared in a wide range of amounts of substitution of both acetate and nitrate groups either through acetylation of cellulose nitrate or nitration of cellulose acetate. The degree of polymerization of the products, as estimated from viscosity data, shows the occurrence of chain degradation for both procedures. The hygroscopicity of the cellulose nitrate-acetate esters was found to be a linear function of total substitution. Films prepared from these mixed esters showed tensile strength at least comparable to that of films of cellulose nitrate or cellulose acetate. The impact sensitivity of the mixed esters varied from 6 to 18 inches for a 2-kilogram weight depending on the substitution of nitrate groups.

The results of the Taliani heat stability test showed inconsistencies, which are discussed. Under the conditions of the explosion temperature test, the mixed esters decomposed violently without igniting. However, the minimum decomposition temperature appears to be the same as for similarly substituted cellulose nitrate. Some mechanistic speculations are advanced to explain the kinetics preceding ignition or decomposition.

CONCLUSIONS

The cellulose nitrate-acetate mixed esters may offer definite advantages over cellulose nitrate when considered for use either in propellant formulations or in the manufacture of combustible cartridge cases. For both types of application, the nitrate-acetate mixed esters, with their relatively high sluggishness to impact detonation (6 to 18 inches as compared to 3 inches for cellulose nitrate of military interest), would certainly be attractive from a safety point of view. In addition, their resistance to ignition might prove to be an interesting feature for some particular application. With regard to other properties examined in this preliminary study, such as hygroscopicity, heat stability, and tensile strength, any improvement over cellulose nitrate would be somewhat marginal. Only with respect to the heat of explosion and residue on ignition do the cellulose nitrate-acetate mixed esters show limitations in comparison with cellulose nitrate. It is realized, however, that some of the results presented in this work are potentially subject to future revision. Time did not allow a thorough study of the various properties examined. Such an endeavor could not be contemplated at this time. For properties such as tensile strength, impact sensitivity, heat stability, and temperature of explosion, a large number of experiments must be conducted to achieve a reasonable degree of confidence. The limited number of determinations undertaken in this study can only suggest trends rather than serve as a basis for definitive conclusions.

Both methods of preparation of the cellulose nitrate-acetate mixed esters, i.e., acetylation of cellulose nitrate and nitration of cellulose acetate, have been shown to have enough merit to warrant further work toward the achievement of optimum conditions. With regard to the nitration of cellulose acetate, as is suggested under "Discussion of Results," one possible means of reducing the degradative processes might be through the use of cellulose triacetate as the starting material. Other nitrating agents such as the complex boron trifluoride-nitric acid, or a nitrating mixture known not to produce degradation (such as the phosphoric acid-phosphorus pentoxide-nitric acid mixture) could be considered.

RECOMMENDATIONS

On the basis of the information gathered from this study as well as the results obtained at other laboratories in the past, the authors would recommend that cellulose nitrate-acetate mixed esters be seriously considered and further evaluated for possible application either as propellant ingredients or in the manufacture of combustible cartridge cases.

INTRODUCTION

In the manufacture of solid propellants, cellulose nitrate occupies a place of unique importance. As a binder, it has shown great versatility and even with the more complex formulations recently developed, cellulose nitrate has been effective in producing a homogeneous grain with satisfactory mechanical properties over a wide range of temperatures. Another feature that makes cellulose nitrate attractive for use in propellant formulations is its high oxygen content; in this respect, it can be properly classed among the few high energy binders so far discovered. However, during recent years, the immense efforts directed towards the development of new propellants and the discovery of a variety of new applications has tightened the requirements which propellant binders must meet. Already cellulose nitrate has shown inadequacy in meeting some of these requirements.

For example, in some new applications the toughness of cellulose nitrate based propellants has been inadequate; in other instances, their dimensional stability with temperature changes, either during cycling or simply under standing conditions, failed to meet the required specifications. In addition, it has been shown that, in the manufacture of propellants containing solid contents in excess of 60% by weight, cellulose nitrate does not possess the necessary binding characteristics to produce a grain of acceptable mechanical properties.

Some of these difficulties were partially resolved through the addition of cross-linking agents in the cellulose nitrate based formulations, which resulted in an increase in toughness, dimensional stability, and binding power of the cellulose nitrate. As would be anticipated, however, the use of cross-linking agents, although very promising at this stage of development, does create new problems and certainly much more work is needed before this approach becomes commonly accepted. This is not surprising when one considers that through cross-linking new chemical bonds are formed which may sometimes change the identity of the binder and destroy some of its desirable properties.

Very little attention has been given to chemical modification of cellulose nitrate as a means of improving its physical and mechanical properties. It is certain that replacing the residual hydroxylic functions by such groups as esters, ethers, and acetals should significantly affect the properties of cellulose nitrate. Although it would be difficult to predict the direction of the changes in these properties, it would nevertheless seem justified that some effort be expended on the study of these cellulose derivatives. Consequently, an investigation of the synthesis and properties of several cellulose mixed esters was initiated in this laboratory, with cellulose nitrate-acetate as the first derivative submitted to our scrutiny.

A comprehensive literature survey on cellulose nitrate-acetate mixed esters was undertaken covering the period 1900 to the present time. In order to disseminate this information, the significant aspects of this survey were organized into a summary which is presented in the next several pages.

LITERATURE SURVEY

During the 1900–1940 period, the needs of the film industry for a less flammable and more stable film stimulated research towards the modification of cellulose nitrate. It was felt that this could be accomplished through acetylation of cellulose nitrate. The preparation of cellulose nitrate-acetate mixed esters was approached from a number of directions. The simultaneous nitration and acetylation of cellulose was attempted by Kruger (Ref 3). This failed to give the expected nitrate-acetate, only the nitrate being obtained. Evidently, under the conditions employed by this author, the acetic anhydride acted as a dehydrating agent only. If, on the other hand, the nitric acid concentration in the esterification mixture was kept very low (approximately 2%), only cellulose acetates were produced (Ref 4). In 1938, a British patent was issued claiming the successful preparation of cellulose nitrate-acetate by reacting anhydrous cellulose at room temperature with a mixture of acetic and nitric acids (Ref 6). However, this is the only reported evidence for the preparation of the mixed nitrate-acetate ester in a single operation. One year later, in 1939, Centola concluded after fruitless attempts that the synthesis of the mixed ester in a single step from cellulose is improbable (Ref 5).

A more promising method consisting in the nitration of cellulose triacetate was recommended by Kaetschet (Ref 15) in 1919.

Centola (Ref 5) in 1939 reported the successful preparation of the nitrate-acetate mixed ester through the nitration of cellulose acetate. This author claimed that this approach leads to homogeneous products. More recently, Gia and Mancini (Ref 13) of the University of Turin, Italy, in the course of their study on cellulose esters, prepared the nitrate-acetate by reacting a mixture of cotton and cellulose acetate in a ratio of 4 to 1 with nitric acid and sulfuric acid. The product, which contained 10.30% nitrogen and 4.71% acetyl group, was shown to have greater thermal stability than either cellulose nitrate or a mixture of cellulose nitrate and cellulose acetate.

By far the most explored method for the nitrate-acetate synthesis has been through acetylation of cellulose nitrate. It was reasoned that since nitrate groups are more resistant to hydrolysis by acids than are acetate groups, acetylation of cellulose nitrate should be favored over nitration of cellulose acetate. As early as 1919, Kaetschet (Ref 15) recommended this method. In 1930 Kruger (Ref 3) investigated this method and reported that cellulose nitrate of a high nitrogen content is resistant to acetylation mixtures containing sulfuric acid. In the same paper, he also reported that, if use is made of cellulose nitrate containing 11% nitrogen or less, acetylation proceeds more readily. It was also observed that, in this latter instance, denitration becomes significant and it was suggested by the author that denitration may have promoted acetylation. Berl and Smith (Ref 6) acetylated cellulose nitrate containing 12.4% and 12.9% nitrogen and obtained products containing between 2.64% and 4.19% nitrogen and 47.74% to 54.84% of combined acetic acid. Evidently the conclusions reached by Kruger, mentioned above, are valid only for one set of conditions. The apparent contradiction between the results of Kruger and Berl is explained in the work of Atsuki (Ref 7), who found that the larger the amount of sulfuric acid in the acetylating mixture the greater the denitration and, as a result, acetylation proceeds further. Atsuki's results were verified by a team of Japanese chemists (Ref 10) in 1939. Comparable results were reported in 1938 in a German patent (Ref 9). Cellulose nitrate containing 12% nitrogen was acetylated by acetic anhydride in the presence of sulfuric acid. The product analyzed for 1.40% nitrogen, 50.28% acetic acid and 3.34% combined sulfuric acid.

As a whole, these investigations indicate that a large number of nitrate groups in cellulose nitrate were hydrolyzed during acetylation. Since both free and regenerated hydroxyl groups were acetylated in the final product, it may reasonably be assumed that denitration precedes acetylation in the sequence of events. In 1950, Danilov (Ref 12), in the course of his studies on cellulose nitrate-acetate mixed esters, reported the reaction of cellulose nitrate with acetic acid and sulfuric acid in a ratio 5 to 1.

Since the presence of sulfuric acid in the acetylation mixture was apparently responsible for the occurrence of denitration, and Oddo (Ref 8) in

1919 conducted the acetylation of cellulose nitrate with boiling acetic anhydride alone. Another modification of the method of acetylation was reported in 1940 in a French patent (Ref 11) which described the preparation of cellulose nitrate-acetate mixed esters by reacting cellulose nitrate with acetic acid or acetic anhydride in the presence of lithium acetate instead of sulfuric acid. A few more publications in the literature were found to deal with cellulose nitrate-acetate mixed esters. However, since their synthetic approaches did not differ from those already discussed, they will not be mentioned here.

It seems to be the consensus that cellulose nitrate-acetate mixed esters have many properties which differ markedly from those of either cellulose nitrate or cellulose acetate or a physical mixture of these two. Relatively high tensile strength and good thermal stability have been reported (Fef 14) for the nitrate-acetate mixed esters. They have been used in propellant applications as a gelatinizer-stabilizer. Replacing the residual hydroxyl groups in cellulose nitrate by acetyl groups does improve the dissolving power of the polymer in a variety of common plasticizers. However, other ester groups beside the acetyl have been shown to increase the compatibility of the polymer towards conventional plasticizers. The same behavior was found, for example, with cellulose nitrate-laurate and cellulose nitrate-palmitate, which were prepared by Gault and Ehrman (Ref 2) in 1927. Although cellulose nitrate-acetates have been found to possess good thermal stability, it has been noticed that, on storage, they develop acidity more rapidly than either of the single esters. There are, however, good reasons to believe that this behavior of the nitrate-acetate may be associated with the use of sulfuric acid in the processing procedure rather than an inherent characteristic of the polymer itself.

In conclusion, it should be said that the ground work laid by these various workers from different countries during the first half of this century on cellulose nitrate-acetate mixed esters has demonstrated that these polymers have attractive features and consequently should be given more serious consideration by propellant chemists. The synthesis of these esters in a variety of ways has been demonstrated to be possible. However, no consistent systematic study dealing with their synthesis or their physical and mechanical properties has yet been reported in the literature. This is accounted for by the difficulties inherent in the study of such molecules and is also due largely to the lack of dependable analytical methods for the quantitative determination of the substituent groups. Although methods have been known for a long time for the determination of nitrate and acetate groups, it would seem that when both these functions are present in the same polymer backbone, each interferes with the determination of the other.

RESULTS AND DISCUSSION

Synthesis

Three synthetic approaches were chosen for the preparation of cellulose nitrate-acetate mixed esters covering a broad spectrum of substitution. The first consisted of reacting cellulose diacetate with a mixture of nitric and sulfuric acids. This approach consistently yielded products having a very low content of acetate groups. In addition, this method appears, from solubility experiments, to give a mixture of products rather than one unique specie. It did not seem that this method would be fruitful; consequently, it was abandoned early in favor of a method whereby cellulose diacetate was nitrated by 98% nitric acid without the intervention of a catalyst. The third method investigated consisted in reacting cellulose nitrate with acetic anhydride in the presence of perchloric acid. Perchloric acid was preferred over sulfuric acid as catalyst because, as far as is known, it does not react with cellulose or the residual hydroxyl groups of cellulose nitrate to form perchlorates. Sulfuric acid, in contrast, reacts with the hydroxyl groups of cellulose or cellulose nitrate to form cellulose sulfates and these sulfate groups have been shown to be responsible for the instability of cellulose nitrate. Only by boiling cellulose nitrate with a dilute sulfuric acid solution for long periods of time, which treatment removes the sulfate groups, can cellulose nitrate with good thermal and storage stability be obtained. It is clear, however, that this stabilization procedure could not be used in the case of the nitrate-acetate mixed esters which contain easily hydrolyzable acetate groups. Therefore, an esterification procedure had to be devised in which the formation of sulfate groups would be avoided.

Accordingly, a number of experiments were conducted using acetic anhydride in the presence of perchloric acid as the acetylating agent. The reaction was allowed to proceed in methylene chloride at the boiling point of the solvent. Two types of cellulose nitrate were subjected to this acetylation procedure. One had a nitrogen content of 12.3% (DS 2.3) and a degree of polymerization of 245 as determined from viscosity measurements in acetone. The second had a comparable degree of polymerization, 240, but a higher nitrogen content, 12.6% (DS 2.6). The degree of substitution of the products in both nitrate and acetate groups was determined by means of infrared spectroscopy. To gain some knowledge of the nature of the reaction, the following parameters were briefly evaluated: the content in acetic anhydride, the content in perchloric acid, and the time of reaction. The results of these experiments are given in Tables 1 and 2 (pp 36 and 37). It should be mentioned that some experiments were also conducted at ambient temperatures. These results, however, were not reproducible and consequently are not reported. It would appear that refluxing in a heterogeneous system of this kind is beneficial probably because there is better penetration of the fibers by the acetylating agent. A number of salient points are revealed upon examination of the data. Perchloric acid is necessary for the reaction to ensue (Experiments 10, 11, and 26). Also quite evident is that the one-hour reaction time is sufficient to give complete acetylation (Experiments 2 and 13 through 22). It is very interesting to note that, although denitration occurs, it seems that in most cases it is confined to the very early period of the acetylation reaction (Experiments 1 through 7 and 13 through 22). This observation, coupled with the previous finding that maximum acetylation is achieved within a one-hour reaction time, provides strong evidence for the stabilizing effect of the acetyl group on denitration. For example, Experiment 26, where no acetylation occurs (because of the absence of the perchloric acid catalyst), gives the rate of nitrate hydrolysis for cellulose nitrate where a large excess of acetic anhydride is used. The degree of substitution in the nitrate group suffers a significant drop for the first hour, from the original 2.6 to 2.1. When this experiment is repeated, however, with 0.2 ml of perchloric acid to catalyze the substitution (Experiment 23), denitration is quite retarded, only 0.2 nitrate group per anhydroglucose unit being lost.

Comparison of Experiments 9, 12, and 23 through 28 shows that perchloric acid is much more instrumental in causing denitration than is acetic anhydride. The extent of denitration appears to be a function of the perchloric acid content, as Experiments 27 and 28 show. When both acetic anhydride and perchloric acid are used in larger quantities (Experiments 9, 24, and 25), the denitrating effects of these two components appear to be additive. As to the mechanism of the acetylation reaction, it is safe to conclude in the light of these results that only the hydroxyl function on the anhydroglucose unit is acetylated. Very little if any acetylation occurs through a transesterification process.

Although molecular weight determinations will be discussed in a following section of this report it may be mentioned at this time that the acetylation procedure leads to some degradation of the cellulosic chain. It is also further indicated that this degradative process is caused principally by the presence of perchloric acid. Hence both processes, degradation of the chains and denitration, have a common promoter, perchloric acid.

The results of the alternate approach (nitration of cellulose acetate by 98% nitric acid) are given in Table 3 (p 38) and Figure 1 (p 46). Smooth curves showing the change with time in degree of substitution for both nitrate and acetate groups are obtained. The following simultaneous reactions probably occur under the conditions of the experiments: hydrolysis of acetate groups (deacetylation), nitration of the free hydroxyl groups, and transesterification of acetate by nitrate groups. Evidently, the observed rate for this reaction is a composite of these individual processes and a kinetic treatment would be outside the scope of this report. It is observed, however, that from 24 hours onward, for each acetyl radical lost a nitrate radical is fixed. Consequently, the observed rate of reaction for this portion of the curve may represent the rate of the transesterification process.

Having prepared from both synthetic methods a number of mixed esters varying in nitrate and acetate content, the possibility that a correlation might exist between the amount and type of substituents on the cellulose chain and various properties of interest to the propellant manufacturer was next explored.

X-ray Diffraction Study

Some knowledge of the crystalline structure of polymers is always desirable not only from a fundamental point of view but also as a means of predicting or at least explaining some of their properties. Although the chemical properties of polymers are evidently for the most part determined by the chemical structure of the monomeric unit, the physical properties and, more specifically, the mechanical properties are, on the other hand, greatly influenced by the degree of organization of the chains and very probably by the architecture of the unit cell of the crystalline elements. The structure of crystalline cellulose has been fairly well established as a result of the extensive work of various investigators and more particularly as a result of the important contributions of Mark, Meyer, and Misch (Refs 16–21). Disregarding the finer theoretical aspects, which still await a final decision, the cellulose crystal structure may be described as, in general, consisting of a monoclinic cell containing two anhydrocellobiose residues, the cell having the following dimensions: a = 8.35 A, b = 10.3 A,

$c = 7.9$ A, $\beta = 84°$ (Ref 18). From the axial length c which measures 7.9 A, it is calculated,that the centers of the planes of the cellulose chain molecules are spaced only 3.93 A apart. If we take into account the thickness of the cellobiose unit, which is approximately 2.5 A, the free space between the chains is found to be of the order of 1.5 A. Similarly, from the axial length a, which measures 8.35 A, it is found that the closest approach in the lateral distance of the cellobiose rings is of the order of 1.1 A.

