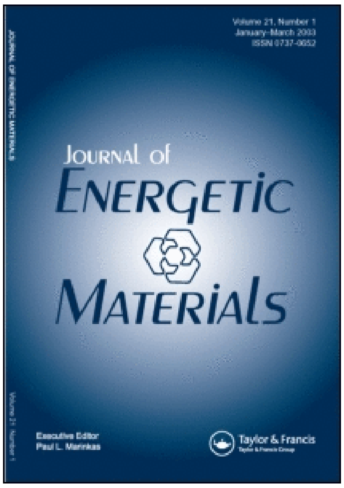

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A review of the synthesis, chemistry and analysis of nitrocellulose

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A REVIEW OF THE SYNTHESIS, CHEMISTRY AND ANALYSIS OF NITROCELLULOSE

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ABSTRACT

Recent avenues of research have improved our understanding of the chemistry of nitrocellulose. With this in mind, a brief review of the chemistry of nitrocellulose is presented. While not comprehensive in nature, this review does point out some of the underlying characteristics of nitrocellulose which are of interest to the propellant community.

INTRODUCTION

Nitrocellulose was the first chemical derivative of cellulose prepared in the lab[1,2,3]. In 1832 Braconnot subjected crude cellulose to treatment with concentrated nitric acid, obtaining a highly degraded and unstable product. Credit for the discovery of nitrocellulose is often given to C. F. Schonbein, who in 1846 produced a stable form of the product using a mixture of nitric and sulfuric acids. Variations of his technique are still used to produce nitrocellulose commercially. Other important years in the history of nitrocellulose (from 3):

1855 - George Audemars first pulls a nitrocellulose filament from an ether/alcohol solution.

1868 - John W. Hyatt produces the first plastic, combining nitrocellulose with camphor under heat and pressure to produce celluloid.

1883 - Sir Joseph Swan patents a process for extruding nitrocellulose into filaments.

Nitrocellulose is the nitrate ester of cellulose, a naturally occurring polymer composed of β-1,4-anhydroglucose units. The name nitrocellulose is a misnomer, for it implies a NO_2

functionality with the nitrogen attached directly to the carbon. It is, in fact, an ester containing nitrato groups with an oxygen bridge between the carbon in the polymer backbone and the nitrogen of the nitrate. The term nitrocellulose is so heavily ingrained in the literature and vernacular of the industry that it likely will remain.

Nitrocellulose is the only inorganic ester of cellulose produced which has proven to be of commercial significance[1,2]. For years, it was used as a base for photographic and X-ray films, but in these applications it has been replaced by cellulose acetate and other polyesters which are less flammable. The largest industrial use of nitrocellulose today is in protective and decorative coatings. These are mostly automobile surface-primer coatings and refinishing lacquers, and clear top coat finishes for wood furniture. The automotive finishes typically contain 4% to 6% nitrocellulose, while a typical wood lacquer contains 12%. The nitrocellulose used in these industrial applications contain 11.8% to 12.2% nitrogen by weight. The types and classification of nitrocelluloses are discussed in more detail later in this paper.

The oldest and presently second largest application of nitrocellulose is the field of explosives and propellants[1,4,5]. The manufacture of nitrocellulose containing propellants dates back to 1896. In the United States, cotton linters are the sole source of cellulose used for production of nitrocellulose for rocket propellant manufacture, while wood pulp can also be used as a cellulose source for gun propellant manufacture. There have been several studies on the effect of the origin of the cellulose on the nitration process, which will be covered in more detail later. The nitrocellulose used in propellants has a higher nitrogen content than lacquer grade material, being 12.2% to 13.5% nitrogen. Propellants containing just nitrocellulose as the polymeric binder have been historically known as single base propellants. Those which combine the nitrocellulose with nitroglycerine, in which it dissolves, are known as double-base propellants. An early problem in the propellant manufacture of nitrocellulose was its having a much more rapid burning rate than black powder, which it replaced. This is now controlled through the addition of burning rate modifiers such as lead-β-resorcylate and lead and copper salicylates. Recent studies in propellant processing have focused upon the molecular weight distribution of nitrocellulose and how it impacts propellant performance. The remainder of this paper will focus on the known chemistry of nitrocellulose, and how that chemistry may affect its applications in industry.

A more recent industrial application of nitrocellulose is in the field of high energy particle detectors[1]. Nitrocellulose films are presently the most sensitive detectors of neutrons, charged particles and fission fragments using the track etching technique. A 10 micron film of nitrocellulose is supported on a polyester or polycarbonate base. When exposed to high-energy particles, latent tracks are created in the film. Visualization of the tracks is carried out by aqueous etching with potassium or sodium hydroxide.

CHEMISTRY OF NITROCELLULOSE

Structure and Properties

To understand the structure of nitrocellulose, it is helpful to look first at the structure of cellulose, the parent compound. Cellulose is a naturally occurring polymer of glucose, linked through β-1,4-glucoside bonds[6]. Its structure can be represented as in Figure 1. A single molecule of cellulose has been estimated to contain 100-200 anhydroglucose units, which represents a molecular weight of from 20,000-40,000 daltons. Neglecting chain ends, each glucose unit within the polymer chain has three hydroxyl groups which are available for esterification. This provides eight possible substitution patterns, illustrated in Figure 2 with nitrate groups. The relative rate of reaction at each hydroxyl is different, and is discussed in detail later in this chapter.

Raw cellulose can be divided into three types: alpha, beta and gamma, based upon their respective solubilities in an 18% aqueous solution of sodium hydroxide[7]. Alpha cellulose, considered to be true cellulose, is insoluble in this solution; while, both the beta and gamma forms will dissolve. The beta form can be reprecipitated by treating the alkaline solution with acetic acid. Beta cellulose is composed of hydrocellulose and oxycellulose, which have shorter chain lengths than alpha cellulose. Gamma cellulose, which remains in the caustic solution upon treatment with acetic acid, is composed of hemicellulose, which consists of pentose's and hexose's as opposed to the glucose units of true cellulose. This classification scheme is not founded on any physico-chemical basis, but has proven to be useful in practice. The minimum alpha cellulose content is an important consideration when a sample of wood pump is to be nitrated.

The crystallographic structure of cellulose has been determined based on X-ray measurements[8]. The unit cell consists of five cellobiose members arranged axially along the cellulose fiber. The dimensions of the cell are given in Figure 3, a pictorial representation of the unit cell of cellulose I. There are believed to be at least four crystalline variations of cellulose. In plants, the majority is of cellulose I. Regenerated cellulose or cellulose precipitated from solution is designated cellulose II. Cellulose II differs from cellulose I in that the angle β is distorted from 84° to 62°. Cellulose III is formed by swelling cellulose I with liquid ammonia and precipitation of the product. It also differs from cellulose I in the deformation of the angle β to 58°. Cellulose IV is formed by the heating of regenerated cellulose in water under pressure or glycerine. It has an X-ray picture roughly the same as cellulose I, but the angle β is wider, 90° versus 84°.

Classes of Nitrocellulose

Fully nitrated cellulose, cellulose trinitrate, has a degree of substitution (DS) equal to 3. Cellulose dinitrate has a DS of 2, and cellulose mononitrate a DS of 1. Such uniform or even levels of nitration are not likely with cellulose and an average DS is generally given for a particular batch. Thus, one is more likely to see nitrocelluloses of DS of 2.7 or average DS of 2.7 reported.

A common method of reporting the nitration level of nitrocellulose in industry is by its nitrogen content, measured in percent by weight. Nitrocellulose of 14.15% nitrogen is fully nitrated, and may be reported as cellulose trinitrate or nitrocellulose of DS=3. Cellulose dinitrate is 11.11% nitrogen and cellulose mononitrate is 6.76% nitrogen.

Rates of Reaction of Cellulose Hydroxyls

The three hydroxyls available for esterification on each anhydroglucose unit are at the C2, C3 and C6 positions on the glucopyranose ring. The rates of reaction at these sites has been known to be different since the 1930's. Spurlin first developed mathematical models to describe the substitution arrangement in 1939, but the analytical techniques available at the time were unable to adequately differentiate the species[9]. Despite the limitations, he was able to postulate that the hydroxyl on the C6 position is the first to react, and that the hydroxyls on the C2 and C3 positions react at nearly the same rate, with the C2 being somewhat faster. The relative rate values given for nitration were from 4-10 for the C6 position, 1-2 for the C2 and 1 for the C3.