It is evident that replacing the hydroxyl groups of cellulose with bulkier substituents would lead to overcrowding of the cell. It would then be anticipated that both axial lengths a and c would have to increase to accommodate the modified chains. In going from cellulose to cellulose nitrate, it has been observed from X-ray study that the outer (002) ring changes its position relatively little but that the inner (101) ring moves steadily towards the center as the nitrogen content increases. The interpretation given to this has been that the addition of the nitrate groups has increased the lateral distance between hexagonal rings in the (001) and (002) planes in which they lie but has not increased the separation of these planes from each other. However, in the monograph of Mathieu (Ref 19), both the lateral distance and the plane's separation are shown to be increased as is shown by the following dimensions for cellulose trinitrate: $a = 12.5$ A, $b = 10.3$ A, $c = 9.0$ A. The number of anhydroglucose residues in the cell has also increased from four to ten. As would be expected from the bulk of the acetate group, the change in the crystalline structure in going from cellulose to cellulose triacetate is more pronounced than in going from cellulose to cellulose nitrate. The unit cell dimensions reported are: $a = 24.5$ A, $b = 10.43$ A, $c = 11.56$ A.

Examination of molecular models is very informative in this respect. Replacing the hydroxylic functions of cellulose by nitrate groups does increase the bulk of the molecule and, as a consequence, the space requirement of cellulose nitrate is raised as compared to cellulose. However, since the nitrate group is planar, and furthermore since hydrogen bonding is still permissible with this group, it may be anticipated that the cell dimensions would not be drastically modified. On the other hand, replacing the hydroxyl function of cellulose by the acetate group is much more effective in disrupting the geometry of the anhydroglucose unit. The space requirement of the acetate group appears to be important enough to force the anhydroglucose rings into preferred configurations relative to each other. If, as is shown by the atomic models, the steric requirements of the acetate group are much higher than those of the nitrate group, it is reasonable to anticipate that, in going from cellulose nitrate to cellulose nitrate-acetate mixed esters, the change in crystalline structure of cellulose nitrate would occur at a rather low degree of substitution in acetate groups.

To test this point of view, three powdered samples of cellulose nitrate-acetate mixed esters prepared in the course of this study were submitted to X-ray analysis using the method of Debye-Scherer. The Debye-Scherer diffraction patterns are given in Figure 2 (p 47) and the calculated spacings are listed in Table 4 (p 38). For purposes of comparison, cellulose, cellulose nitrates of various degrees of substitution (DS), and cellulose acetate with a DS of 2.45 are also included. It is worth noting that the crystalline structure of the nitrate-acetate samples changed from that of nitrocellulose to that of cellulose acetate somewhere between 0.4 and 1.0 degree of substitution in acetate groups. If attention is focused on the sharpness of the rings, it is observed that the strong characteristic ring spaced at 6.4 A in the nitrate-acetate sample containing only 0.4 acetate group per anhydroglucose unit is substantially more diffused than the corresponding ones in the cellulose nitrate samples. It is evident then that the arrangement of the chains in cellulose nitrate becomes disorganized quite early upon addition of acetate groups. Since the nitrate-acetate samples containing a degree of substitution in acetate groups of one or above have no vestige of a cellulose nitrate structure, it is reasonable to assume that the nitrate-acetate mixed esters are homogeneously substituted along each chain.

The results of this X-ray study suggest that the nitrate-acetate mixed esters with a low substitution in acetate groups should have physical and mechanical properties more akin to those of cellulose acetate than those of cellulose nitrate. This last observation will, of course, be accurate only to the extent that the crystal structure of these polymers is effective in controlling these properties.

Viscosity

The acetylation of cellulose nitrate and the nitration of cellulose acetate have been done under conditions which in all probability would induce some cleavage of the acetal links between anhydroglucose units. Of the various methods available for the determination of molecular weights or degrees of polymerization, viscosity is one of the most simple with regard to design of apparatus and experimentation. However, the relationship between viscosity and molecular weight still rests on empirical grounds with no well established quantitative theory to permit calculation of the contribution of various other factors besides molecular weight to the viscosity. Consequently, viscosity cannot be used directly to determine the molecular weight of polymers. The equation relating viscosity and molecular weight contains two constants, K_m and a, which have to be determined empirically for each type of polymer and which vary not only with the temperature and the solvent but also with the chain length itself (Refs 23, 24). Although the values for K_m and a have been determined for cellulose nitrate and cellulose acetate, in the case of the nitrate-acetate mixed esters, no such information is available. Therefore, the use of viscometry in determining the molecular weights of nitrate-acetate mixed esters would seem a very questionable choice. Viscometry certainly could not be considered as dependable as, for example, the more direct methods, osmometry and ultracentrifugation. Unfortunately, viscometry was the only method available during the course of this work.

Having no other alternative, the possibility of using the intrinsic viscosity data to determine the molecular weights of the products was investigated. Evidently this is not an easy task and the approach offered in the following discussion is only tentative, being justified simply by the lack of a better procedure. It would be pertinent at this point to mention briefly one previous publication (Ref 13) describing the preparation of cellulose nitrate-acetate mixed esters in which the authors claim the determination of molecular weights from intrinsic viscosity data. However, as is shown below, their mathematical treatment is not acceptable, the fundamental error being that Equation 1 presupposes no change in molecular weight in going from the starting material (cellulose acetate) to the product (cellulose nitrate-acetate). Consequently, in a roundabout way, they have simply determined the molecular weight of the starting material, cellulose acetate. They proceeded as follows:

$$\frac{[\eta_o]}{[\eta]} = \frac{K_{m_o}}{K_m} \qquad (1)$$

$[\eta_o]$ intrinsic viscosity of cellulose acetate (I)

$[\eta]$ intrinsic viscosity of cellulose nitrate-acetate product

K_{m_o} Staudinger constant for cellulose acetate

K_m unknown constant for cellulose nitrate-acetate

The value of K_m was then substituted in the Mark-Houwink equation

$$[\eta] = K_m M^a \qquad (2)$$

where M was supposed to represent the molecular weight of the product nitrate-acetate. It is evident, however, that if the value of K_m in Equation 1 is substituted into Equation 2, this results in the cancellation of $[\eta]$, the intrinsic viscosity of the product

$$[\eta] = K_{m_o} \frac{[\eta]}{[\eta_o]} M^a$$

$$[\eta_o] = K_{m_o} M^a \qquad (3)$$

Therefore, M in Equation 3 stands for the molecular weight of the starting material, cellulose acetate.

Consequently, since no information can be found in the literature in regard to the Staudinger relation for cellulose nitrate-acetate mixed esters, the only possible means for estimating viscosity-molecular weights for these mixed esters will rest completely on speculations based on the known relations for cellulose nitrate and cellulose acetate. In the case of cellulose nitrate, it has been shown by Wannow (Ref 25) that the intrinsic viscosity $[\eta]$ rises with the nitrogen content of the sample (Fig 3, p 18). This increase in $[\eta]$ was not only caused by the increase in molecular weight due to the introduction of additional nitrate groups but, as could be anticipated, by a marked change in the rheological properties of the molecules in solution. In order to make use of the intrinsic viscosity-molecular weight relationship for cellulose nitrate samples of different nitrate substitution, Lindsley and Frank (Ref 26) have proposed that the intrinsic viscosity of the sample be corrected to that of cellulose trinitrate $[\eta_T]$, suggested as a common reference, and that this value of $[\eta_T]$ be inserted in Equation 4 for the calculation of the molecular weight.

$$[\eta]_T = K_m M^a \qquad (4)$$

$$\log \frac{[\eta_T]}{[\eta]} = \log f_N + (14.15 - N) B \qquad (5)$$

$$f_N = 1.833 - 0.0589 N$$

$$B = 0.114$$

$$\log R_N = \log f_N + 0.113\,(14.15 - N)$$

$$[\eta_T] = [\eta]\, R_N \qquad (6)$$

$$[\eta_T]_{g/dl} = K_m\, M^a \qquad (7)$$

$[\eta]$ – Observed or calculated intrinsic viscosity for the sample of cellulose nitrate

$[\eta_T]$ – Adjusted intrinsic viscosity for the corresponding cellulose trinitrate

K_m – Staudinger constant for cellulose trinitrate

a – Taken as unity
N – Nitrogen content (%) of the cellulose nitrate sample

Consequently, by simply multiplying the sample intrinsic viscosity by a factor R_N, itself a function of the degree of substitution (Fig 4, p 49), a value is obtained for the intrinsic viscosity which can be inserted into Equation 7. The best value of K_m for unfractionated cellulose trinitrate material in acetone appears to be 19.4×10^{-4}. This value is only provisional, however, since K_m is a function of the polydispersity of the sample.

It has been reported (Ref 22) that, in contrast to that of cellulose nitrate, the intrinsic viscosity of cellulose acetate in various solvents, including acetone, happens to be a decreasing function of the degree of substitution (DS). This finding rested on measurements done on samples ranging in DS from 2.2 to 2.7. In acetone, however, the decrease in viscosity was only about 7% for this range in DS. The K_m values for unfractionated cellulose acetate, taken from the data of Howlett, et al (Ref 22), were plotted against the degree of substitution (Fig 5, p 50), and the straight line obtained by the method of least squares was extrapolated to a DS 3. The extrapolated K_m value is 3.7×10^{-4} for cellulose triacetate in acetone. To summarize the information available at present, it seems that the best K_m values for unfractionated cellulose trinitrate and cellulose triacetate in acetone are 19.4×10^{-4} and 3.7×10^{-4}, respectively. The dependence of these K_m values to both derivatives on the degree of substitution is also established and finally, both cellulose derivatives have been shown to obey the Mark-Houwink relationship between intrinsic viscosity and molecular weight or degree of polymerization. With this knowledge available about cellulose nitrate and cellulose acetate, the determination of the molecular weight of the nitrate-acetate mixed esters can be estimated in more than one way, depending on what assumption one wishes to introduce.

The simplest approach would, of course, rest on the assumption that the acetate groups in the mixed esters bring a contribution to the intrinsic viscosity comparable to that of the nitrate groups. In such a case, then, the intrinsic viscosity can be adjusted by means of the Lindsley and Frank treatment according to Equations 5, 6, and 7 to yield $[\eta_T]$. However, the value of N would be that corresponding to the total substitution, i.e., that of both nitrate and acetate groups. Evidently it would be anticipated that such an approach is unrealistic since, as was shown above, the K_m values for cellulose acetate and cellulose nitrate differ by a factor as high as 5, and in addition, these two derivatives show opposite dependences of substitution on their respective K_m values.

A second approach to the calculation of molecular weights for nitrate-acetate mixed esters would take into account the K_m values of cellulose nitrate and cellulose acetate. Then, on the assumption that these K_m values are not changed by having both functional groups in proximity on the same molecular chain, one would be justified in using their weighted value in the Mark-Houwinck equation as shown in Equation 8.

$$\frac{[\eta]}{\frac{DS_o}{DS_t} \times K_{m_o} + \frac{DS_1}{DS_t} \times K_{m_1}} \qquad DP \tag{8}$$

DS_o – Degree of substitution in nitrate groups

DS_1 – Degree of substitution in acetate groups

DS_t – Total degree of substitution (DS_o plus DS_1)

DP – Degree of polymerization

K_{m_o} – Staudinger constant for cellulose nitrate for a degree of substitution corresponding to DS_t. These K_{m_o} values were taken from Wannow's data (Fig 3, p 48).

K_{m_1} – Staudinger constant for cellulose acetate for a degree of substitution corresponding to DS_t. These K_{m_1} values were taken from Howlett's data (Fig 5, p 50).

$[\eta]$ – Experimental intrinsic viscosity, g/li, obtained from a one-point determination and application of the Baker-Philipoff equation, as shown in Equation 9

$$[\eta]_{g/li} = \frac{8(\eta_r^{\frac{1}{8}} - 1)}{C} \qquad (9)$$

η_r – Relative viscosity

C – Concentration in gram per liter.

If for the moment attention is focused on the intrinsic viscosity alone (Table 5, p 39), it is observed that $[\eta]$ decreases with the time of reaction (Experiments 1–3 and 10–12). Also, while acetic anhydride does not bring about any lowering of the viscosity (Experiments 1, 4, and 7), perchloric acid is very effective in this respect (Experiments 4, 7, 8, and 9).

The degrees of polymerization corresponding to these viscosities were obtained as follows: for the nitrate-acetate mixed esters (Experiments 1–6 and 10–12), use was made of Equation 8; for the products containing only the nitrate function (Experiments 7, 8, 13, and 14), the Lindsley-Frank method of calculation was applied (Equations 4–7); in the case of cellulose acetate (Experiment 15), a K_m value of 4.01×10^{-3} taken from the curve (Fig 5, p 50) was used. It should be realized, however, that these methods of calculation are only valid for degrees of substitution above 2. This stems from the fact that the Lindsley-Frank relation becomes very inaccurate at nitrogen contents below 11%. The reason for this limitation is evident from examination of Figure 4 (p 49). The derivative dR_N/dN takes up increasingly large values in going toward lower nitrogen contents. Hence, below 11% nitrogen, the experimental error in the determination of the nitrogen content introduces excessive deviations in the resulting R_N values. In addition, for low degrees of substitution the solubility of these cellulose derivatives in acetone even at low concentration is never complete and a filtration step is necessary to remove the insolubles. This explains why no degree of polymerization values are quoted for Experiments 8 and 9.

The results given in Table 5 clearly show that acetylation of cellulose nitrate under the conditions described in this work leads to degradation of the polymer chain and almost to complete splitting of the acetal bonds with increasing amounts of perchloric acid. To minimize such degradation in the preparation of the mixed esters, the reaction time, perchloric acid content, and acetic anhydride content should be kept to a minimum. Hence, it would probably be advantageous to modify the procedure by adding both the acetic anhydride and perchloric acid dropwise during the reaction.

Experiments 10–12 in Table 5 (p 39), which refer to the nitration of cellulose acetate (DP 340), demonstrate the strong degradative effects of nitric acid as a reaction medium. After 16 hours reaction time the average degree of polymerization value has dropped to less than ¼ the original value, and the degradation reactions are still proceeding at 72 hours reaction time. Since degradation of the chains still progresses at long reaction times, this would suggest that the nitrate-acetate products are being split in contact with nitric acid. It would be interesting to know whether the starting material, cellulose acetate, and the nitrate-acetate products are equally sensitive to degradation under these conditions. Evidently, such information would help greatly in determining the optimum conditions for the preparation of the nitrate-acetate mixed esters by this method with a minimum of degradation. Considering that a large excess of nitric acid was used, the degradation process should have proceeded in accordance with first order kinetics if no selectivity occurred during the destruction of the acetal bonds. Using the average number of acetal bonds available in lieu of the concentration, and applying the integrated form for a first order process (Equation 10), the rate constants k were calculated and their magnitude was found to change with time, as shown in Table 6 (p 40).

$$k = \frac{2.303}{t} \log \frac{a}{a-x} \qquad (10)$$

a	available positions on anhydroglucose unit at beginning of period
$a-x$	available positions on anhydroglucose unit at end of period
t	time, or length of period, in hours

There is a significant drop in the rate constant k (factor of 5) in going from 16 hours to 24 hours reaction time while, for the remaining 48 hours, the rate constant remains practically the same. This change in the rate constant from 16 hours on cannot be explained by a change in the nitrating medium brought about by the progress of the reaction. Nitric acid was used in such a large excess that its concentration varied only negligibly and, similarly, the total water content in this medium did not change to any significant extent from its initial value. One is then led to believe that possibly the nitrate-acetate mixed ester products are less sensitive to degradation than the starting cellulose acetate. This increased resistance to degradation may be caused either by the presence of nitrate groups in the molecular chain or, as seems to these authors more probable, by a higher degree of substitution in the products (DS 2.9) than in the cellulose acetate (DS 2.45).

If this speculation should prove to be correct, it would then be expected that using cellulose triacetate instead of the commercial cellulose acetate used for this study (DS 2.45) should lead to much less degradation of the chains under the same conditions.

Hygroscopicity

Since dimensional stability in propellants is closely connected to the moisture uptake or regain of the binder, hygroscopicity experiments were conducted at a temperature of 20°C and a constant relative humidity of 67%. The profiles of the hygroscopicity curves are given in Figure 6 (p 51). Except for cellulose acetate (DS 2.45), all of the samples reached their equilibrium absorption before one hour of exposure at this temperature and humidity level. At this point, it would seem pertinent to recall a hypothesis formulated in 1926 by Will (Ref 27) which stated that the absorbed water in cellulose nitrate esters is fixed by the free hydroxyl groups. A simple linear expression was found which relates the hygroscopic absorption H, in grams per 100 grams of cellulose nitrate, to the nitrogen percentage of cellulose nitrate esters. This relation, known as Will's rule, states that the sum of the hygroscopicity (%) and nitrogen content (%) values of any cellulose nitrate ester should give a constant, 14.6, as expressed in Equation 11.

$$H = 14.6 - N \qquad (11)$$

This rule rests on a great number of experimental investigations carried out at 25°C and at approximately 100% relative humidity. Later on, Démougin, who carried out further investigations on the subject, concluded that Will's hypothesis can be true only for low saturation of vapor where probably only chemisorption would be active (Ref 28). Whatever the fundamental relation between hygroscopicity and degree of substitution (DS) for cellulose derivatives may be, it is nevertheless a fact that, in the case of cellulose nitrates, a very simple mathematical expression can adequately express this relation. However, if Will's hypothesis, i.e., the absorbed water being fixed by the free hydroxyl groups alone, is correct to a first approximation, then the simple relation as expressed by Equation 11 should still persist upon replacement of some of the nitrate groups with other functional groups. This extension of Will's hypothesis was tested with some of the cellulose nitrate acetate samples prepared as described earlier. As Figure 7 (p 52) shows, a linear relationship was found between the percent water absorbed and the total degree of substitution of the cellulose nitrate-acetates. The data fit the simple linear expression (Equation 12) similar to that of Will.

$$H = 7.15 - 2\ DS \qquad (12)$$

$$H = 14.6 - N \qquad (11)$$

DS – Number of substituents per anhydroglucose unit.

It is evident from Equation 12 that, for a degree of substitution of zero (i.e., that of cellulose itself), the hygroscopicity value is calculated to be 7.15%. The hygroscopic value for cellulose under a relative humidity atmosphere of 70–75% extracted from Démougin's work is 7.0–7.3%, which is in perfect agreement with Equation 12. This could of course be a coincidence and certainly more work is needed to confirm these results.

Tensile Strength

Films of cellulose nitrate-acetate mixed esters were cast from ethyl acetate, and their tensile strength was determined on an Instron Tester under constant load. For these samples, which were prepared by acetylation of cellulose nitrate, an apparent correlation was found between the degree of substitution in acetate groups and the tensile strength. As Figure 8 (p 53) shows, the tensile strength decreases with an increase in acetate content. The least square line through the experimental points obeys Equation 13.

$$\text{Tensile strength, psi} = 17{,}300 - 7{,}100\ DS_{OAc} \qquad (13)$$

By way of comparison with these values, which were obtained for cellulose nitrate-acetates, the tensile strength of the cellulose nitrate used in the synthesis (DS 2.3) was found to be 12,900 psi, which is in good agreement with the value of 12,500 psi frequently quoted by other authors (Ref [illegible]). It is interesting to note in this connection that the values taken from the literature apply to films cast from an acetone solution, while for this study the films were cast from ethyl acetate. Although it has often been observed that the casting solvent is an important parameter in tensile strength measurements, it would seem that ethyl acetate and acetone contribute the same overall cohesive energy towards cellulose nitrate and hence these solvents could be interchanged without substantial effect on the tensile strength values.

It has been reported (Ref 29) that cellulose acetate, 52.8% acetic acid yield, under experimental conditions very close to those used in this study, yields films having an average tensile strength and elongation in the neighborhood of 13,000 psi and 5%, respectively. In addition, the tensile strength did not change to any significant extent when the films were prepared from fractions ranging in DP from 240 down to 82. For all practical purposes, then, the cellulose nitrate and cellulose acetate unplasticized films have comparable tensile strengths, approximately 12,500 and 13,000 psi, respectively. If we compare the results shown in Figure 8 (p 53) and Table 7 (p 41) with these values, it would appear that nitrate-acetates with low DS in acetate can form films as strong as or possibly stronger than those of either cellulose nitrate or cellulose acetate. With regard to the apparent correlation exhibited in Figure 8 between the tensile strength and the DS in acetate, the authors cannot at this time decide whether this relationship is real or only coincidental. No really convincing arguments can be advanced to explain such a trend. For example, it cannot be explained on the basis of molecular weight variation since the relation cannot be extended to either time of acetylation or intrinsic viscosity of the nitrate-acetates. Neither could it be explained by invoking the concept of hygroscopicity of the films (water plasticizing action) or the extent of solvent retention in these films. In addition, no similar relationship could be observed with either DS in nitrate or total DS. The possibility that the relationship indicated in Figure 8 is real cannot be disregarded; however, more work is needed to clarify this point.

The formation of films from samples prepared by nitration of cellulose acetate proved to be extremely difficult. For most trials, the films could not be removed from the glass plate. They were too brittle and usually broke into small pieces. Only with one sample could films be prepared and tested. As Table 7 shows, the tensile strength is very low, indicating that this sample has a DP approaching the critical value.

Impact Sensitivity

The impact sensitivity of the cellulose nitrate-acetate mixed esters was measured on a Picatinny Arsenal machine using a two-kilogram drop weight. The procedure used has been described in detail before (Ref 30). The impact test values quoted in this report correspond to the minimum height in inches from which the impact of the falling weight causes explosion of the sample in at least one of ten trials. In studies of the shock sensitivity of propellants, attempts have been made to relate sensitivity to certain propellant properties. For example, at Allegany Ballistic Laboratory (Ref 31), it has been proposed that the card-gap sensitivity of propellants could be related to the heat of explosion according to the following equation:

$$V = A + B \cdot \Delta H_E \cdot V_o \qquad (14)$$

V	card-gap value
ΔH_E	heat of explosion of binder plus the solid oxidizer
A and B	constants which apparently characterize the oxidizer
V_o	specific volume of the propellant

In an attempt to find a similar relationship, the heat of explosion of various cellulose nitrate-acetate mixed esters prepared in the course of this study was plotted against the drop height in inches, with a two-kilogram weight, necessary to produce an explosion (this value being proportional to energy); and, by means of the least squares method, a line was then drawn through the experimental points as shown in Figure 9 (p 54). A relationship seems to exist although a large deviation is observed. This function is given by Equation 15.

$$H = 25.8 - 0.08\,\Delta H_E \qquad (15)$$

H	drop height in inches (2-kg wt)
ΔH_E	heat of explosion, Kcal/mole

A much better relationship was found, however, between the degree of substitution in nitrate and the drop height or energy as shown in Figure 10 (p 55). The straight line through the experimental points was obtained by the method of least squares and obeys Equation 16.

$$H = 27.3 - 8.3\,DS_{NO_3} \qquad (16)$$

If extrapolation of the curve beyond the experimental points is valid, then these values would lead to the prediction that the sensitivity of cellulose trinitrate (DS 3) would be approximately 2.5 inches while for cellulose triacetate, explosion or violent decomposition would occur at around 27 inches. Evidently, the curve in Figure 11 (p 56) must bend upward for degree of substitution (nitrate) below 1 since cellulose acetate is known to be insensitive to impact for drop heights over 40 inches.

It has been reported (Ref 52) that cellulose nitrate whose nitrogen content varies from 12.6% up to approximately 14.0% will under the same experimental conditions give an impact sensitivity value of 3 inches, which is surprisingly close to the extrapolated value of 2.5 (from Figure 10). Consequently, it can be said that nitrate-acetate mixed esters are characterized by a resistance to impact significantly superior to that of cellulose nitrate of military grade. It is not possible, however, to reach a definite conclusion as to whether this increased resistance to impact is simply due to a decrease in the number of nitrate groups on the anhydroglucose unit or whether the presence of acetate groups is largely responsible. Some arguments could be advanced in favor of the latter point of view. For example, as is pointed out above, in going from a cellulose nitrate with nearly theoretical substitution down to 12.6% N (DS 2.4–2.5), the impact sensitivity was the same, 3 inches. It has been found recently in this laboratory that cellulose nitrate of 11.6% nitrogen (DS 2.1) has an impact sensitivity of 3 inches. So, for cellulose nitrates, decreasing the number of nitrate groups per anhydroglucose unit from 3 to 2 does not produce any change in impact sensitivity while, in the nitrate-acetate mixed esters, the same degree of substitution in nitrate raises the impact value to 10 inches. In addition, closer examination of Figure 10 (p 55) will show that the two points below the curve (DS 1.7 and 2.3) correspond to samples with low substitution in acetate (Table 8, p 42). This again could be taken as an indication that the acetate function in the polymer could act as an efficient stabilizer relative to the hydroxylic function.

Heat Stability

An examination of the literature reveals that many procedures have been developed to evaluate the stability of organic nitrates, that is, their resistance to spontaneous decomposition. Of the three methods currently in use, the 134.5 C heat test, the Bergman-Junk test, and the Taliani test, the last was considered most suitable for this investigation. This judgment rested on the extensive work carried out jointly by the United States Forest Products Laboratory and Picatinny Arsenal (Ref 33) on the stability of cellulose nitrates. The interpretation of nitrate stability was found to be strongly dependent upon which of these current methods is used in making the measurements since each is differently influenced by a number of variables. However, the conclusion was reached that the Taliani procedure provides the most meaningful interpretation of nitrate stability.

The apparatus and test procedure adopted some years ago at Picatinny Arsenal are essentially those established by Pauling and co-workers (Ref 34) and described in a Bureau of Ordnance Publication (Ref 35). In this modified Taliani test, powder samples are heated at 110 C in a closed system, at constant volume, under an atmosphere of nitrogen or air, and in contact with gaseous decomposition products. The relative stability of different compositions can be correlated by comparing their pressure vs time curves.

The pressure-time curves for a series of nitrate-acetate mixed ester samples prepared in the course of this work and a sample of the starting cellulose nitrate are given in Figures 11 and 12 (pp 56 and 57).

On the basis of an examination of the thermal behavior of a number of samples prepared through acetylation of cellulose nitrate (Fig 11), it is observed that four out of five samples tested have their pressure-time curves closely grouped, the onset of the accelerated decomposition rates (used as end point) ranging from 120 to 155 minutes heating time. The accelerated decomposition rate for the fifth sample was not recorded. From the shape of the curve, however, it could be tentatively located somewhere between 400 and 500 minutes heating time. In contrast, the starting cellulose nitrate has its thermal end point located at 340 minutes.

For the sake of clarification, it should be remarked at this point that the criteria commonly used to express stability on the basis of Taliani pressure-time curves are varied and somewhat different from the one chosen for this study. In general, the stability is expressed by quoting the slope at a given pressure in millimeters, by recording the time necessary to reach 100 mm pressure in the system, or by recording the slope at 100 minutes. This lack of uniformity in expressing the thermal stability as measured by the Taliani method can be understood from examination of a large number of curves obtained for various compositions susceptible to thermal decomposition. The profiles of these curves are extremely varied and no criterion can alone satisfactorily describe the decomposition phenomena for a broad range of compositions. For this study, however, the curves have in general been characterized by one very sharp change in the rate of gas evolution, and the time at which this change occurs, here called the end point, is offered as the criterion which best reflects the thermal stability of the samples.

The unique behavior of the sample labeled 2 cannot be traced to the substitution in nitrate, acetate, nor the time of reaction. Consequently, this could be taken as an indication that the lower stability of the other samples of nitrate-acetate may be due to causes other than structural. Among various possible causes for the low stabilities, the stabilization treatment deserves particular mention. All samples, including the cellulose nitrate in question, had been stabilized by boiling in a very dilute solution of sodium carbonate for four hours after a preliminary wash with distilled water. That this mild base was effective in removing the major portion of the residual acids in the samples with a resulting improvement in stability is well illustrated in Table 8 (p. 32). However, no assurance can be given that the amount of base or time of treatment was extensive enough to remove all residual acid in the samples. Another aspect to consider is the fact that the mixed ester samples were prepared in the presence of methylene chloride. It is conceivable that in spite of drying of the products a small amount of residual solvent could have easily escaped removal. This hydrophobic solvent could have acted as a protective shell for small amounts of acid during the stabilization treatment.

Only three samples of nitrate-acetate mixed esters prepared by the alternate synthetic route, i.e., nitration of cellulose acetate, were available for thermal stability studies. As is indicated in Table 9 (p. 33), one of the samples shows a stability at least as good as that of stabilized cellulose nitrate while the second gives no sign of decomposition up to 400 minutes of heating time. The end point for the third samples is comparable to the end points observed with the four samples prepared by acetylation of cellulose nitrate. Although there is apparently some correlation between the thermal stability values for these three samples and their substitution patterns, in the light of the preceding discussion and the limited number of tests, there does not seem to be sufficient justification for suggesting that this correlation is real.

Combustible and Consumable Cartridge Cases

When this study was initiated one important objective was to investigate the possibility of applying these cellulose nitrate-acetate mixed esters as substitutes for cellulose nitrate in the manufacture of combustible and consumable cartridge cases. It was reasoned that the presence of acetyl groups in the polymer might raise the deflagration temperature and consequently eliminate "cook-off" during continuous firing. Furthermore, the presence of acetyl groups could possibly improve both the thermal stability and the storage stability of the case. On the other hand, the residue on ignition, which is of fundamental importance in connection with cartridge case applications, would of course increase upon substitution of acetyl groups. Evidently, the upper tolerance limit in extent of substitution is expected to be somewhat low for true combustible cartridge cases, while for consumable cases this limit could be raised to considerably higher values.

Consequently, in addition to the information already provided on the mechanical and thermal properties, it seemed pertinent to include the results of tests done on the explosion temperature, the heat of explosion, and, finally, the residue on ignition.

Temperature of Explosion

The temperature of explosion was determined on four samples of cellulose nitrate-acetate mixed esters covering a wide range in substitution and on three samples of cellulose nitrate having degrees of substitution of 2.1, 2.3, and 2.8. The determinations were carried out by means of the standard test (Ref 30) which simply consists of immersing hollow copper cylinders loaded with 5 mg of sample into a metal bath maintained at the desired temperature, and recording the time at which an explosion or flash occurs. Although it has been common practice to use 20 mg of sample for this test, the results discussed in this report were obtained from determinations done on 5 mg samples. The smaller samples were used because the amount of material available was limited. However, since it has been previously reported (Ref 42) that the time to explosion is very nearly independent of the size of sample, it is believed that the results are not affected by this modification.

The temperature-time curves are given in Figures 13 and 14 (pp 58 and 59). Each point on the graphs represents an average of five determinations. The average standard deviation for the low temperature (210°C) determinations was 10% while for the high temperatures (270°C) with short time to decomposition the standard deviation amounted to 12%. This reproducibility across the whole range of temperatures is considered exceptionally good, when the crudity of the technique is considered. The plots obtained with the three types of cellulose nitrate (Fig 13) are indicative of an exponential function with an asymptotic value estimated somewhere between 200° and 210°C. The nitrate-acetate mixed esters (Fig 14) give similar curves with the exception of the sample with the highest acetyl content. In this last instance, the asymptotic value apparently lies close to 220°C. In fact, the results at this temperature were very erratic, violent decomposition being observed at 12 seconds for some determinations, while at other times there was no sign of decomposition after 30 seconds immersion.

The asymptotic values quoted from these experiments may not represent the lowest possible explosion temperatures for the compounds under study.

They should only be regarded as representative of the relative ease with which these compounds reach uncontrollable decomposition. This opinion has already been expressed by Henkin and McGill (Ref 42) in their paper on the rates of decomposition of explosives.

All samples of cellulose nitrate-acetates differed from the samples of cellulose nitrate in their thermal behavior in one major aspect. While the samples of cellulose nitrate literally exploded or deflagrated at these temperatures, the nitrate-acetate mixed esters did not ignite but rather exhibited decomposition with evolution of smoke. This difference in behavior between cellulose nitrates and cellulose nitrate-acetates even with low substitution in acetyl can perhaps be explained in the light of the information available from the literature. It has been known for some time that, when cellulose nitrate is heated above 180°C, it will ignite after a short induction period (Ref 39). This induction period, called "time lag to ignition," has been found to obey an Arrhenius-type relationship.

It has often been suggested that the controlling reaction in the complex decomposition process is the dissociation of the nitrate grouping. Study of the thermal decomposition of cellulose nitrate by differential thermal analysis (Ref 43) seems to bear out this hypothesis. The thermogram exhibits a sharp symmetrical exothermic peak in the 160–190°C region. Other organic compounds containing the nitrate group (for example, the pentaerithritol series) show similar thermograms. However, the decomposition of cellulose nitrate does not always lead to ignition. Churchill and his collaborators (Ref 36) have found, for example, that under a stream of hot carbon dioxide or nitrogen gases pyrocellulose does not ignite consistently and have concluded that oxidation reactions are controlling in the mechanism of ignition. Consequently, although the cellulose nitrate-acetate samples decompose in a fashion similar to that of cellulose nitrate, as is indicated by the similarity of the curves in Figures 13 and 14 (pp 58 and 59), the former suppresses ignition, possibly by the release of acetic acid into the atmosphere above the sample, which could change the composition of the gas phase enough to prevent ignition.

It is not probable, however, that acetic acid would be released through dissociation of the acetate group. The pyrolysis of organic acetates to yield unsaturation and acetic acid (Ref [illegible]) becomes significant only in the neighborhood of 500°C. Also, differential thermal analysis of cellulose triacetate (Ref 37) gives a thermogram characterized by a broad irregular exothermic peak with the maximum located at [illegible]°C. Consequently, the dissociation of acetate groups in cellulose nitrate-acetate at the temperatures used here, 210–270 C, would be expected to be negligible. A second possibility, however, would be that acetic acid is released during the initial phase of the decomposition, through acid hydrolysis of the acetate groups. This hydrolysis would be promoted by the presence of a small amount of water in the sample. At these temperatures and in the presence of water and acidic oxides of nitrogen, hydrolysis could proceed extremely fast. The saponification of cellulose acetate by a solution of nitric acid has been shown to proceed with an energy of activation of 14.4 Kcal/mole (Ref 44). Evidently, the hydrolysis would become immeasurably fast at the temperatures used in these experiments (Ref 45).