Advances in the technique of ^{13}C-NMR have led to more recent studies on the reaction rates of cellulose hydroxyls. The application of ^{13}C-NMR to the analysis of nitrocellulose is discussed under Analytical Methods, but the results obtained are of interest here. In 1980, Wu, using ^{13}C-NMR, was able to distinguish whether an available site (C2, C3, C6) was occupied by a hydroxyl or a nitrate group[10]. By collecting data on the fraction of groups substituted for nitrocelluloses of average degree of substitution over the range of 0.4 to 2.2, and applying equilibrium rate equations, relative rate constants for nitration at each available site were determined. For the positions C6:C2:C3, relative rates of nitration were determined to be 5.8:1.8:1. These fall well into line with the values postulated earlier by Spurlin. Figure 4 from Wu's paper shows the fractions of specific glucose units (i.e., non-substituted, mono, di, and tri-nitrated) as a function of average degree of substitution. What is evident from this figure is that at any average degree of substitution between 0 and 3, the nitrocellulose molecules are comprised of a mixture of glucose units of differing nitration levels.

Viscosity of Nitrocellulose

The viscosity of nitrocellulose solutions is influenced by the level of nitration. Table 1, from Reference 11, shows the relationship between nitrogen content and viscosity, when nitration conditions and purification procedures are held constant. The data show that as cellulose is nitrated to higher levels, the viscosity of the product increases dramatically. This is even more apparent in Figure 5. Lindsley and Frank have plotted the intrinsic viscosity of nitrocelluloses of increasing degree of polymerization as a function of percent nitrogen[12]. The higher the degree of polymerization, the greater the increase in intrinsic viscosity observed with increasing nitration. Note that the cotton and absorbent cotton samples, which have a higher degree of polymerization than the rest, have a separate intrinsic viscosity scale covering a much larger range of values. The increase in intrinsic viscosity with increasing nitration for these samples is considerably greater as well. These authors felt that the changes observed could be attributed not only to the average degree of nitration of the samples, but also to the distribution of the nitrate groups along the polymer chain.

TABLE 1

Relationship of Viscosity to % Nitrogen

Nitrogen Content, %	Viscosity, Sec.
9.09	447
10.41	1,800
12.48	16,200
13.02	18,600
13.50	322,500

As can be seen in Figure 5, there is a good correlation between intrinsic viscosity and percent nitrogen within a given series, and increases in percent nitrogen lead to increases in molecular weight when no degradation of the material occurs during nitration. Lindsley and Frank stated that the major effect of introducing increasing numbers of nitrate groups into the cellulose chain was not the increase in molecular weight, but a change in the rheological properties in solution[12]. This change might be intermolecular bonding or some other physicochemical factor. The importance of the origin of cellulose used for nitration will be discussed in more detail later, but it is certainly evident that cellulose obtained from different sources, and having different degrees of polymerization, nitrated to the same level can have vastly different intrinsic viscosities.

The change in viscosity of nitrocellulose solutions based on nitrogen content is important to process engineers. The measurement of solution viscosity is the most widely used method for obtaining the average molecular weight of a polymer[13]. The intrinsic viscosity, defined earlier and represented as [n], in general is related to the viscosity average molecular weight, $\bar{M}_v$, as

$$[n] = K \bar{M}_v^{a},$$

where K and a are constants which depend on the polymer, the solvent, and the temperature at which the measurement is taken. For cellulose derivatives, including nitrocellulose, the value of a is nearly 1, so that the intrinsic viscosity is linearly related to the molecular weight through the constant K[12]. It is convenient to approximate the viscosity average molecular weight as the weight average molecular weight, $\bar{M}_w$, though for broad distribution polymers it is not always reliable[13]. This is due to the solvent dependence of $\bar{M}_v$, through the exponent a, and this dependence is greater for broad distribution polymers.

Solubility of Nitrocellulose

The solubility of a particular nitrocellulose sample in a given solvent is also dependent upon its nitration level. The relationship between solubility in an ether:alcohol solution (2:1) with percent nitrogen is shown in Figure 6. There is a marked increase in solubility around 9% nitrogen, and a marked decrease around 13% nitrogen. Nitrocelluloses with nitrogen contents between 10.5 and 12.2% nitrogen are completely soluble. Solutions of nitrocellulose are reversible lyophilic colloids[15]. While colloids are not generally thought of as solutions, the term "lyophillic colloid" traditionally describes soluble macromolecular material[16]. Some important characteristics of such solutions are: (1) prior to dissolution, the material undergoes swelling; (2) the viscosity of the solution is high, even at low concentrations; (3) the material does not form a saturated solution in a single solvent. The dissolution of nitrocellulose, and indeed other cellulose esters, is thought to be dependent on adhesion forces between individual molecules. In cellulose, each substituent position is occupied by a hydroxyl group, and hence, there is strong intermolecular interaction from hydrogen bonding. A disubstituted cellulose, such as cellulose dinitrate, has an irregular structure, and no such adhesion exists, or exerts much influence. In a fully-substituted cellulose, again a regular structure is obtained, and now adhesion is again possible through van der Waal's forces between substitutent groups. This was first hypothesized by Spurlin and is seen pictorially in Figure 7 taken from Urbanski[17].

It is also thought that nitrocellullose forms solvates with solvents in which it dissolves[18]. It is likely that the solvent is bound to free hydroxyls. This might explain why nitrocellulose is soluble in an alcohol/ether solution, when neither solvent alone can dissolve the material. First an alcohol solvate may be formed, which then dissolves in the ether.

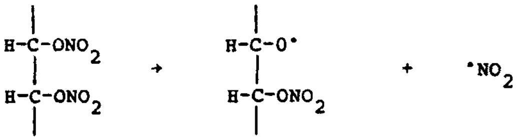
Plasticization of Nitrocellulose

The solubility of nitrocellulose in nitroglycerine is the basis of manufacture of double-base propellants and blasting gelation. In this context, nitroglycerine (NG) also acts as a plasticizer, improving the processability of the nitrocellulose. The nitrocellulose is first "dissolved" in the nitroglycerin, forming a dough which can be shaped and pressed in what is termed "solventless" propellant manufacture. The action of a plasticizer is to lower the polymer glass transition temperature (Tg), decrease the modulus and tensile strength and increase the impact strength and elongation of the polymer[19]. The first plasticizer for NC was camphor, used to produce celluloid. In the lacquer industry, tricresylphosphate has been used as a plasticizer. Some double-base propellant formulations have added an additional plasticizer in an effort to reduce the amount of nitroglycerin, due to the dangers of working with it on a large scale. Triacetin and di-n-propyl adipate have been used in this manner[20].

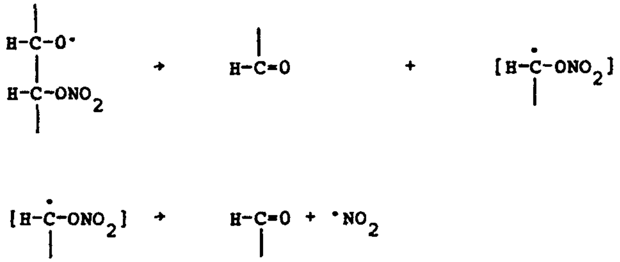
Renner has followed the rate of plasticization of nitrocellulose using polarized light microscopy[21] and with time-lapse video microscopy[22]. He found that the higher the nitrogen content of the nitrocellulose, the slower the rate of dissolution, the greater the range of nitrogen contained within the sample the greater the time difference to dissolve 90% of the fibers and to dissolve 100% of the fibers, the time-lapse photography enabled Renner to view the nature of the dissolution process for individual fibers. He noted some fibers uncoiled and gradually dissolved in the plasticizer, while others gelled and dissolved without uncoiling thereby leaving a skeletal residue in the solution. This difference was attributed to the presence of submicroscopic crystalline fibers which persist after the morphology of the fiber has vanished.

Degradation of Nitrocellulose

Thermal processes provide the major route for degradation of nitrocellulose. In this respect, it is similar to decomposition of organic peroxides[23]. The reaction proceeds with loss of NO_2 forming an organic free radical:



The organic free radical is much more reactive than the NO_2 and carbon-carbon bond cleavage can occur:



The major products are aldehydes, with evolution of NO_2 gas. It is also possible for the organic free radical to dehydrogenate organic matter present, producing alcohols.

Beard and Sharma studied the surface changes of thermally aged nitrocellulose[24]. Using X-ray photoelectron spectroscopy they found that while cleavage of the -O-N-bond with NO_2 loss was the initial step at the surface as well as the bulk, the rate of loss was three times greater at the surface. In addition, their data suggest amines, oximes, and urethanes as products of secondary reactions of NO_2 with the nitrocellulose residue.

More recently, Druet and Asselin have reviewed the chemistry of propellent aging[25]. They point out that the NO_2 produced in the thermal degradation of nitrocellulose can itself promote further thermolysis. This autocatalytic reaction, if left to itself, could create a hazardous situation. In propellent manufacture, stabilizers which scavenge the NO_2 produced, such as diphenylamine, are added. As long as the stabilizer is present, the autocatalysis is slowed and the useful lifetime of the propellent extended.