From these considerations, the mechanism for the thermal decomposition of cellulose nitrate-acetate mixed esters as carried out under the conditions of the explosion temperature test is tentatively submitted as proceeding according to the following sequence of events: the nitrate groups are, upon absorption of heat, dissociated (or possibly hydrolyzed) to produce nitrogen oxides following the same kinetics of decomposition as are observed with cellulose nitrate. After only a small amount of these nitrogen oxides are formed, the fast hydrolysis of the acetate groups occurs to form acetic acid, which is released above the surface of the sample. The presence of acetic acid in the gas phase would result in a dilution effect in the mixture of oxygen and the reactive gases which would interfere with the oxidation reactions.

Some very interesting information was obtained when the data of Figures 13 and 14 (pp 58 and 59) were fitted into an Arrhenius-type equation.

$$\frac{1}{\theta} = A\,e^{\frac{-E_A}{RT}} \qquad (17)$$

θ time lag to ignition

E_A energy of activation

A frequency factor

$$\text{Log}\ \theta = \frac{E_A}{2.303RT} - \text{Log}\ A \qquad (18)$$

Plots of log θ versus the reciprocal of absolute temperature for cellulose nitrates and cellulose nitrate-acetate mixed esters yield the curves shown in Figures 15 and 16 (pp [illegible] and [illegible]). The straight lines were obtained by the method of least squares. The energies of activation (E_A) and the frequency factors (A) were calculated and the values are given in Table 10 (p 44). According to the data on cellulose nitrate, both the energy of activation and the frequency factor have values proportional to the substitution in nitrate. This is in contradiction to the results reported by Henkin and McGill (Ref 12), who observed that two samples of cellulose nitrate of degrees of substitution of 2.4 and 2.8, respectively, were characterized by the same energy of activation of 26.5 Kcal (Ref 11). However, the magnitude of E_A found in the present work (25–30 Kcal) is comparable to this value of 26.5 and in turn both values are substantially lower than those found in the thermal decomposition of nitrate esters in general which, depending on the nitric ester, ranged from 36 to 40 Kcal/mole. These last values are associated with the energy required for the fission of an O–N bond in agreement with the value of 38 Kcal reported for the dissociation energy of the O–N bond from spectroscopic data. Similarly, the temperature-independent factors (A) observed for the thermal decomposition of nitrate esters are of an order of magnitude (10[illegible] – 10[illegible]) significantly higher than those observed in the present work for cellulose nitrate (10[illegible] – 10[illegible]). Consequently, one would be more justified in regarding the mechanism of decomposition of cellulose nitrate and other nitrate esters under the conditions of the explosion temperature test as proceeding through hydrolysis of the nitrate function rather than by a simple thermal dissociation of the O–N. This view appears well founded when one considers that the activation energy for the hydrolysis of aliphatic nitrate esters ranges between 21 and 28 Kcal/mole (Ref 40).

Examination of Table 10 reveals that the activation energy (E_A) and frequency factor (A) values for the cellulose nitrate-acetate samples have magnitudes comparable to the values obtained with cellulose nitrate and that, except for one sample, the shifts in the E_A and A values for the cellulose nitrate-acetates seem to be functions of the substitution in nitrate groups alone. This is better seen when the energy of activation (E_A) or the frequency factor (A) is plotted versus the substitution in nitrate as shown in Figures 17 and 18 (pp [illegible] and [illegible]). The extrapolated curves for cellulose nitrate in both E_A and A pass very close to the actual values obtained for cellulose nitrate-acetate.

Consequently, aside from the fact that cellulose nitrate-acetate mixed esters decompose without ignition, they offer no advantage over cellulose nitrate of the same degree of substitution in nitrate groups with regard to the explosion temperature.

Heat of Explosion and Residue on Ignition

The heat of explosion and the residue on ignition were determined for a few samples of the cellulose nitrate-acetates. The results of these tests are given in Table 11 (p 45). All samples burned under an inert atmosphere. The lowest value (349.5 cal/g) for ΔH_E corresponds to a sample containing DS 1.1 (NO_2) and DS 1.8 (OAc). The residue on ignition for this sample is evidently too high for it to be considered as a possible candidate for a truly combustible cartridge material. It would appear that cellulose nitrate-acetate mixed esters containing up to one acetate group per anhydroglucose unit could, under gun firing conditions, give clean burning without the formation of excessive smoke.

EXPERIMENTAL PROCEDURES

Nitration of Cellulose Acetate

Cellulose acetate (20 g, 0.075 mole) of 39.8% acetyl content, corresponding to a DS of 2.45, was added to 400 ml of 98.7% (by weight) nitric acid and the mixture was kept at room temperature for sixteen hours with occasional stirring. At the end of this period, the mixture was poured with stirring into 2 liters of water containing cracked ice. The product was isolated by filtration and washed on the filter with distilled water. The product was then boiled for 4 hours in water and for an additional 4 hours in a 0.01 M aqueous sodium carbonate solution, and was then filtered and further washed with distilled water. The product was dried by heating at 55 C for 3 hours under reduced pressure. Analysis: N, 5.58%; CH_3CO, 27.60%. Corresponds to $C_6H_7O_2(NO_3)_{[illegible]}(CH_3CO_2)_{[illegible]}H_{[illegible]}$. This experiment was repeated at the same temperature but with reaction times of 24 and 72 hours.

Acetylation of Cellulose Nitrate

To cellulose nitrate (5.0 g, 0.017 mole, 12.8% nitrogen corresponding to a DS of 2.5) suspended in 150 ml of methylene chloride, 2 ml of acetic anhydride was added and the mixture was agitated for 15 minutes at room temperature. This was followed by the addition of 0.5 ml of 70% perchloric acid and by heating to reflux for [illegible] hours under a nitrogen atmosphere. Evolution of brown fumes was observed during the refluxing period. The product was isolated by filtration, washed on the filter with methylene chloride, air dried, then washed with aqueous sodium carbonate and, finally, with distilled water. After the product was boiled for 4 hours in water followed by 4 hours boil in a 0.01 M aqueous sodium carbonate solution, it was filtered and further washed with distilled water. The product was dried by heating at 55°C for 3 hours under reduced pressure. Analysis: N, 11.24%; CH_3CO, 5.58%. Corresponds to $C_6H_7O_2(NO_2)$[illegible] (CH_3CO)[illegible] H[illegible]. In a number of experiments the following parameters were varied: time of reaction, acetic anhydride content, and perchloric acid content.

X-ray Diffraction Photographs

The X-ray diffraction patterns were obtained from a Philips Electronic Corporation X-ray unit, with Cu target and Ni filter. The powdered samples, mounted in a capillary and rotated, were exposed for 10 hours. The measurements were done following the Debye-Scherer technique.

Viscosity Determination

Reagent-grade acetone was further purified by keeping it overnight over potassium permanganate followed by distillation over calcium sulfate. The distillate was kept over calcium sulfate overnight and then distilled into a dry flask and stored.

Dilute solutions of the samples in acetone (1 gram per liter) were prepared and their viscosity was determined in a Cannon-Ubbelohde viscometer at 25° ± 0.1°C. The relative viscosity value found at this concentration was then entered into the Baker-Philippoff equation (Equation 9) to give intrinsic viscosity.

$$(\eta)_{c \to 0} = \frac{8(\eta_r^{1/8} - 1)}{c} \qquad (9)$$

η_r = relative viscosity

c = concentration, g/liter

Hygroscopicity

The samples had been previously dried at [illegible]°C under a reduced pressure of 0.22 mm. A quantity of these dried samples, approximately 1 gram to the nearest milligram, was weighed in covered weighing bottles and subsequently, placed in a constant temperature ([illegible]°C) and humidity ([illegible] RH) room for various time periods, 0.5, 1, 2, 3, and 4 hours. The gain in weight was then recorded as percent of the original weight.

Tensile Strength Measurements

Preparation of Films

A weighed quantity of each sample was dissolved in reagent grade ethyl acetate to form a 6.7% solution. By means of a variable thickness spreader, the solution was spread on a 16-by-20-inch glass plate which had been previously thoroughly cleaned and made free of dust. The solvent was left evaporating at room temperature overnight. A trickle of water was then poured on the dry film to facilitate its removal from the plate. 1-by-5-inch strips of film were cut with a scaple knife and conditioned for two weeks in a room maintained at 25 C and 50% relative humidity. Only films having thicknesses between 0.001 and 0.0015 inch were used for tensile strength measurements.

The individual strips of film were pulled in a recording Instron tensile tester with a 50-pound scale load and cross-head and chart speeds of 2 inches per minute. The distance between the jaws was kept at 2 inches. Fifteen strips of films were pulled for each sample. Those films which showed evidence of slippage or which broke at the jaws were not included in the results.

Impact Sensitivity

This test was done with a Picatinny Arsenal apparatus on 5-mg quantities of sample for each trial. The procedure is described in detail in Reference 30.

Heat Stability Test (Taliani)

The apparatus and test procedure adopted for determining the rates of decomposition at 110 C are described in Reference 35. The powdered samples (0.100 g) were heated at 110 C in a closed system at constant volume, under an atmosphere of air and in contact with the gaseous decomposition products. Every half hour, the pressure developed in the system was recorded in millimeters. Each sample was run in duplicate. As is mentioned early in this section, the samples had been previously stabilized by boiling for 4 hours with a 0.01 M aqueous solution of sodium carbonate.

Temperature of Explosion

This procedure is described in detail in Reference 30. Ten hollow copper cylinders (No. 8 commercial blasting caps) were loaded with 0.005 g of powdered sample each and the samples were compacted gently. The loaded caps were then immersed in a metal bath, and the temperature and time of immersion required to cause each to flash or explode was recorded. The apparatus consisted of a multiple-unit electric furnace, equipped with a rheostat to control the temperature and a calibrated thermocouple immersed in the molten metal bath. The bath itself consisted of 75 cc of an alloy (mp, 65.5 C) of the following composition: 50% bismuth, 25% lead, 12.5% tin, and 12.5% cadmium.

Heat of Explosion and Residue on Ignition

These determinations were done on 3.0-g samples using a regular Parr Calorimetric stainless steel bomb of 350 ml capacity. The samples were exploded under helium at a pressure of thirty atmospheres.

Nitrate and Acetate Determination

An analytical procedure based on infrared spectroscopy was developed for the quantitative determination of nitrate and acetate groupings in cellulose nitrate-acetates. Accurate weights of the samples, previously dried under vacuum, were dissolved in spectro-grade tetrahydrofuran to make an approximately 0.5% solution. The determinations were done on a Perkins-Elmer Double Beam Model 21 spectrophotometer equipped with sodium chloride optics. The solutions were transferred into calibrated cells with lead spacers and compensated with pure solvent in the reference beam. The peak heights for the absorption bands at 6.1μ (1640 cm^{-1}) and 5.7μ (1755 cm^{-1}) were measured and, from comparisons with standard curves established with cellulose nitrate and cellulose acetate, the concentrations were calculated. The concentrations expressed as percent NO_2 and percent CH_3CO can be converted to degree of substitution by means of the simple relation

$$DS\,(NO_2) \quad \frac{X/46}{R/159} \qquad (19)$$

$$DS\,(CH_3CO) \quad \frac{Y/43}{R/159}$$

X percent by weight of nitro group in sample

Y percent by weight of acetyl group in sample

R percent by weight of residue $C_6H_7O_5$ in sample

R 100 - X - Y

Although in this approximate equation the residual hydrogens in the unsubstituted OH functions are not considered, the maximum relative error is found to be less than 2% in the calculated DS values.

The nitrate determinations were also done by the ferrous-titanous titrimetric method described in Reference 40.

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TABLE 1

Acetylation of 5.0 g Cellulose Nitrate, 12.3% Nitrogen (DS 2.3)
Solvent: Methylene Chloride (Reflux)

	Acetic Anhydride, g		Perchloric	Time,	Substitution		
Sample	Added	Stoichiometry*	Acid, ml	Hours	Nitrate	Acetate	Total
1	1.0	1.6	0.20	0.5	2.3	0.3	2.6
2	1.0	1.6	0.20	1	2.3	0.4	2.7
3	1.0	1.5	0.08	6	2.2	0.4	2.6
4	1.0	1.4	0.04	10	2.3	0.4	2.7
5	1.0	1.5	0.08	16	2.2	0.5	2.7
6	2.0	1.6	0.20	20	2.2	0.8	3.0
7	2.5	1.5	0.10	6	2.2	0.8	3.0
8	2.5	1.5	0.10	16	2.0	1.0	3.0
9	20.0	3.3	1.00	1	0.8	2.2	3.0
10	1.0	1.3	None	6	2.3	None	2.3
11	1.0	1.3	None	20	2.3	None	2.3
12	None	1.6	0.20	16	1.8	None	1.8

---

*Milliliters of acetic anhydride calculated for complete reaction with the hydroxyl function and the water present in perchloric acid

TABLE 2

Acetylation of 5.0 g Cellulose Nitrate, 13.1% Nitrogen (DS 2.6)
Solvent: Methylene Chloride (Reflux)

Sample	Acetic Anhydride		Perchloric Acid, ml	Time, Hours	Substitution		
	Added	Stoichiometry*			Nitrate	Acetate	Total
13	2.0	1.0	0.20	1	2.4	0.6	3.0
14	2.0	1.0	0.20	2	2.2	0.6	2.8
15	2.0	1.0	0.20	3	2.2	0.5	2.7
16	2.0	1.0	0.20	4	2.4	0.5	2.9
17	2.0	1.0	0.20	5	2.4	0.6	3.0
18	2.0	1.0	0.20	6	2.5	0.5	3.0
19	2.0	1.0	0.20	7	2.3	0.5	2.8
20	2.0	1.0	0.20	9	2.4	0.6	3.0
21	2.0	1.0	0.20	11	2.3	0.6	2.9
22	2.0	1.0	0.20	12	2.4	0.6	3.0
23	20.0	1.0	0.20	1	2.4	0.5	2.9
24	20.0	2.7	1.30	1	0.8	2.2	3.0
25**	20.0	2.7	1.30	1	0.6	2.4	3.0
26	20.0	2.7	None	1	2.1	None	2.1
27	None	1.0	0.20	1	2.2	None	2.2
28	None	2.7	1.30	1	1.4	None	1.4

---

*Milliliters of acetic anhydride calculated for complete reaction with the hydroxyl function and the water present in perchloric acid.

**Chloroform was used as solvent for this experiment (reflux).

TABLE 3

Nitration of Cellulose Acetate (DS 2.5) at Room Temperature

Sample	Reaction Time, Hours	Substitution		
		Nitrate	Acetate	Total
29	16	1.1	1.6	2.7
30	16	1.1	1.7	2.8
31	16	1.1	1.8	2.9
32	24	1.4	1.5	2.9
33	72	2.2	0.7	2.9

TABLE 4

X-ray Diffraction Study

	d(A)*	Intensity
Cellulose	9.30	W broad
	5.80	M
	5.18	M
	4.30	M
	3.80	VVS
	2.57	M
Cellulose Acetate (DS 2.45)	9.11 (Halo)	M
	5.15	M
	3.83 (Halo)	M
	3.76	M
Cellulose Nitrate (DS 2.1)	9.93	W broad
	6.50	VVS broad
	3.86	M broad
	3.41	M
	2.96	W sharp
Cellulose Nitrate (DS 2.3)	11.48	W broad
	6.46	VVS broad
	3.85	M broad
	3.24	M broad
	2.98	W sharp
Cellulose Nitrate (DS 2.8)	11.47	W broad
	6.52	VVS broad
	3.86	M broad
	3.69	W sharp
	3.40	M broad
	2.97	W sharp
Cellulose Nitrate-Acetate (DS 2.2)-(DS 0.4)	6.41	VVS broad
	3.20	M broad
	2.96	W sharp
Cellulose Nitrate-Acetate (DS 1.8)-(DS 1.0)	9.11 (Halo)	M
	3.80 (Halo)	M
Cellulose Nitrate-Acetate (DS 1.1)-(DS 1.9)	9.05 (Halo)	M
	3.80 (Halo)	M

---

*d(A) Spacing

TABLE 5

Degree of Polymerization of Cellulose Nitrate-Acetate Mixed Esters

Experiment	Procedure	Acetic Anhydride	Perchloric Acid	Time, hours	Substitution			Intrinsic Viscosity, g l.	Degree of Polymerization
					Nitrate	Acetate	Total		
1	Acetylation of cellulose nitrate	1	0.20	0.5	2.3	0.3	2.6	0.294	250
2		1	0.04	10	2.3	0.4	2.7	0.288	[illegible]
3		1	0.20	20	1.7	0.3	2.0	0.162	
4		20	0.20	1	2.4	0.5	2.9	0.286	180
5		20	1.30	1	0.8	2.2	3.0	0.003	[illegible]
6		20	1.30	1	0.6	2.4	3.0	0.003	[illegible]
7		20	None	1	2.1	None	2.1	0.286	200
8		None	0.20	1	2.2	None	2.2	0.208	[illegible]
9		None	1.30	1	1.4	None	1.4	0.176	–
10	Nitration of cellulose acetate	–	–	16	1.1	1.6	2.7	0.069	80
11		–	–	24	1.4	1.5	2.9	0.043	40
12		–	–	72	2.2	0.7	2.9	0.020	15
13	Cellulose nitrate				2.3	–	2.3	0.250	230
14	Cellulose nitrate				2.6	–	2.6	0.327	240
15	Cellulose acetate				–	2.5	2.5	0.138	340

TABLE 6

Rate of Depolymerization During Nitration of Cellulose Acetate by Nitric Acid

Period	Time, Hours	Rate Constant, k, Hrs^{-1}
0 – 16	16	$6.2 \cdot 10^{-\text{[illegible]}}$
16 – 24	8	$1.2 \cdot 10^{-\text{[illegible]}}$
24 – 72	48	$1.6 \cdot 10^{-\text{[illegible]}}$

$$k = \frac{2.303}{t} \log \frac{a}{a - x}$$

a = DP at beginning of period

a – x = DP at end of period

t = time in hours

TABLE 7

Tensile Strength and Elongation of Cellulose Nitrate-Acetate Mixed Esters

Procedure	Substitution			Tensile Strength, psi	% Deviation	% Elongation
	Nitrate	Acetate	Total			
Acetylation of cellulose nitrate	2.3	0.2	2.5	15,660	2.0	3.0
"	1.7	0.3	2.0	15,630	2.1	5.5
"	2.3	0.4	2.7	14,160	0.6	5.5
	2.2	0.8	3.0	11,700	2.1	4.0
	2.1	0.9	3.0	10,850	3.0	5.0
Nitration of cellulose acetate	1.1	1.8	2.9	1,340	–	–
"	1.0	1.4	2.4	–	–	–
"	1.9	0.7	2.6	–	–	–
Cellulose nitrate	2.3	–	2.3	11,950	25.3	7.0

TABLE 8

Impact Sensitivity of Cellulose Nitrate-Acetate Mixed Esters

Degree of Substitution		Impact Sensitivity, in. 2kg
Nitrate	Acetate	
2.3	0.2	6
2.2	0.7	10
2.2	0.8	10
2.1	0.9	10
1.8	0.9	14
1.7	0.3	11
1.4	1.5	16
1.1	1.6	18

TABLE 9

Heat Stability of Cellulose Nitrate-Acetate Mixed Esters (Taliani Test, 110 C)

Procedure	Reaction Time, hours	Sample No.*	Substitution			End Point, minutes
			Nitrate	Acetate	Total	
Acetylation of cellulose nitrate	0.5	1	2.2	0.4	2.6	400
"	6	2	2.2	0.4	2.6	150
"	10	3	2.2	0.3	2.5	120
"	16	4	2.2	0.8	3.0	155
	20	5	1.7	0.3	2.0	140
Cellulose nitrate	(No Na_2CO_3 treatment)	6	2.3	–	2.3	340
"	"	6A	2.3	–	2.3	120
Nitration of cellulose acetate	16	7	1.1	1.8	2.9	295
"	24	8	1.0	1.4	2.4	400
"	72	9	1.9	0.7	2.6	150

---

*Corresponding to the numbers in Figures 11 and 12 (pp 56 and 57).

TABLE 10

Energy of Activation and Frequency Factor for Cellulose Nitrate and Celluiose Nitrate-Acetate

Substitution		E_A,	A,
Nitrate	Acetate	Kcal	sec^{-1}
2.8	–	29.4	$1 \cdot 10^{12}$
2.3	–	26.2	$5 \cdot 10^{1}$
2.1	–	25.0	$2 \cdot 10^{10}$
2.4	0.4	27.8	$3 \cdot 10^{12}$
2.1	0.9	23.4	$3 \cdot 10^{9}$
2.0	0.9	29.0	$8 \cdot 10^{11}$
1.1	1.8	17.9	$1 \cdot 10^{7}$

TABLE 11

Heat of Explosion and Residue on Ignition

Procedure	Reaction Temperature, °C	Reaction Time, hours	Substitution			Heat of Explosion, ΔH_E, cal gram	Residue, mg per g sample	Ash, mg per g sample
			Nitrate	Acetate	Total			
Acetylation of cellulose nitrate	25	16	2.0	0.3	2.3	767.7	2.18	0.29
"	40	0.5	2.3	0.3	2.6	739.3	1.03	0.61
"	40	6	1.7	0.8	2.5	644.2	2.21	None
"	40	16	1.8	1.0	2.8	604.2	10.05	0.44
"	40	20	1.7	0.3	2.0	753.7	1.72	0.21
Nitration of cellulose acetate	25	16	1.1	1.7	2.8	349.5	197.7	1.57
Cellulose nitrate	–	–	2.3	–	2.3	855	–	–

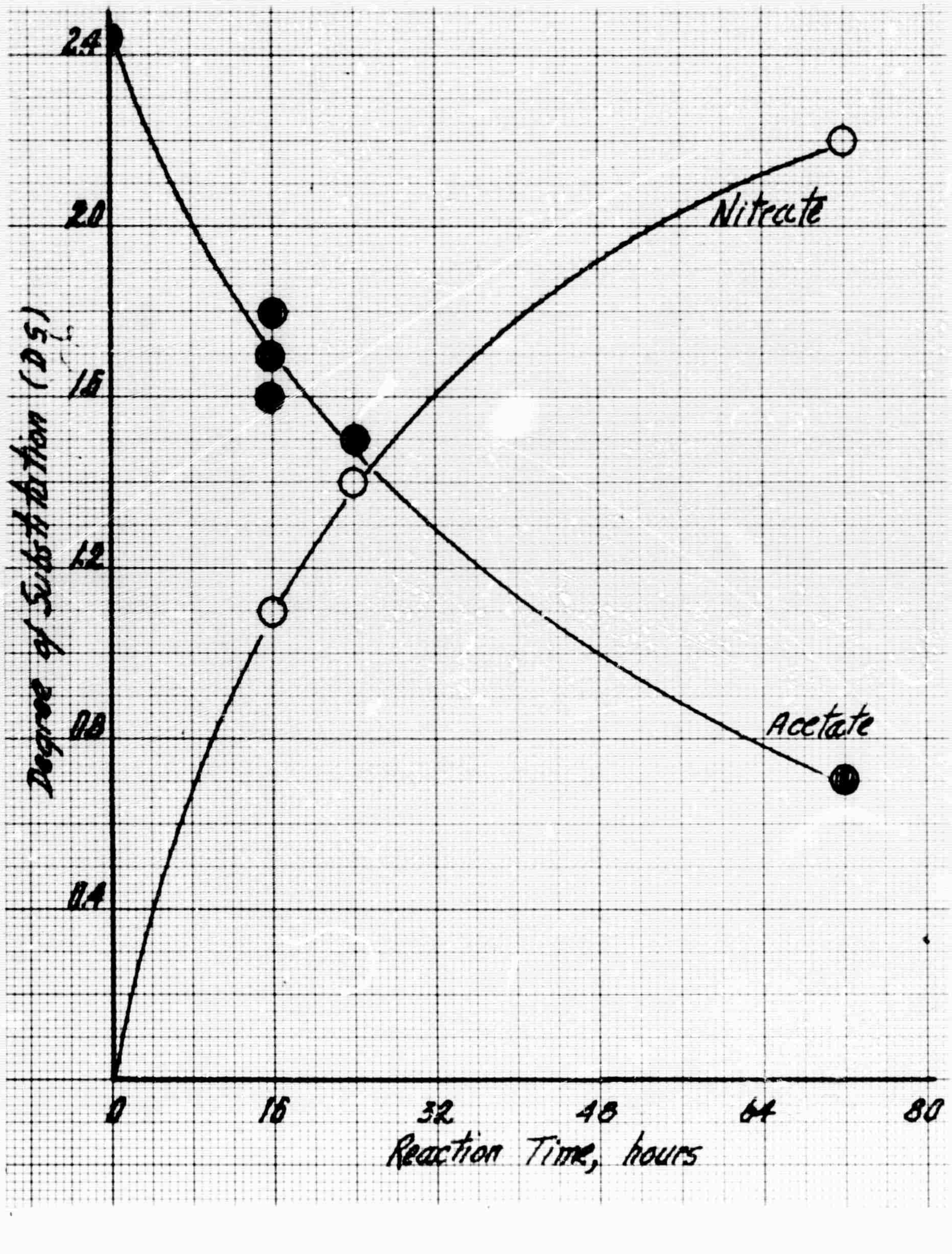
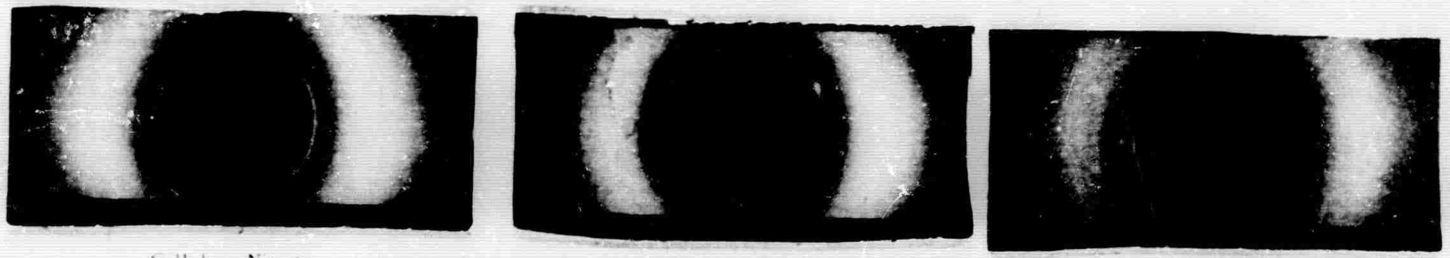


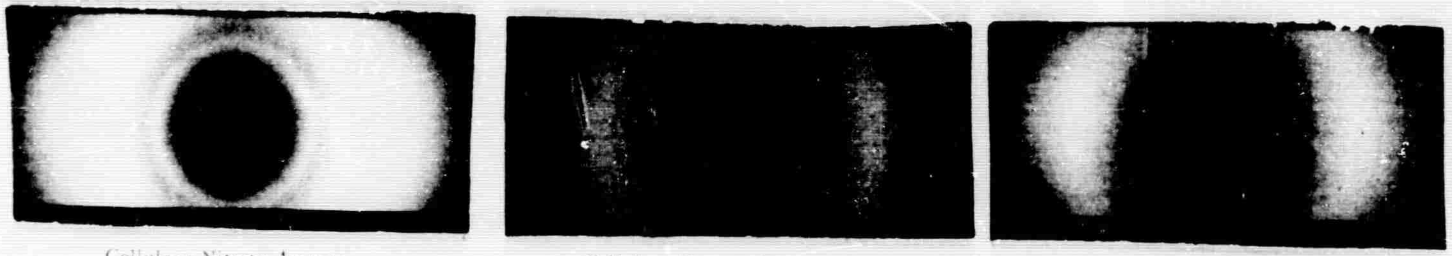
Fig 1   Nitration of cellulose acetate at 25°C



Cellulose Nitrate
DS 2.1

Cellulose Nitrate
DS 2.3

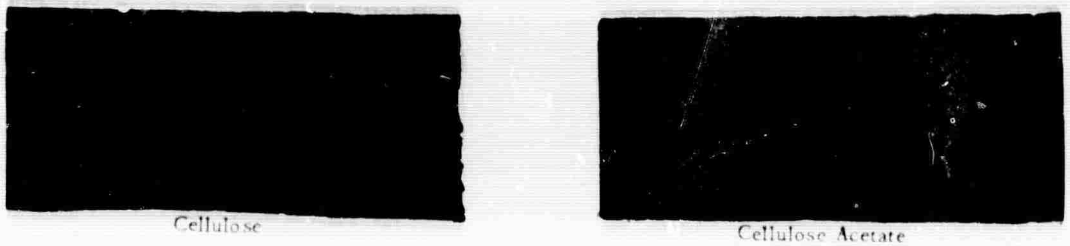
Cellulose Nitrate
DS 2.8



Cellulose Nitrate-Acetate
DS: 2.2 0.4

Cellulose Nitrate-Acetate
DS: 1.8 1.0

Cellulose Nitrate-Acetate
DS: 1.1 1.6

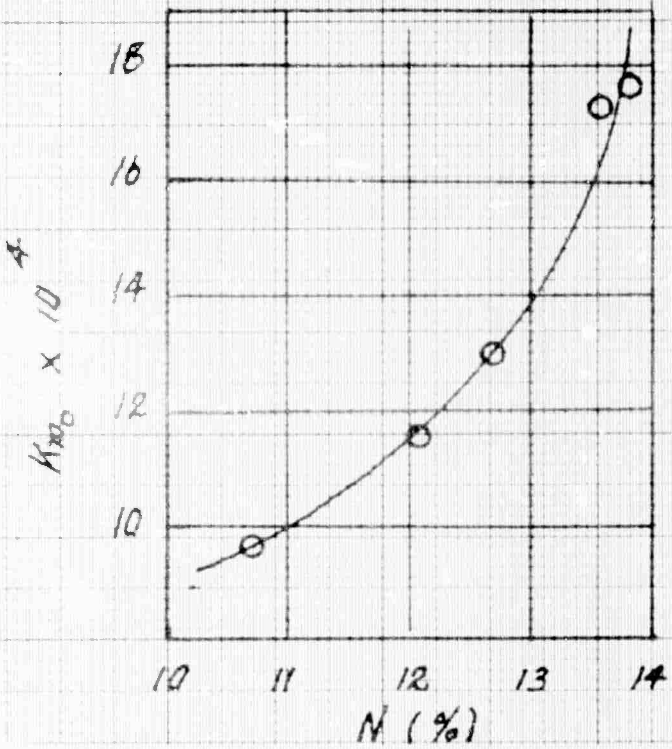


Cellulose

Cellulose Acetate
DS 2.5

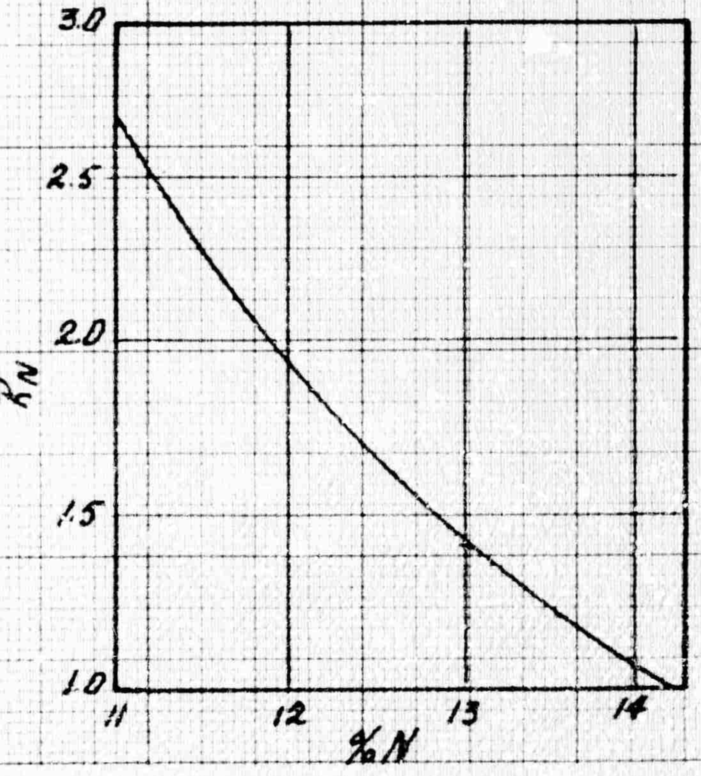
Fig 2 Debye-Scherer diffraction patterns

½ frame



From the data of Wannow.
Kolloid Z., 102, 29 (1943)
Ref. Miles, p.359

Fig 3 Relation of K_{m_o} to nitrogen content



From the data of Lindsley + Frank, Ind. + Eng. Chemistry, 45, 2491-97 (1953).