SYNTHESIS OF NITROCELLULOSE

The first nitrocellulose was produced by treating crude cellulose such as sawdust, paper or linen with concentrated nitric acid[3]. The product was unstable and highly degraded. In 1846, Schonbein developed the mixed nitric and sulfuric acid method and is generally credited with the discovery of nitrocellulose[26]. The mixed nitric and sulfuric acid method is still used in industry today.

Nitration With Nitric Acid

The nitration of cellulose is an equilibrium esterification, wherein the elements of water are eliminated between nitric acid and one anhydroglucose hydroxyl unit. In its simplest form, the reaction can be written as:

$$ROH + HONO_2 \rightleftarrows RONO_2 + H_2O$$

It can be readily seen that hydrolysis of nitrocellulose can be a competing reaction depending on the equilibrium position, thereby leading to denitration. The reaction is not so simple, however, since unlike other esterification reactions of cellulose, nitration takes place without dissolution of cellulose, retaining the fibrous nature of the substrate throughout the reaction[27]. The nitrating solution reaches surface sites first, as opposed to interacting with the molecule as a whole. The absorption of nitric acid into the fibers is a step which precedes nitration[28]. The most efficiently absorbed nitric acid is concentrated (85%) acid which provides the highest nitration level (8%). One problem encountered in nitrations with nitric acid alone is the gelatinization of surface fibers upon contacting the acid. This prevents diffusion of the acid into the fibers and gives a nonuniform product. The low nitration levels obtained by this technique have no commercial value and nitration with nitric acid alone is rarely performed outside the laboratory.

Nitric acid vapors and 98% nitric acid were used in Germany during World War II to obtain nitrocellulose of 13.6-13.8% nitrogen. The cellulose was first treated with saturated nitric acid vapors, then immersed into 98% acid. The vapor phase pretreatment prevented the aforementioned gelatinization, and the product was reportedly easy to stabilize since no other acid residues were present.

Nitration With Mixed Nitric and Sulfuric Acids

In the mixed nitric and sulfuric acid process, it is believed that the sulfuric acid acts as a dehydrating agent[29] When the molar ratio of sulfuric acid to water in the nitric acid equals one the following reaction is operative:

$$HNO_3 \cdot \eta H_2O + \eta H_2SO_4 \rightleftarrows HNO_3 + \eta H_2SO_4 \cdot H_2O$$

It is postulated that nitration is favored in the presence of anhydrous nitric acid. Experimental evidence to support this theory was reported by Lunge, and described by Urbanski[28]. The highest nitration level (13.92%) achieved by various compositions of mixed acids was obtained with a composition of 25.3% nitric acid, 63.4% sulfuric acid and 11.3% water. This corresponds to a mole ratio of approximately 2:3:3. Increasing the water content resulted in a lowering of the percent nitrogen in the product. Lowering the water content to essentially anhydrous conditions does not alter the nitrogen level obtained, but does slow down the rate of reaction such that the same nitration level is achieved after 12 hours, versus 1 hour when some water is present. This is believed to be due to rapid swelling at the fiber surface which slows diffusion of the anhydrous nitric acid into the fibers. The rate of reaction is also slowed if the amount of sulfuric acid in the mix is increased. The optimal range has been found to be a ratio of $H_2SO_4:HNO_3$ of 3:1 to 1:1. It is thought that the higher sulfuric acid concentrations promote the formation of unstable sulfuric esters of cellulose.

Nitration With Nitric and Phosphoric Acids

A mixture of nitric and phosphoric acids has been used commercially to obtain 13.7% nitrogen nitrocellulose[30]. In this study it was difficult to obtain nitrocelluloses of lower nitrogen content, however, as any deviation in the composition of the nitrating mixture caused the fibers of the material to crystallize or harden[30]. Ratios of $H_3PO_4:HNO_3$ from 3:1 to 1:1 were found to be optimal. The stability of nitrocellulose prepared by nitration with nitric and phosphoric acids is excellent. Apparently there are no phosphoric esters produced, or if they are, they do not decompose as the sulfuric esters do. The limited range of nitrogen levels obtainable and the tendency of phosphoric acid to corrode iron and steel have made commercialization of the method an unlikely proposition.

Nitration With Nitric and Acetic Acid

Nitric acid mixed with acetic acid and/or acetic anhydride has been used to obtain nitrocellulose of over 14% nitrogen[32,33]. The product was stabilized by three extractions with boiling alcohol. A drawback to this technique is the potential formation of acetyl nitrate, which explodes at elevated temperatures.

Nitration With Nitric Acid and Organic Solvents

The mixing of nitric acid with organic solvents as a nitrating solution was first performed in the 1930's[34]. Only high percent nitrogen nitrocelluloses were obtained using solvents such as carbon tetrachloride, methyl nitrate, or chloroform. These have had limited commercial application. In 1983, Turngren and Carignan reported on the nitration of wood pulp with mixtures of 99% nitric acid and methylene chloride[35]. By increasing the percent of nitric acid in the mixture from 2.5 to 25%, they obtained nitrocelluloses ranging from 1.1 to 13.4% nitrogen, all in yields of greater than 95%. They found that the polymer chain and fibrous structure of wood pulp was not degraded by the nitration, a characteristic which is important to the mechanical strength of the product.

Effect of Origin of the Cellulose on Nitration

As mentioned earlier, cellulose obtained from cotton and from wood pulp has been used in the manufacture of nitrocellulose. The investigation of wood pulp as a source began in the period around World War I, when an increase in nitrocellulose manufacture and an overall increase in the demand for cotton strained the available supply[36]. Initially, there were significant problems with nitrating wood pulp. The pulp swelled considerably during nitration, and the product retained much more acid than nitrocellulose made from cotton. After World War I the problems with wood pulp were solved, and nitrocellulose made from wood pulp was used extensively during World War II.

Cellulose obtained from wood pulp is separated by one of two methods prior to nitration[35]. These are termed the sulfite and the sulfate processes. The sulfite process consists of cooking wood chips in a solution of calcium bisulfite at elevated temperature and pressure. The product obtained has a high percentage of alpha cellulose and low content of lignins and pentosans. The sulfate process involves cooking the wood chips at elevated temperature and pressure in a solution of sodium hydroxide, sodium sulfide and sodium carbonate (65:15:20). The cellulose is separated from the lye and washed and bleached. The lye is evaporated to dryness and sodium sulfate added. The sulfate is reduced to sulfide. This allows industry to recover the spent chemicals for further use. This product contains more lignins than the sulfite product and is darker in color. Which process is used to separate the cellulose will ultimately affect some of the properties of the nitrocellulose made from it. Strecker and Turngren have found that sulfite pulps produce nitrocellulose with a more variable degree of polymerization[37]. They also found that sulfite pulps produced nitrocellulose with more high molecular weight material than either sulfate pulp or cotton linters, both of which produced material with a more symmetrical molecular weight distribution. The distribution will affect the processability of the nitrocellulose into propellant.

Stabilization of Nitrocellulose

The final step in the synthesis of nitrocellulose is the stabilization of the final product. The first step in the process is the removal of the spent acids. In the batch process this was often done by simple centrifugation, resulting in a high retention of acids[38]. In the continuous process, counter current washes are used which result in less retained acids. After removal of the spent acids, the nitrocellulose is mechanically chopped to reduce the fiber length. The cut fibers are then treated to a poaching operation, which consists of boiling the fibers in a sodium carbonate solution. This removes the last of the spent acids and reduces the viscosity of the material. A homogenous product is obtained by blending a water suspension of the nitrocellulose in large vessels. The material is then passed through a screen to remove particulates and long fibers, and the water removed by decantation. The water content is further reduced to 20-30% by centrifugation. This is the form in which nitrocellulose is transported.

ANALYTICAL METHODS FOR NITROCELLULOSE

Fractionating Methods

That nitrocellulose consists of a range of molecular weight material has been known for some time. Early researchers took advantage of the differing solubilities of low, medium and high molecular weight material in an acetone/water solution to effect separations and characterize the individual fractions[39]. In this method, as more water is added to the system the higher molecular weight fraction precipitates out.

Fractionation methods have for the most part been replaced by chromatographic techniques, particularly Gel Permeation Chromatography (GPC). In GPC, separation of the individual fractions is based on hydrodynamic volume. The nitrocellulose molecules pass through a set of columns containing material of a defined pore size. Molecules small enough to fit within the pores are retained, while the large excluded molecules pass on through the column bed. Thus, larger size molecules of higher molecular weight material will elute from the column earlier than smaller lower molecular weight material. By connecting a series of columns of different pore sizes, efficient separation of molecules of differing size contained within a sample can be effected. Common detectors used with GPC include differential refractive index (DRI), ultraviolet (UV), and differential viscometric.

GPC has become the standard method for estimating the molecular weight and polydispersity of nitrocellulose samples. The first evaluation of GPC as a production quality assurance method was in 1976[40]. Since that time a number of papers on the accuracy of the technique have appeared. There appears to be a problem in the standard method of calibration of the GPC equilibration curve. In general, narrow molecular weight range polystyrene standards are used to calibrate the elution volume of the chromatographic system. Since the separation is based upon hydrodynamic volume and not molecular weight, a molecule of nitrocellulose having the same elution volume as a molecule of polystyrene may well have a different molecular weight. If a correction is not applied to the results, an error in absolute molecular weight measurement occurs. French and Nauflett addressed this problem in 1981[41]. By plotting the number average molecular weight of several nitrocellulose samples, determined by membrane osmometry, against elution volume of the same samples run by GPC, in an iterative process they were able to establish a true calibration curve for nitrocellulose (Figure 8). The calibration curve fell below that of polystyrene standards run on the same system. This would indicate that a nitrocellulose molecule of the same molecular weight as a polystyrene molecule has a larger hydrodynamic volume.

Law and Coleman also used membrane osmometry to independently calibrate the GPC technique[42]. They also found that the nitrocellulose calibration curve fell below that of polystyrene. In their results, however, there was a crossover point at the low molecular weight end due to a difference in the slopes of the curves of these two polymers. This type of behavior would lead to high calculated values of weight average molecular weight and polydispersities, but low values of number average molecular weight.

Despite questions as to the absolute molecular weight obtained from GPC, the results from the technique have still proven useful in evaluating nitrocelluloses for propellant manufacture. Goldwasser, Carlson and Nauflett found that GPC traces of nitrocellulose samples which produced acceptable propellent were different from those which produced unacceptable propellent[43].

The GPC trace of acceptable material contained a lower molecular weight region not found in the unacceptable material. They conclude that even though molecular weight values determined are only relative to polystyrene, the technique can be useful in process quality control. Thomas found much the same to be true for nitrocellulose used in Ball Powder propellants[43]. Here the GPC trace of the nitrocellulose was found to be indicative of whether the propellant grains would have poor or good shaping quality. The polydispersity of the nitrocellulose appeared to be the most important factor.

Another problem in the GPC analysis of nitrocellulose is its solvation by tetrahydrofuran (THF), one of the most common GPC solvents. This was examined by Siochi, who found that it can take up to seven days for a solution to obtain stable molecular weight results[45] She attributes the change, which was a steady lowering of values, to solvation of the sample by THF. This is also supported by the observed shift in the molecular weight distributions. Over time, the high molecular weight portion shifted to the low molecular weight end of the GPC chromatogram, with a concurrent increase in the concentration of the low molecular weight end. The fact that no shift of the low molecular weight end to even lower values was observed suggests to her that chain degradation does not occur, as chain scission would be expected to be random and the entire distribution would be shifted to lower values. Most researchers doing GPC of nitrocellulose shake the sample overnight and perform the analysis the following day.

Ultraviolet Spectroscopy

Ultraviolet absorption has already been mentioned as a detector in GPC. Fixed wavelength detectors typically monitor the total absorption at 254 nm. This is not a particularly good wavelength for nitrocellulose, as it does not contain a conjugated double bond system. Urbanski, reporting on the work of Jones and Miles, lists a maximum UV absorption around 220 nm[46]. More recently, Carlos, Dow and Nauflett used a diode array UV detector in the GPC analysis of nitrocellulose from several double base propellants[47]. They observed a maximum at a somewhat lower wavelength (210 nm). Figure 9 from their work shows the GPC/UV spectrum from 190 to 400 nm of a nitrocellulose sample in THF. The sample elutes from about 3.5 minutes to 6.5 minutes with an impurity eluting around 8 minutes. If one were to take a slice along the wavelength axis a typical UV trace would be obtained. If a slice were taken along the time axis a typical chromatogram would be obtained. Above 280 nm, there appears to be no significant absorbance. Among the factors examined in this work were the relationship of UV absorbance at any wavelength and the processability of nitrocellulose in propellant formulations. Of interest was the finding that in propellant processing, the nitrocellulose undergoes some sort of change, as yet undefined, which is manifested as an increase in the absorbance in the range 250 to 280 nm. Their results indicate that this change is beneficial to processing of good propellant, as "good" (extrudable) batches of propellant always had a greater absorbance in this region than "bad" (non-extrudable) propellant.

Carbon 13 NMR

Carbon 13 NMR has proven to be an extremely valuable spectroscopic technique for nitrocellulose. As mentioned in Chapter 2, it has been used to quantify the fraction of mono-, di- and tri-substituted anhydroglucose units as a function of the average degree of substitution. Most notably, the work of Wu and Clark, Stephenson and Heatley has established the relative rates of reaction at the three hydroxyls[10,48]. Using a 25.2 MHz proton decoupled ^{13}C-NMR and analyzing samples from very low (DS=0.4) to very high (DS=3.0) nitration levels, a number of complex spectra were deconvoluted with respectnm[47] to band assignments. Once band assignments were established, integration of the peaks yielded the relative degree of substitution at each substitution site. Figure 10 shows a representative spectrum, with band assignments given in Table 2.

Leider and Pane used the same technique to examine the stability of the nitrate groups to thermal aging[49]. It is interesting to note that the C6 site, which is the one which reacts the fastest, is also the most stable to the aging process. The reaction rates proceed as C6>C2>C3, while the thermal decomposition rates found by Leider and Pane proceed as C2>C3>C6. No explanation was given for the difference in nitration/ denitration reaction order.

TABLE 2

Band Assignments of ^{13}C Peaks

Peak Number	Assignment
1	C1 in 3,6 disubstituted
2	C1 in 6 monosubstituted
3	C1 in trisubstituted
4	C1 in 2,6 disubstituted
5	C3 in 3,6 disubstituted
6	C2 in 2,6 disubstituted
7	C3 in trisubstituted
8	C4 in trisubstituted
9	C2 in trisubstituted
10	C2 in 3,6 disubstituted
11	C5 & C6

X-ray Techniques

It was also mentioned in Chapter 2 that X-ray analysis has been used to obtain dimensions of the unit cell of nitrocellulose. The diffraction of X-rays by crystals was first discovered in 1912 and was the first means for measuring the wavelength of the rays[50]. X-ray Crystallography makes use of the same principles to measure the spacing between crystal planes of a material. Figure 11 illustrates how interchain spacing reflects X-rays. The spacing, d, is related to the wavelength of radiation by Bragg's Law:

$$n\lambda = 2d \sin\theta$$

The technique has been applied in an effort to study the distribution of nitrate groups along the chain on nitrocellulose molecules. Clark and Stephenson noted that the interchain spacing of nitrocelluloses of a given DS prepared by denitration of more highly nitrated material was always greater than for material with the same DS prepared by direct nitration[51]. Since the interchain spacing is higher for more highly nitrated materials, the most likely conclusion is that the denitrated materials has a more regular configuration and intermolecular interactions are dominated by the substituted residues (recall Figure 7).

Infrared Spectrometry

Almost from the inception of infrared analysis, the technique has been applied to nitrated compounds. One of the earliest was the identification of components in a mixture of nitroparaffins in 1943[52] A compilation of the infrared spectra of ingredients used in explosives and propellants was published in 1960 by a group working at the Picatinny Arsenal, Dover, NJ[53]. They were developing an infrared method for use in propellant quality control and, as a first step, generated neat spectra of 68 ingredients, additives, and related components of the more common explosive formulations in use at the time. This included nitrocellulose, which was cast as a film for the analysis. The development of Fourier transform infrared instruments (FT-IR) has made the collection of infrared spectra simpler and faster. This has permitted the application of IR techniques in kinetic studies where changes in the entire IR spectrum can be evaluated rather than monitoring of a single wavelength. This technique has been applied to decomposition studies of nitrocellulose by researchers at Universite Laval, Quebec, Canada[54]. They examined the degradation of nitrocellulose films heated from 413 K to 473 K. Figure 12 shows the FT-IR spectrum of a nitrocellulose film in the region from 4000 to 500 cm^{-1}. The assignments of the frequencies are given in Table 3.

TABLE 3

FT-IR Band Assignments

Wavenumber	Assignment
3512, 3315	OH stretching
2973, 2883	CH_2 stretching
2927	CH stretching
1653	NO_2 asymmetric stretching
1282	NO_2 symmetric stretching
1070	C-O stretch, C1-O-C4
1025, 1004, 910	C-O stretching
840	O-NO_2 stretching
749, 692	O-NO_2 deformation

The degradation studies are represented in Figure 13, showing only the region from 2000 to 800 cm^{-1}. What is evident is that the O-NO_2 bond is the most labile in the nitrocellulose molecule. This is seen in the loss of the band at 1653 cm^{-1}, with a concomitant increase in a band at 1740 cm^{-1} from a carbonyl stretch. Recall from the discussion on degradation that the principal products of thermolysis are aldehydes.