Fig 4 Relation of R_N to nitrogen content

½ frame →

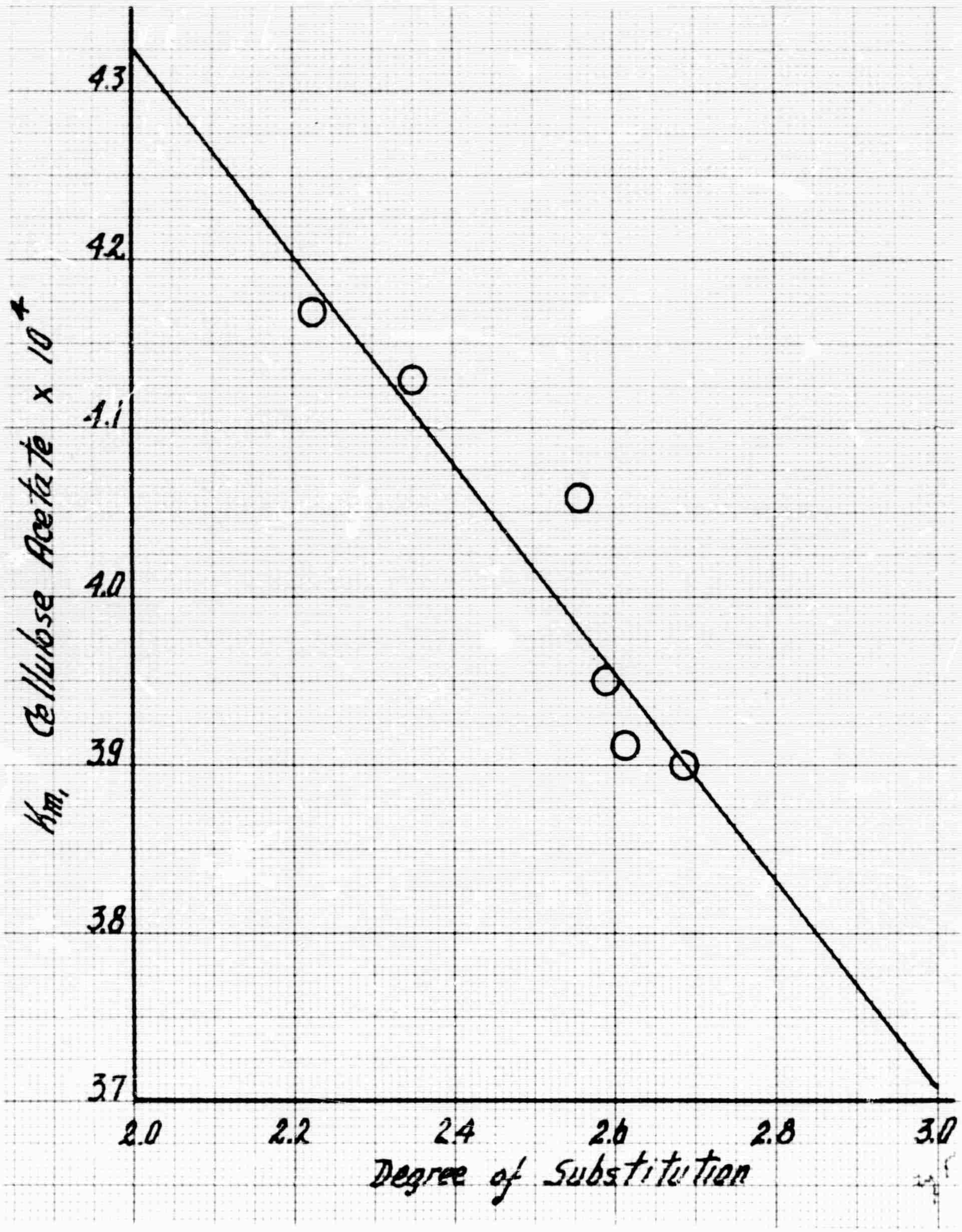


Fig 5   Cellulose acetate K_m values in acetone vs degree of substitution (From the data of F. Howlett, *J. Textile Inst.* 35, T133 (1944))