Other applications of infrared analysis to nitrocellulose have focussed upon quantitative procedures. Norwitz and Chansan used the intensity of the band at 1653 cm^{-1} for the determination of percent nitrogen in raw nitrocellulose samples[55]. They found that a method could be developed which could quantity the percent nitrogen with a standard deviation of 0.028%. To achieve this level of precision, it was necessary to control the sample mass, in grams, and quantity based on the percent nitrogen through a previously established standard curve. They found no interference from the inorganic salts present, but the water present in commercial THF (0.02%) does absorb near 1650 cm^{-1}. This required ratioing against a blank for each sample run.

Raisor and Law used the same wavenumber in the GPC/FT-IR of nitrocellulose for computation of the molecular size distribution[56]. They found standard deviations of 6-8% with pristine samples and 9-10% for samples extracted from lacquers.

Thermal Methods

Thermal methods of analysis are often applied to polymeric systems to test stability. In the case of nitrocellulose, thermal aging at elevated temperatures is used to estimate the long term storage stability of the final product. Carignan and Turngren monitored decomposition and chain degradation of 13.20% nitrogen nitrocellulose, using the standard heat test for propellants[56]. In this test, the sample is placed in a test tube and fitted with a slotted stopper to allow slow escape of evolved gases. The setup is heated to 134.5°C and decomposition monitored by measuring the percent nitrogen and weight loss of the residue and the percent NO_2 evolved. Sampling intervals were two hours for the first 12 hours, five hours up to 24 hours of heating, and every 24 hours thereafter . Their results show a moderate weight loss (5 to 6%) for the first 10 hours, followed by a period of rapid weight loss. After 72 hours, the rate of loss falls off and 25% of the original sample remains. While they admit to too few data points, they feel the decomposition kinetics can be represented by the general differential:

$$dX/dt = k\, X^{1-p}\, (1-X)^{1-q}$$

where X is the fractional decomposition, t the time constant, k the rate constant, and p and q are system parameters with values between 0 and 1. Roughly 50% of the weight lost is as NO_2 , the rest as CO_2, CO and H_2O.

Barendregt and Verhoeff used thermogravimetry as a substitute method for the standard heat test as used in the Netherlands[58]. The standard test in the Netherlands uses a temperature of 85°C, as compared with the 134.5°C used in the U. S. Thermogravimetry makes use of a recording microbalance to measure the weight of the sample during the heating process. In addition, the heating rate can be varied such that the weight loss can be condensed into a smaller time frame, or different weight loss regions can be monitored. This work compared isothermal with temperature programmed measurements, and calculated the rate constant according to the equation:

$$dX/dt = k\ (1-X)^n$$

This equation is similar to that given above, with $p=1$ and $n=1-q$. A major difference in this work was the testing of the order of the rate equation, n, by evaluating the standard deviations of the rate constant, k. A second order fit gave the lowest standard deviations, based on five replicate analyses. This would seem to be in conflict with the equation as given by Carignan and Turngren, and no explanation can be given. Support for the second order conclusion can be found in a paper by Pfeil, Eisenreich, and Krause, who used GPC to analyze samples quenched at different temperatures[59]. They also found a second order rate of degradation. In addition, they compared the change in nitrate ester group IR absorption with the decrease in molecular weight, and found that the molecular weight decreases significantly before any decrease in IR absorption is detected. The average molecular weight of the material decreased to about one tenth its initial value when the IR signal began dropping off. The decay of the nitrate concentration is reported to be autocatalytic, and the weight loss profile takes the characteristic S-shaped curve (Figure 14).

Both Differential Thermal Analysis (DTA) and Differential Scanning Calorimetry (DSC) have also been applied to the analysis of propellants to establish the heat of explosion at atmospheric pressure. DSC gave the more reproducible values, which were about half those reported by the technique of bomb calorimetry[60]. The reason given was the incomplete combustion under high pressure. Since the conditions of actual use of the propellant generate high pressures, the bomb calorimetric values are probably more realistic. The DTA data were also much lower than the bomb calorimetric data with a much wider range of values[61]. These results indicate that these types of analyses are better suited to nonpropellant formulations of nitrocellulose where high pressures in actual conditions of use are not achieved, and the data are more likely to represent actual energies released.

SUMMARY

Nitrocellulose has found many applications in commerce in its 140 year history. Many of these applications were developed without much understanding of the underlying chemistry. What has been learned well is the mechanism for controlling the nitration level of commercial nitrocellulose using the mixed nitric and sulfuric acid method. What is not yet clear is the distribution of the nitrate groups along the polymer chain. Current research using ^{13}C-NMR holds promise in answering this question.

The chemistry of nitrocellulose is most often explained in terms of the number and likely distribution of nitrate groups and hydroxyl groups on individual chains. Experimentally, this is observed in the variation of solubilities of nitrocelluloses of different nitrogen content in the same solvent system. As new and more powerful analytical techniques are developed, they are often applied to the characterization of nitrocellulose which in turn suggest the great complexity of the nitrocellulose system. The number of variables which influence the chemistry of nitrocellulose include: (1) origin of the cellulose starting material, (2) the amount and distribution of non-glucopyranose units in the cellulose chain, (3) nitrating conditions, (4) efficiency of final washes, and (5) the age of the final material. Each of these variables needs to be better understood

before it can be said that the chemistry of nitrocellullose is understood.

ACKNOWLEDGMENT

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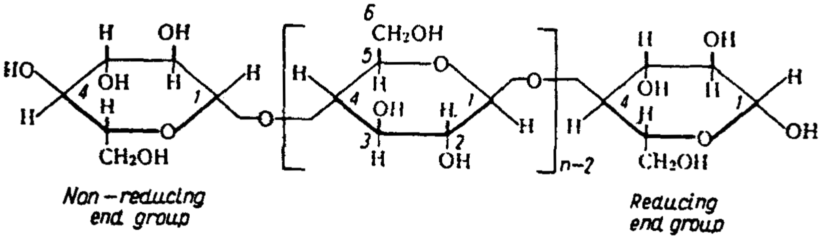


FIGURE 1

Cellulose Molecule

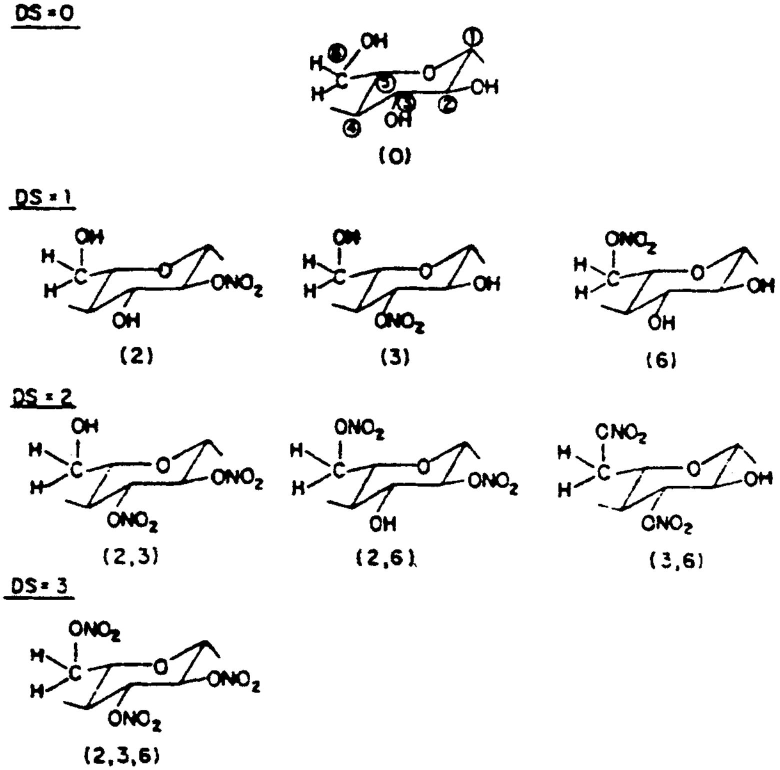


FIGURE 2

Eight Substitution Patterns for Nitrated Cellulose

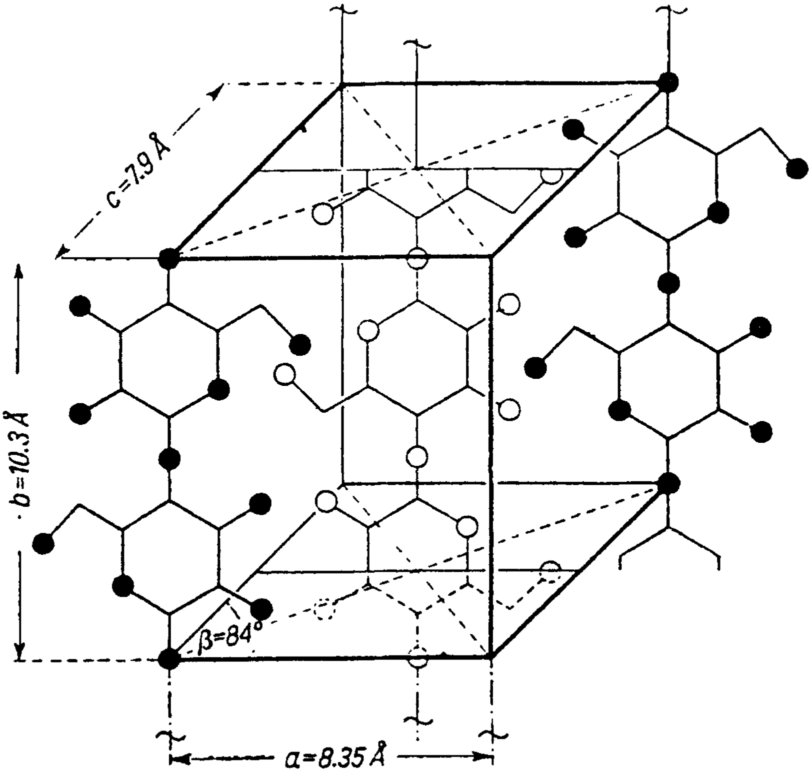


Figure 3

Unit Cell of Cellulose I

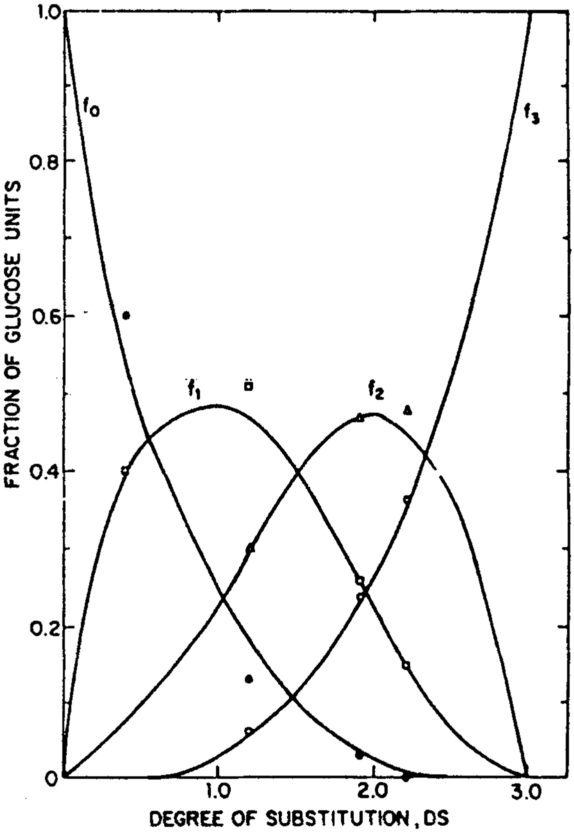


FIGURE 4

Fraction of Substituted Glucose Units, f_x, Where x=0 For Unsubstituted, 1 For Mono-Nitrate, 2 For Dinitrate, and 3 For Trinitrate

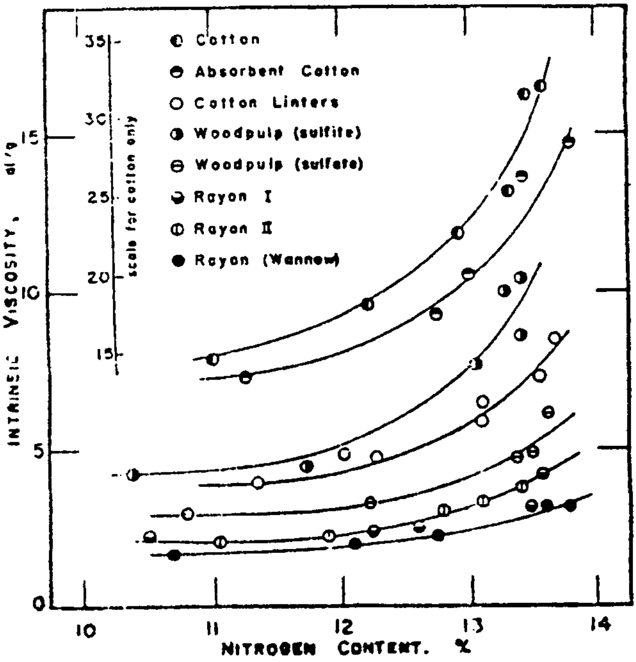


FIGURE 5

Change in Intrinsic Viscosity With Nitrogen Content

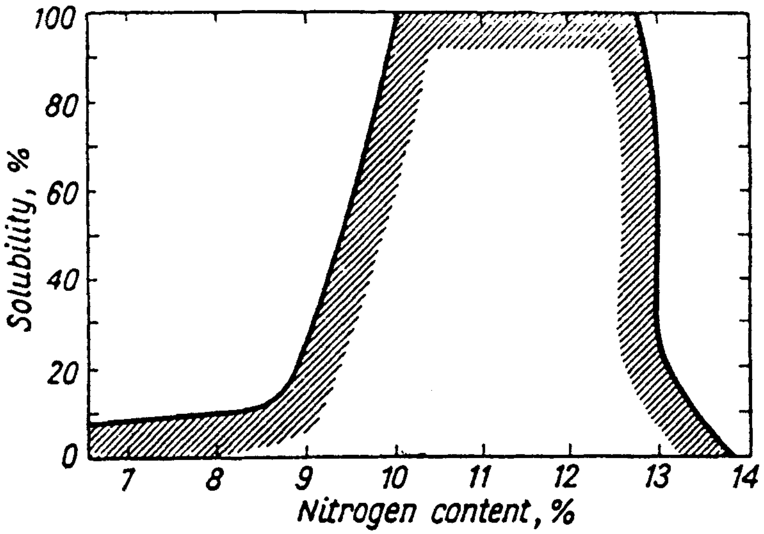
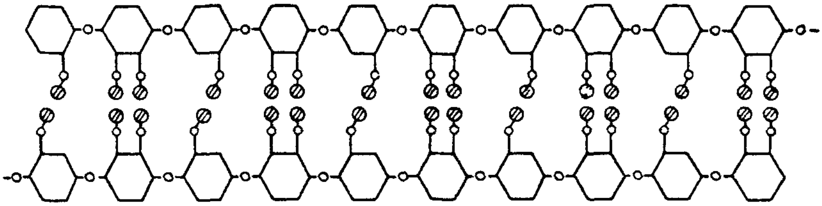
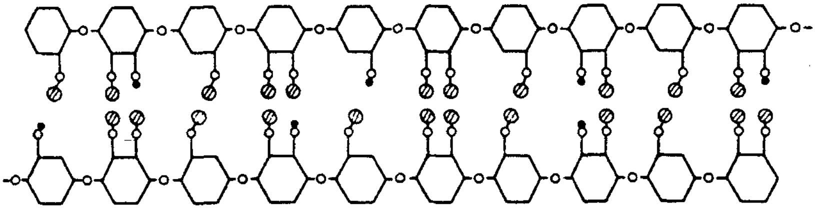


FIGURE 6

Solubility In Ether/Alcohol Versus Nitrogen Content of Nitrocellulose



(a) Completely substituted derivatives



(b) Derivatives of substitution 2.3

○ Oxygen ● Hydrogen ⊘ Substituents

FIGURE 7

Illustration of Substituent Interaction for Completely and Partially Substituted Cellulose