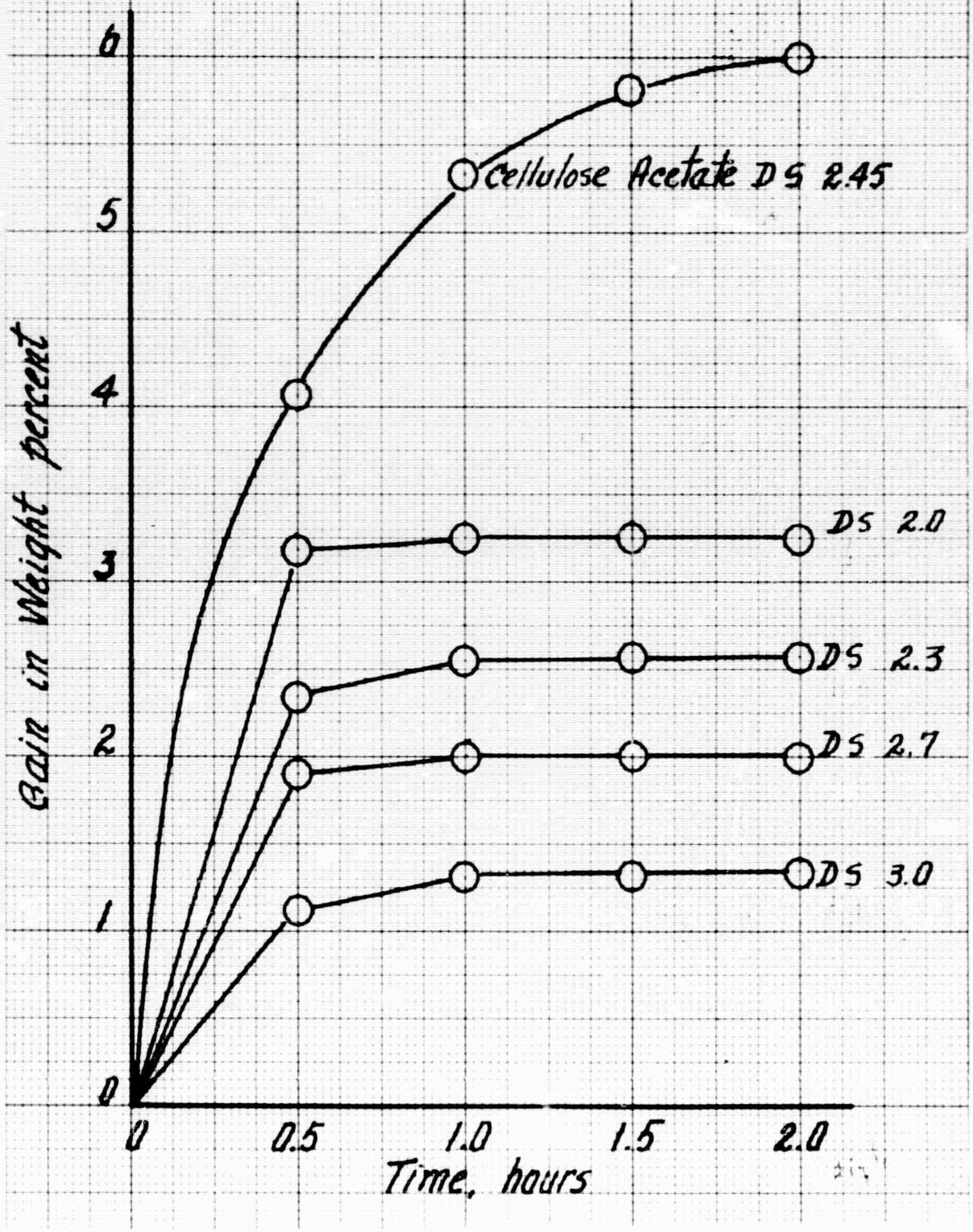


Fig 6 Rate of water absorption

½ frame

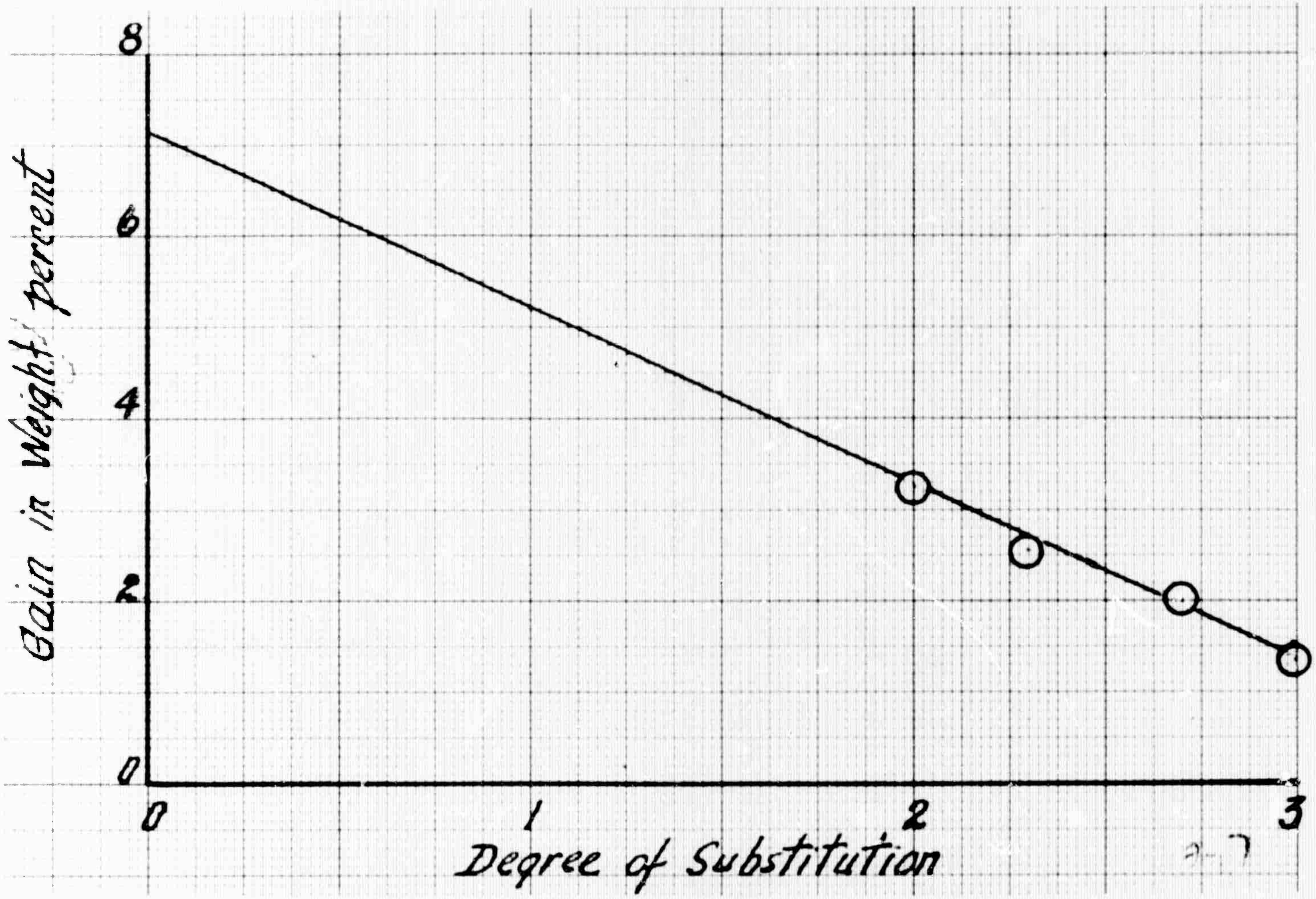


Fig 7 Hygroscopicity vs degree of substitution, total

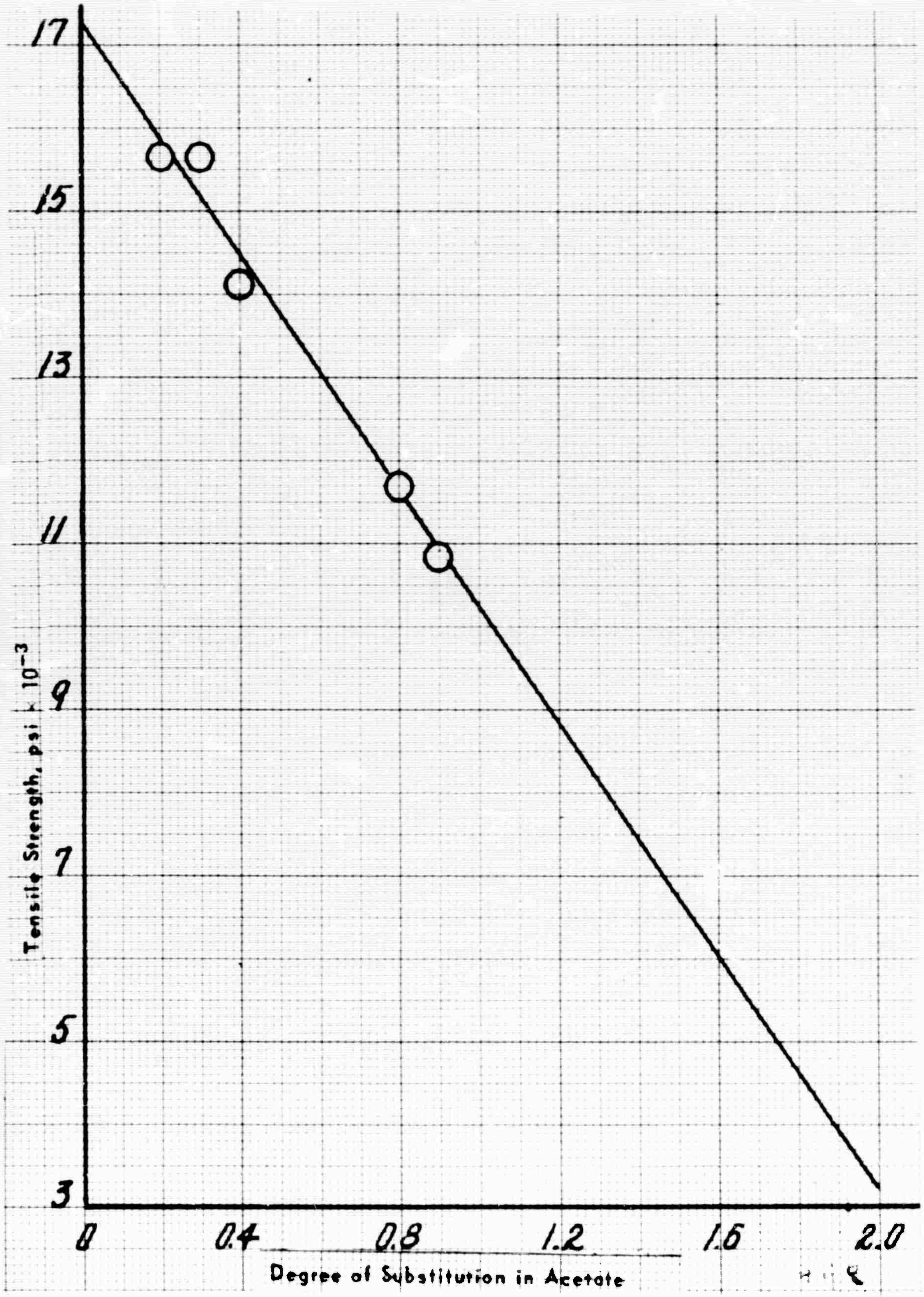


Fig 8 Tensile strength versus acetate substitution

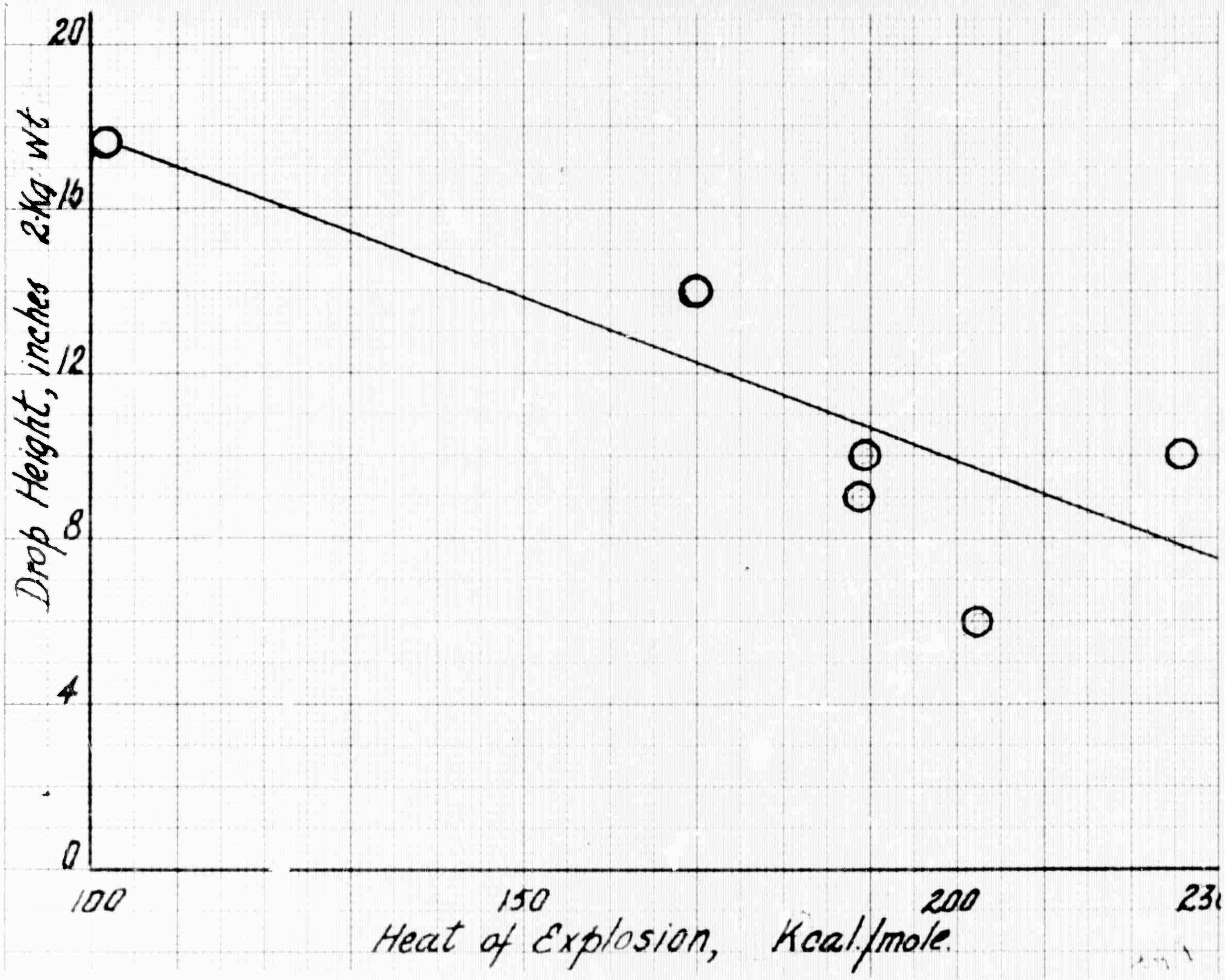


Fig 9 Impact sensitivity vs heat of explosion

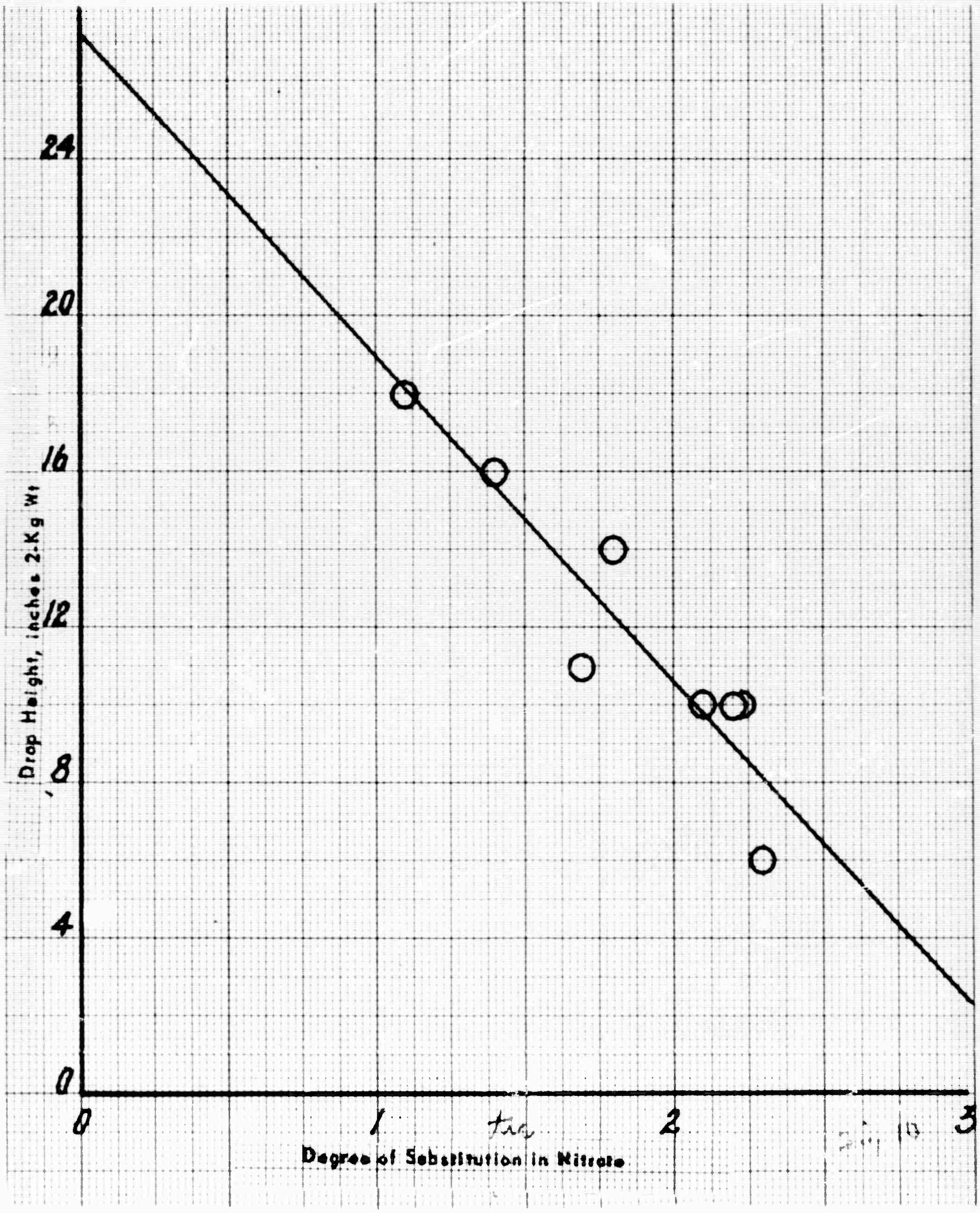


Fig 10 Impact sensitivity vs DS in nitrate

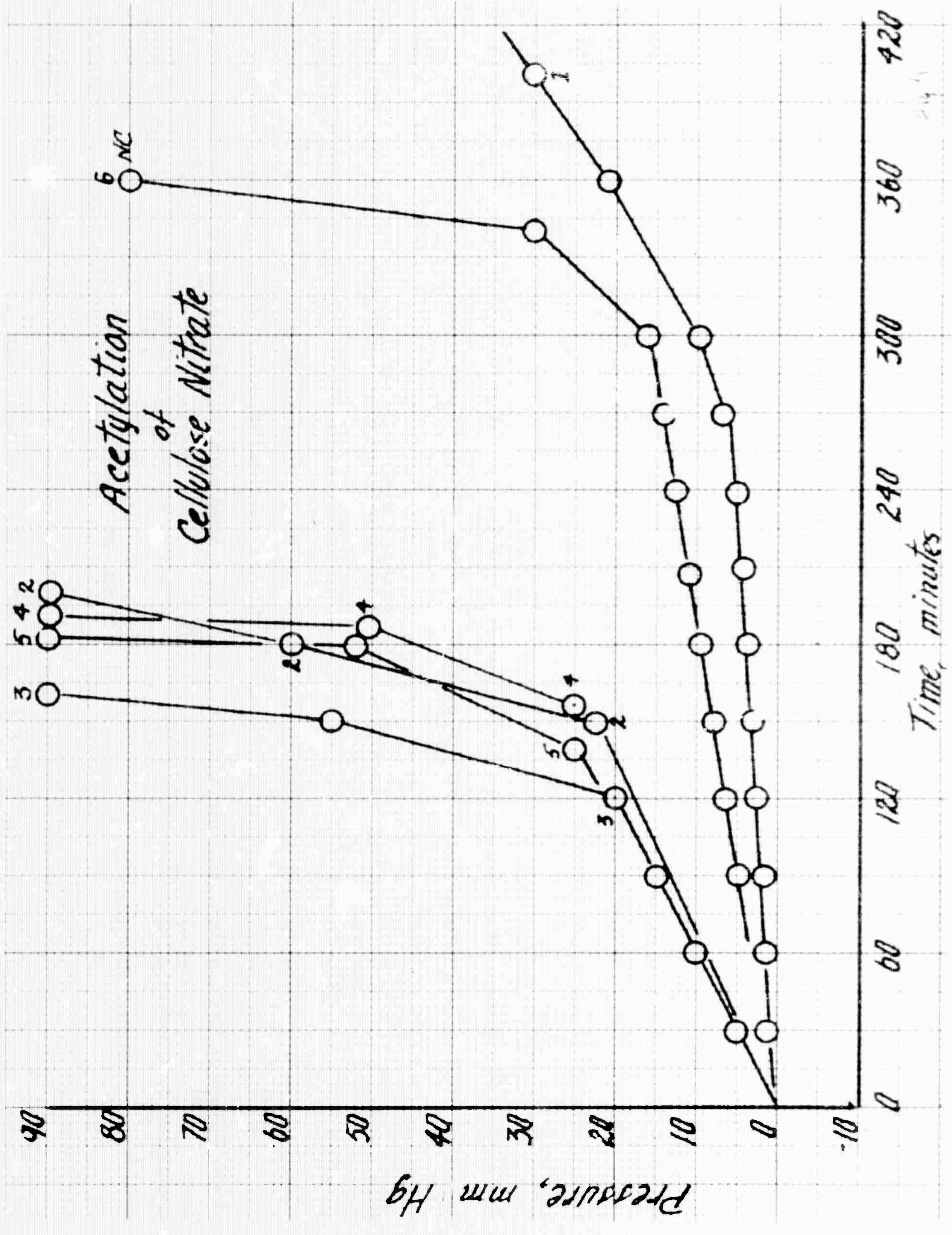


Fig 11   Heat stability of cellulose nitrate-acetates (Taliani)

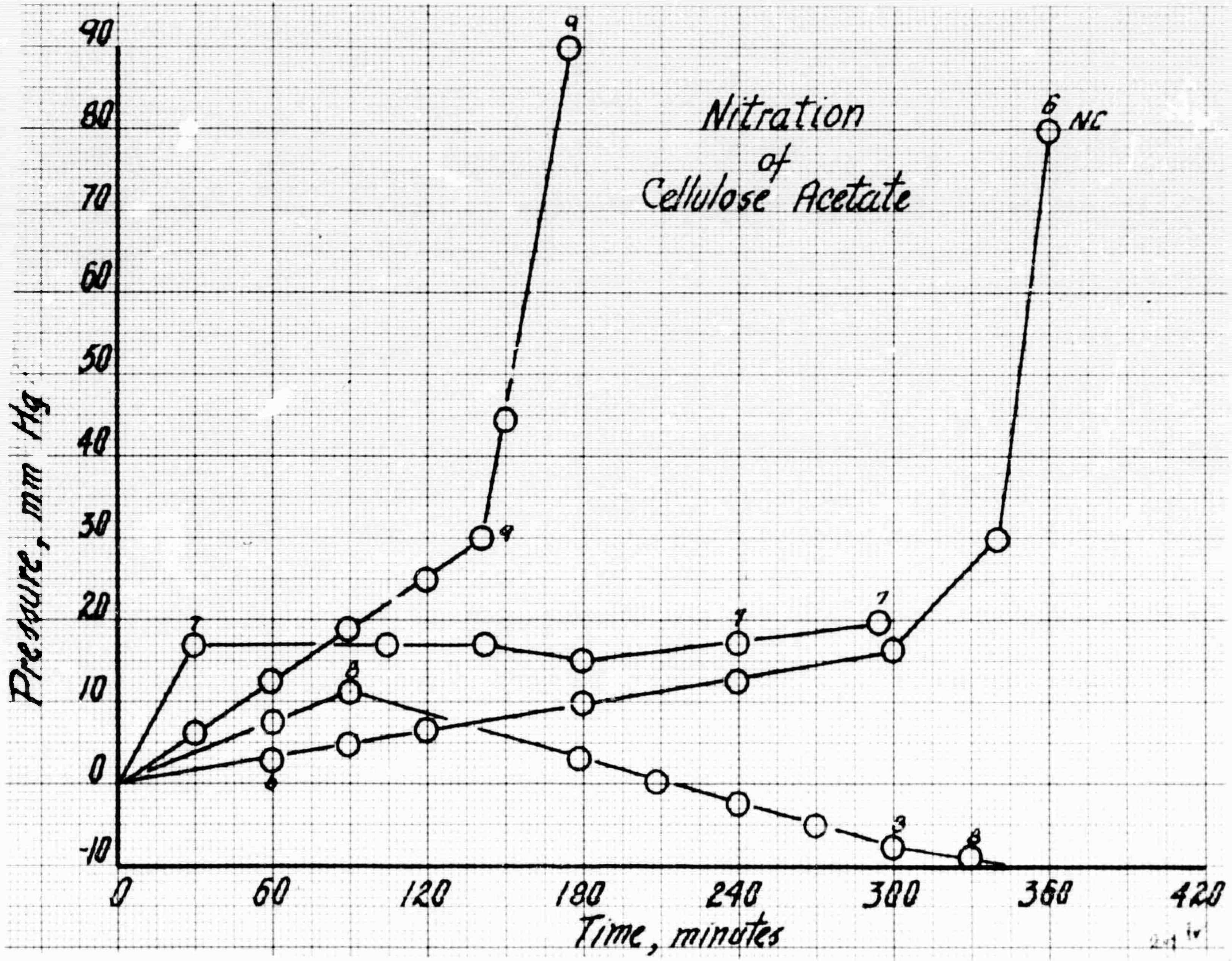


Fig 12 Heat stability of cellulose nitrate-acetates (Taliani)