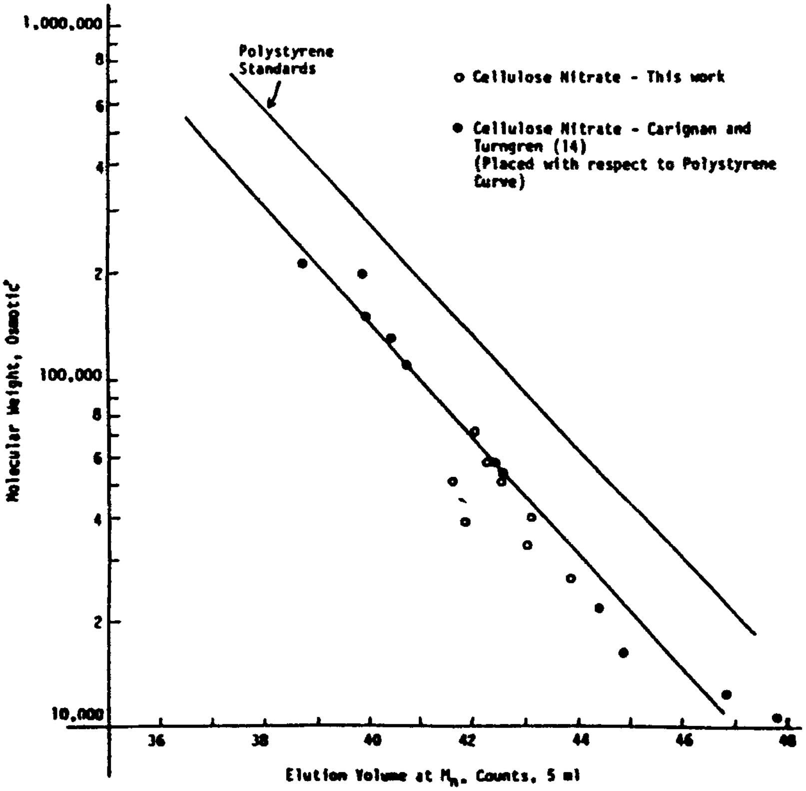


FIGURE 8

GPC Calibration Curve for Nitrocellulose

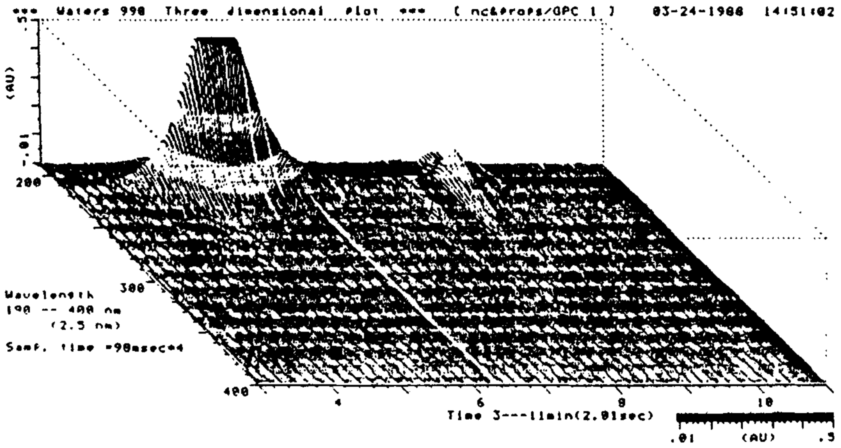


FIGURE 9

UV Spectrum of Fractionated Nitrocellulose From 190-400 nm

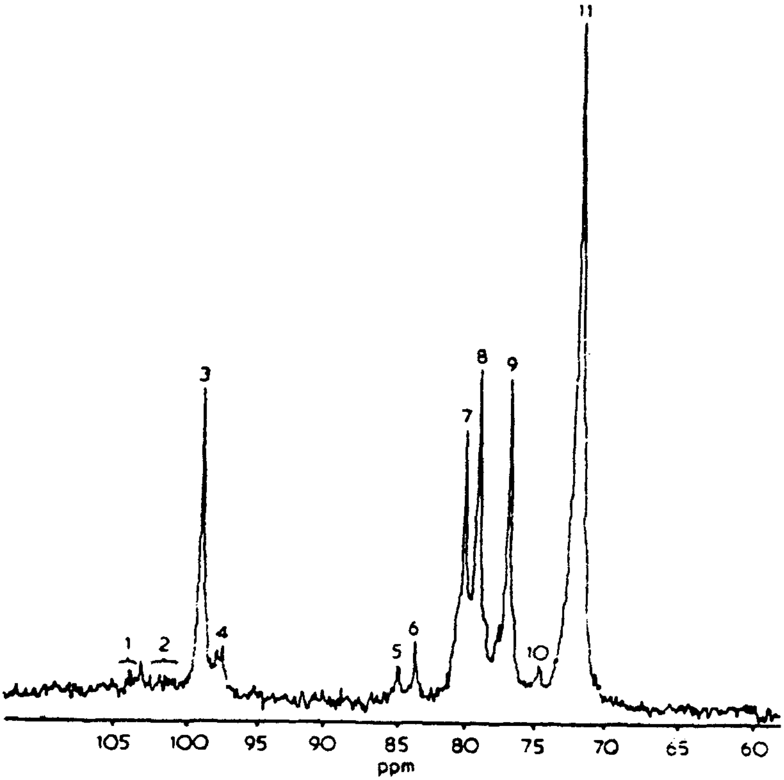


FIGURE 10

^{13}C NMR Spectrum of Nitrocellulose of DS=2.8

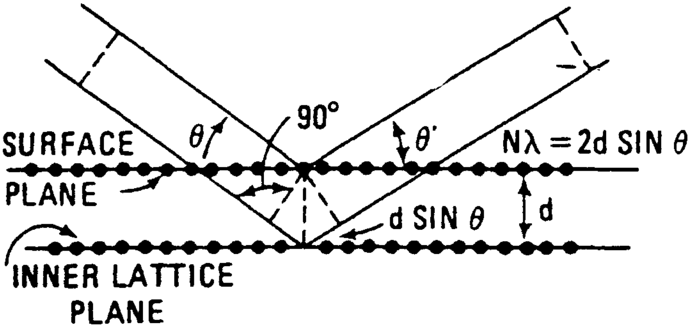


FIGURE 11

Reflection of X-rays From a Crystalline Structure

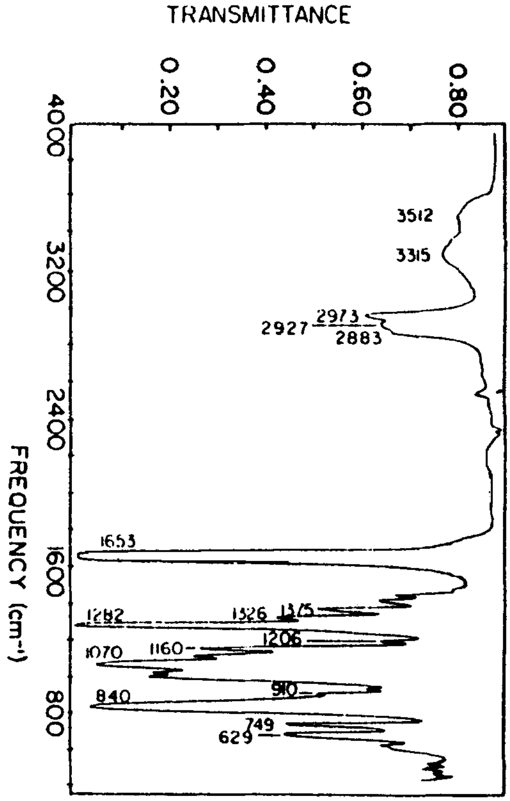


FIGURE 12

FT-IR Spectrum of Nitrocellulose Film

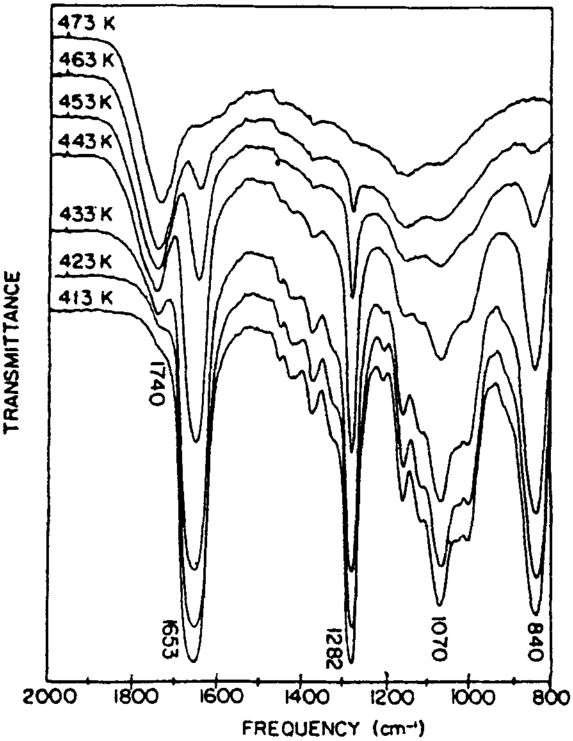


FIGURE 13

FT-IR Spectra of Nitrocellulose Film Heated to 480 K

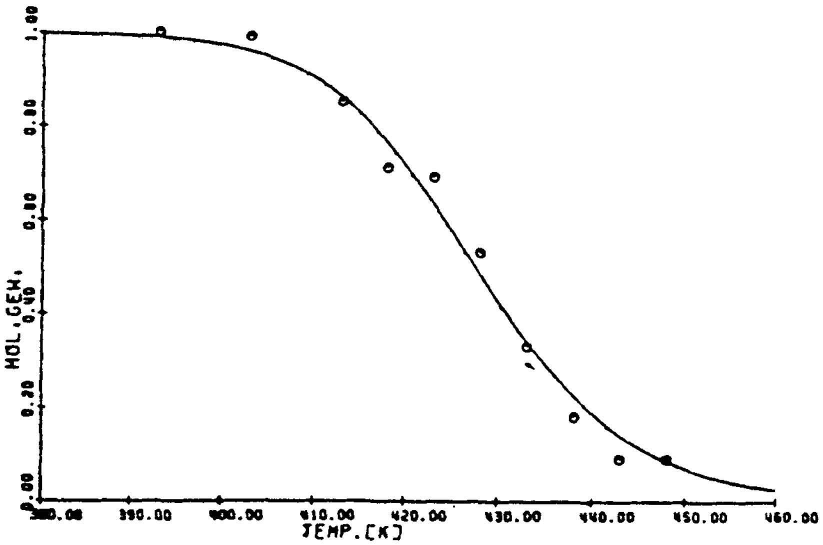


FIGURE 14

Normalized Average Molecular Weight as a Function of Temperature at a Heating Rate of 0.5 K/min

REFERENCES

1. Encyclopedia of Polymer Science and Engineering, Second Edition 1985, Volume 3 "Cellulose Esters, Inorganic", p. 139.

2. Kirk-Othmer Encyclopedia of Chemical Technology, Third Edition 1979, Volume 5 "Cellulose Derivatives, Esters", p. 129.

3. A. Reveley in "Cellulose and Its Derivatives", J. F. Kennedy, G. O. Phillips, D. J. Wedlock and P. A. Williams, Editors, Ellis Horwood Ltd., Chichester.

4. "Chemistry and Technology of Explosives", T. Urbanski; Pergamon Press, New York, NY, Volume 3, Part 3, p. 528.

5. Kirk-Othmer Encyclopedia of Chemical Technology, 3rd Ed., 1979, John Wiley & Sons, New York, NY, Volume 9, "Explosives and Propellants", p. 577.

6. "Chemistry and Technology of Explosives", T. Urbanski; Pergamon Press, New York, NY, Volume 2, p. 216.

7. Ibid, p. 230.

8. Ibid, p. 219

9. H. M. Spurlin in **High Polymers**, Volume 5 "Cellulose", 2nd Ed., Part II, E. Ott, H. Spurlin and M. Grafflin, Editors; p. 676.

10. T. K. Wu, Macromolecules, 13, 1980, p. 74.

11. "Chemistry and Technology of Explosives", T. Urbanski, Pergamon Press, New York, NY, Volume 2, p. 271.

12. C. H. Lindsley and M. B. Frank, Ind. Eng. Chem., 45, 1953, p. 2491.

13. "The Elements of Polymer Science and Engineering", A. Rudin, Academic Press Inc., Orlando, FL, 1982, Secton 3.3.

14. "Chemistry and Technology of Explosives", T. Urbanski, Pergamon Press, New York, NY, Volume 2, p. 259.
15. Ibid, p. 244.

16. "Introduction to Colloid and Surface Chemistry", 3rd Ed., D. J. Shaw, Butterworth & Co., Inc., 1980, p. 5.

17. "Chemistry and Technology of Explosives", T. Urbansksi, Pergamon Press, New York, NY, Volume 2, p. 247.

18. Ibid, p. 248.

19. Kirk-Othmer Encyclopedia of Chemical Technology, Volume 18, "Plasticizers", p. 116.

20. "A Comprehensive Government/University/Industry Double Base Propellant Characterizaton Effort", G. Nauflett, Presented at the 1988 JANNAF Propellant Characterization Subcommittee Meeting, Las Curses, NM, Nov. 1-3, 1988.

21. R. H. Renner, 1986 JANNAF Propellant Characterization Subcommittee Meeting, CPIA Pub. #459, p. 149.

22. R. H. Renner, 1987 JANNAF Propellant Characterization Subcommittee Meeting, CPIA Pub. #470, p. 275.

23. E. Ott in **High Polymers** Volume 5, "Cellulose", 2nd Ed., Part II, E. Ott, H. Spurlin and M. Grafflin, Eds., p. 1047.

24. B. C. Beard and J. Sharma, 1987 JANNAF Propellant Characterization Subcommittee Meeting, CPIA Pub. #470, p. 259.

25. L. Druet and M. Asselin, J. Energetic Materials, 6, 1988, p. 27.

26. "Chemistry and Technology of Explosives", T. Urbanski, Pergamon Press, New York, NY, Volume 2, Chapter 1.

27. H. M. Spurlin in **High Polymers** Volume 5, "Cellulose", 2nd Ed., Part II, E. Ott, H. Spurlin and M. Grafflin, Eds., p. 718.

28. "Chemistry and Technology of Explosives", T. Urbanski, Pergamon Press, New York, NY, Volume 2, p. 321.

29. Ibid, p. 327.

30. Ibid, p. 341.

31. H. M. Spurlin in **High Polymers** Volume 5, "Cellulose", 2nd Ed., Part II, E. Ott, H. Spurlin and M. Grafflin, Eds., p. 728.

32. Ibid, p. 729.

33. "Chemistry and Technology of Explosives", T. Urbanski, Pergamon Press, New York, NY, Volume 2, p. 344.

34. Ibid, p. 345.

35. E. V. Turngren and Y. P. Carignan, 1983 JANNAF Propulsion Meeting, Monterey, CA, CPIA Pub. #370, Volume 2, p. 175.

36. "Chemistry and Technology of Explosives", T. Urbanski, Pergamon Press, New York, NY, Volume 2, p. 364.

37. "Cellulose Source and Nitration Process Effects on Nitrocellulose", R. A. Strecker and E. V. Turngren, Presented at the Joint Symposium on Compatibility of Plastics and Materials With Explosives and Processing Explosives, Propellants and Ingredients, October 14-16, 1980, Blacksburg, VA.

38. "Nitrocellulose Manufacturing Processes and Properties", R. A. Mundy, C. D. Chandler and W. T. Bolleter, Hercules, Radford, VA, Internal Document Delivered to Picatinny Arsenal, Dover, NJ.

39. "Chemistry and Technology of Explosives", T. Urbanski, Pergamon Press, New York, NY, Volume 2, p. 278.

40. Bulletin of the 7th JANNAF Propellant Characterization Meeting, June 1976, CPIA Pub. #279.

41. D. M. French and G. W. Nauflett, J. Liquid Chromatography, 4(2), 1981, p. 197.

42. R. D. Law and D. W. Coleman, 1987 JANNAF Propellant Characterization Subcommittee Meeting, CPIA Pub. #470, p. 269.

43. J. M. Goldwasser, D. Carlson and G. W. Nauflett, 1985 JANNAF Propellant Characterization Subcommittee Meeting, CPIA Pub. #435, p. 291.

44. K. A. Thomas, 1986 JANNAF Propellant Characterization Subcommittee Meeting, CPIA Pub. #459, p. 143.

45. E. J. Siochi, "Absolute Molecular Weight Distribution of Nitrocellulose", Ph.D. Dissertation, VPI & SU, 1988.

46. "Chemistry and Technology of Explosives", T. Urbanski, Pergamon Press, New York, NY, Volume 2, p. 287.

47. D. Carlson, T. Dow and G. Nauflett, Presented at the 1988 JANNAF Propellant Characterization Subcommittee Meeting, Las Cruses, NM, November 1-2, CPIA Pub. in Press.

48. D. T. Clark, P. J. Stephenson and F. Heatley, Polymer, 22, 1981, p. 1113.

49. H. R. Leider and A. J. Pane, "Proceedings of the ADPA Symposium on Compatibility of Plastics and Other Materials With Explosives, Propellants, Pyrotechnics and Processing of Explosives, Propellants and Ingredients, October 27-29, 1986, Long Beach, CA.

50. Van Nostrand's Scientific Encyclopedia, 6th Ed., 1983, p. 3041.

51. D. T. Clark and P. J. Stephenson, Polymer, 23, 1982, p. 1295.

52. J. R. Nielsen and D. C. Smith, Ind. Eng. Chem., Analytical Ed., 15, 1943, p. 609.

53. F. Pristera, M. Halik, A. Castelli and W. Fredericks, Anal. Chem., 32, 1960, p. 495.

54. J. J. Jutier, Y. Harrison, S. Premont and R. Prud'homme, J. Applied Polymer Sci., 33, 1987, p. 1359.

55. G. Norwitz and D. E. Chasan, Talanta 20, 1973, p. 73.

56. R. C. Raisor and R. D. Law, 1984 JANNAF Propellant Characterization Subcommittee Meeting, CPIA Pub. #413, p. 39.

57. Y. P. Carignan and E. V. Turngren, 7th JANNAF Propellant Characterization Meeting, CPIA Pub. #279, p. 45.

58. Int. Jahrestag-Fraunhofer-Inst. Treib.-Explosivst., (Mess-Pruefmethoden Treib.-Sprengst.), 87-107, "TGA Experiments With Propellants", R. Barendregt and J. Verhoeff.

59. Int. Jahrestag-Fraunhofer-Inst. Treib.-Explosivst., 17th (Anal. Propellants Explos.: Chem. Phys. Methods), 8/1-8/5, "A Kinetic Link Between Nitrate Group Loss and Molecular Weight Degradation of Nitrocellulose", A. Pfeil, N. Eisenreich and H. Krause.

60. J. E. House and P. J. Zack, J. Forensic Sci. 22(2), p. 332.

61. J. D. DeHaan, J. Forensic Sci., 20(2), p. 243.