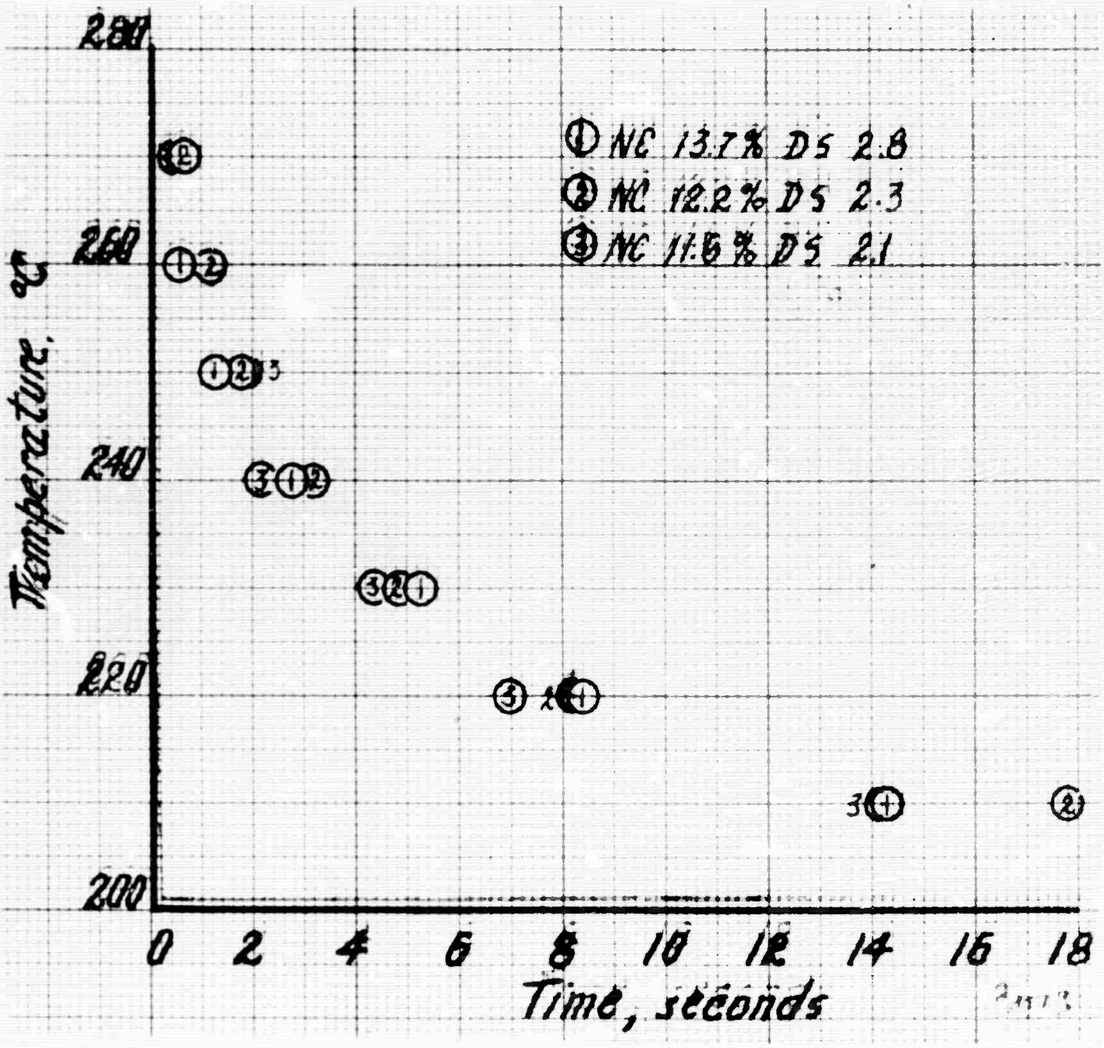


Fig 13 Explosion temperature of cellulose nitrates

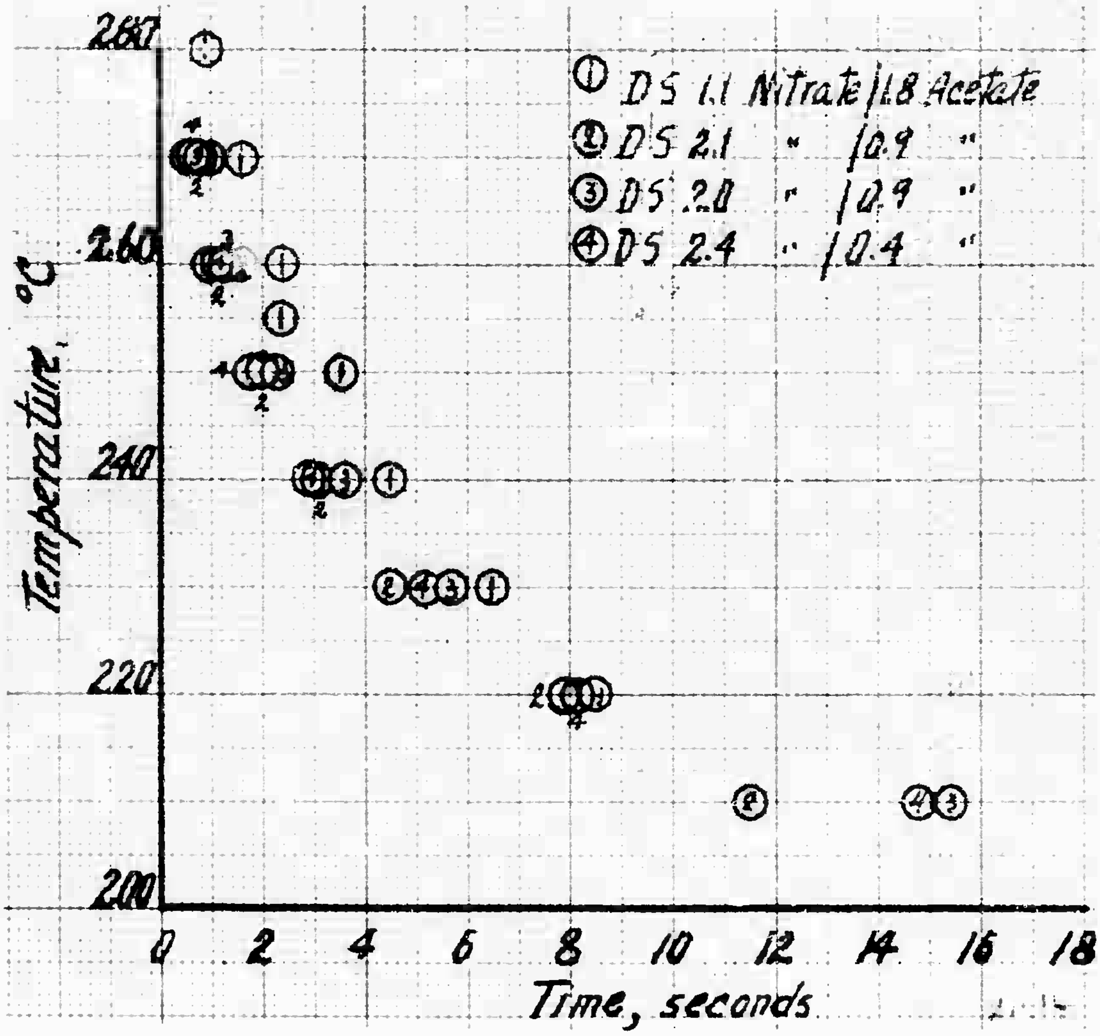


Fig 14   Explosion temperature of cellulose nitrate-acetates

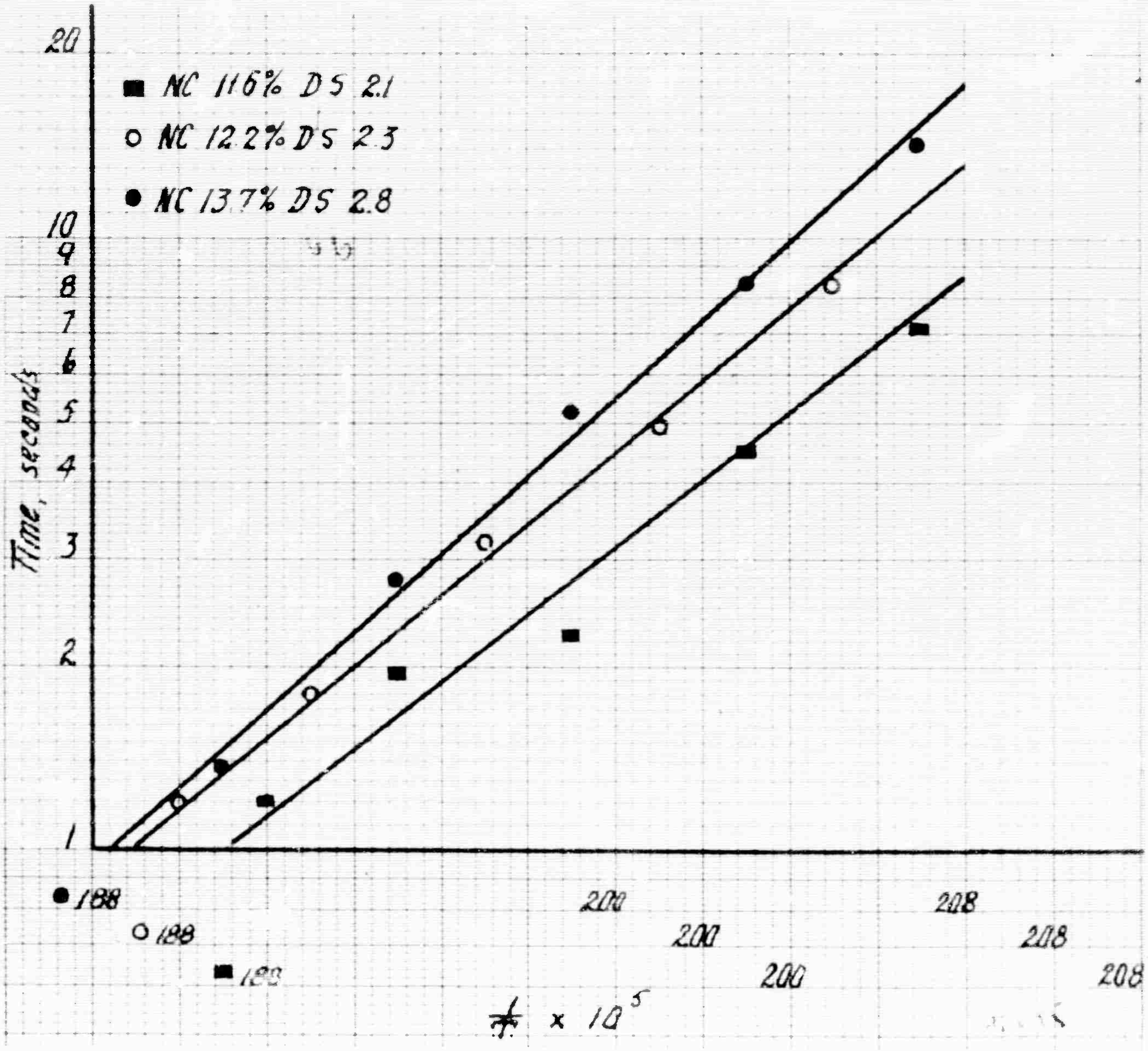


Fig 15 Rates of decomposition for cellulose nitrates

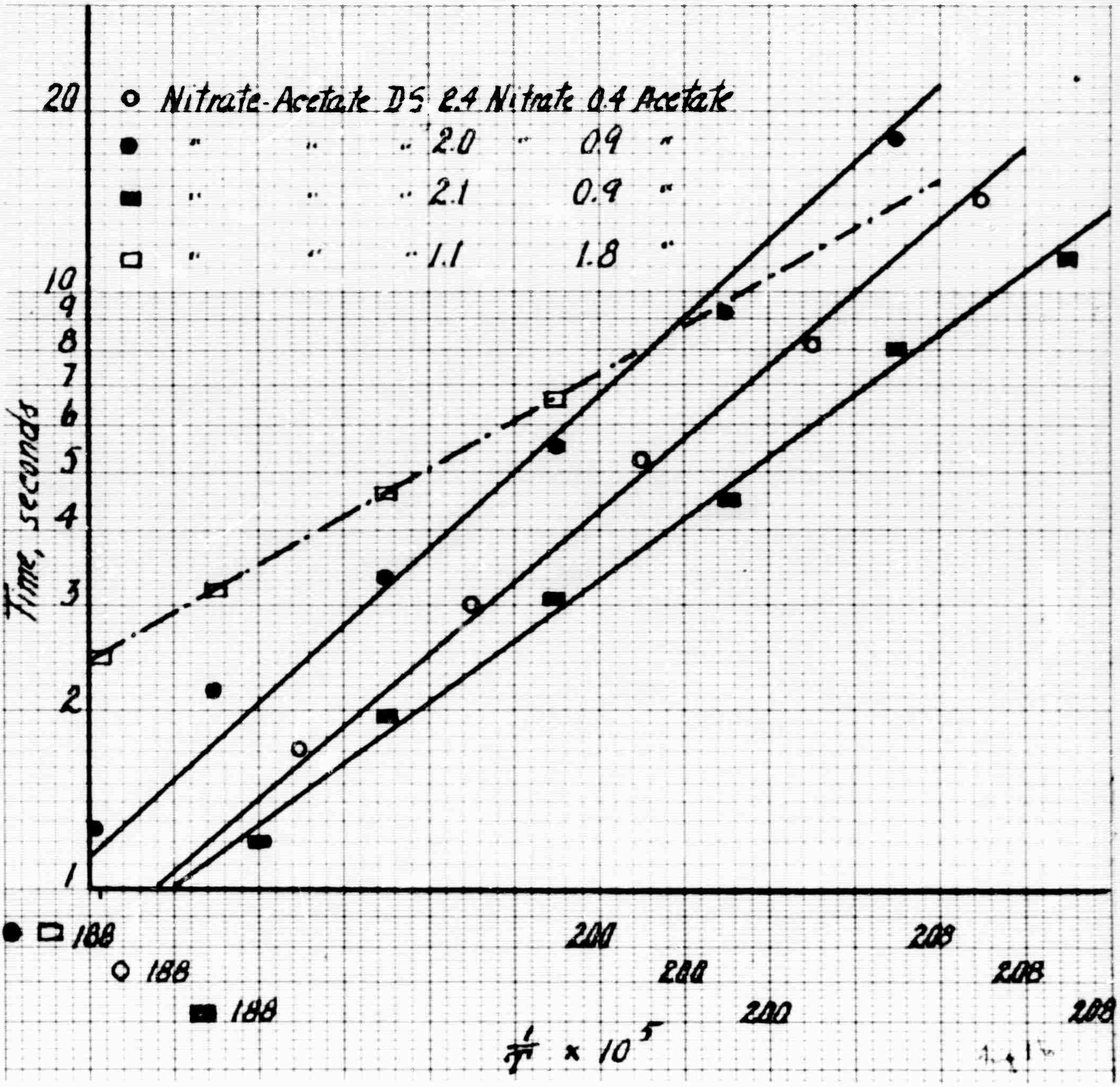


Fig 16 Rates of decomposition for cellulose nitrate-acetates

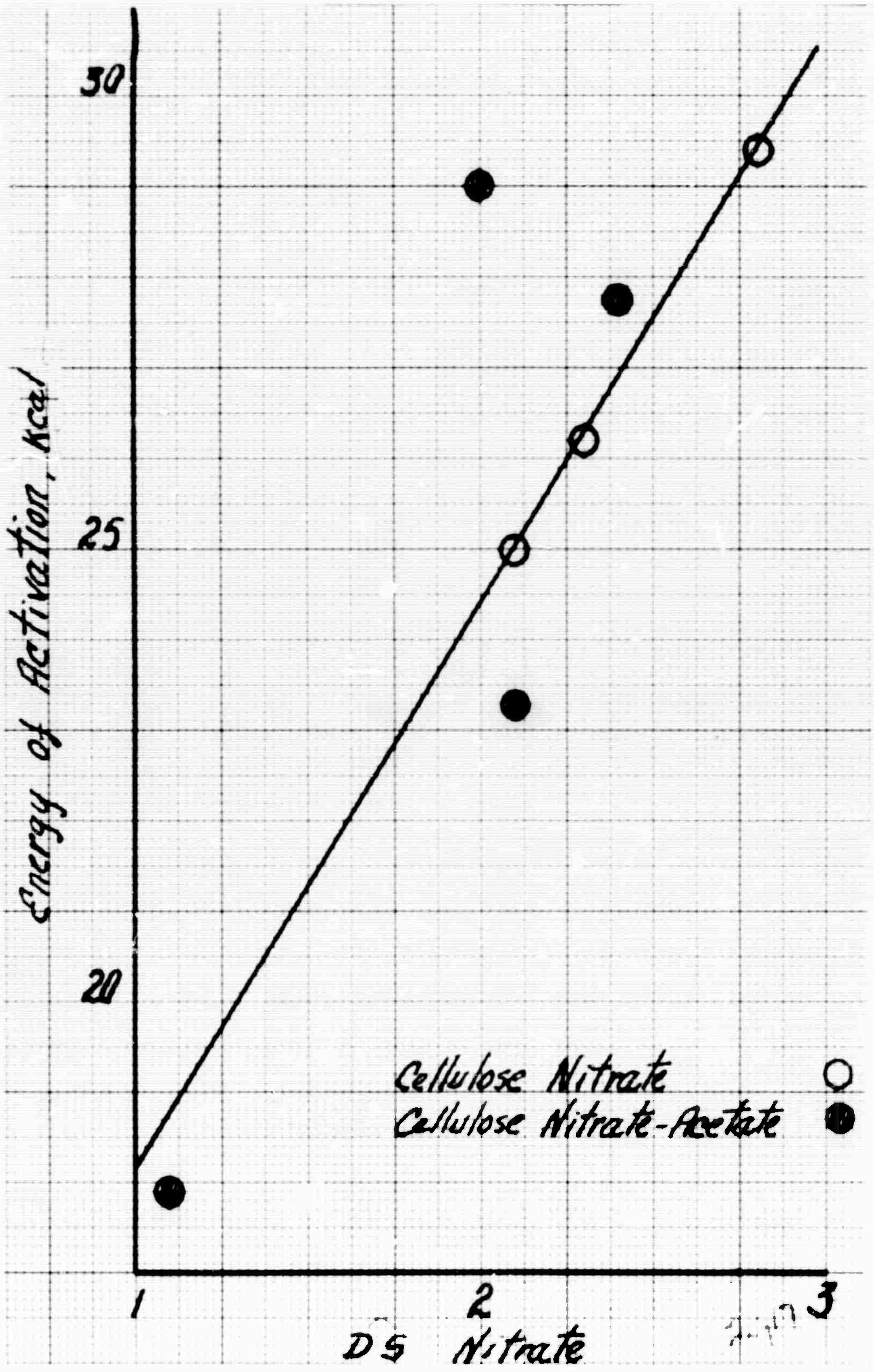


Fig 17 Energy of activation versus nitrate substitution

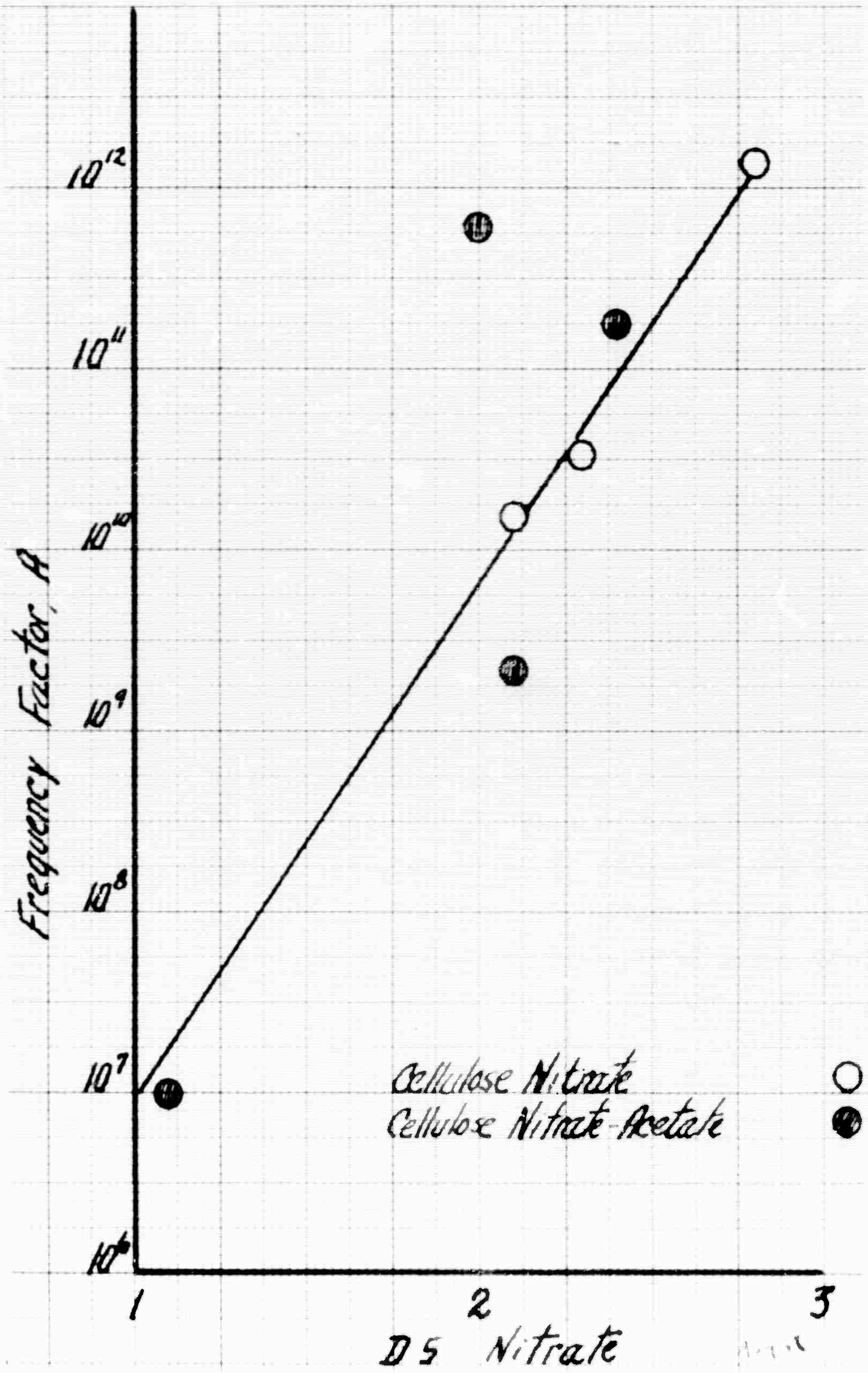


Fig 18   Frequency factor versus nitrate substitution