

NITROCELLULOSE LITERATURE REVIEW  
CHARACTERIZATION AND APPLICATION  
TO MODERN GUN PROPELLANTS

by

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## Table of Contents

Chapter 1	Introduction .....	1
Chapter 2	History of Nitrocellulose .....	3
Chapter 3	Description of Cellulose .....	5
3.1	Microstructure of Cellulose .....	8
3.2	Macrostructure of Cellulose .....	12
3.3	Purification of Cellulose .....	14
Chapter 4	Manufacture of Nitrocellulose .....	16
Chapter 5	Gun Propellant Manufacture and Mechanical Properties .....	19
5.1	Background .....	19
5.2	Gun Propellant Manufacture .....	19
5.3	Gun Propellant Mechanical Properties .....	20
Chapter 6	Nitrocellulose Characterization .....	33
6.1	Background .....	33
6.2	Solubility Studies of Nitrocellulose .....	34
6.3	Viscosity Studies of Nitrocellulose .....	41

6.4	Molecular Weight Determination .....	45
6.4.1	Methodology .....	45
6.4.2	Molecular Weight Determination of Nitrocellulose .....	49
<b>Chapter 7</b>	<b>Conclusions and Recommendations for Further Study .....</b>	<b>56</b>
7.1	Conclusions .....	56
7.2	Recommendations for Further Study .....	57
7.2.1	Nitrocellulose Characterization .....	57
7.2.2	Integration of Nitrocellulose Characteristics with Propellant Mechanical Properties and Ballistic Performance .....	58
<b>References</b>	<b>.....</b>	<b>59</b>

## List of Illustrations

Figure 3.1	Chemical Structure of Cellulose .....	6
Figure 3.2.1	Model of Basic Cell Structures of Cotton and Wood Cellulose .....	13
Figure 4.1	Graphical Comparison of Degree of Substitution and Weight Percent Nitrogen .....	17
Figure 5.3.1	Tan $\delta$ versus Temperature Plot for Blended Nitrocellulose Films .....	24
Figure 5.3.2	Mechanical Response of Double-Base Propellant Under High Strain Rate .....	29
Figure 6.2.1	Nitrogen Distribution for Nitrocellulose from Sulfate Pulp .....	38
Figure 6.2.2	Nitrogen Distribution for Nitrocellulose from Sulfite Pulp .....	39
Figure 6.2.3	Nitrogen Distribution for Nitrocellulose from Cotton Cellulose .....	40
Figure 6.3.1	Intrinsic Viscosity versus Shear Rate for Nitrocellulose in Ethyl Acetate .....	44
Figure 6.4.2.1	Time Dependence of Average Molecular Weight Determined by GPC of 12.58 Percent N Nitrocellulose .....	55

## List of Tables

Table 3.1	Molecular Weight and Degree of Polymerization Range for Cellulose .....	7
Table 3.1.1	Percentage of Amorphous Material in Various Celluloses .....	10
Table 3.1.2	Percent Crystallinity of Cellulose from Several Different Sources as Measured by X-ray Diffraction .....	11
Table 5.3.1	Results from Dynamic Mechanical Analysis of Double-Base Propellant .....	30

## INTRODUCTION

Nitrocellulose is the most important inorganic ester of cellulose and is the oldest cellulose derivative (1,2). Nitrocellulose has been used in diverse applications for the past century. Although nitrocellulose was originally used primarily in military applications as a key ingredient in gun propellants and explosives, it subsequently found use as a commercial plastic and is still used in large quantities in the films and coatings industries (3,4).

Owing to its long history, diverse applications, relative expense, chemical complexity and strategic importance, nitrocellulose has been the subject of intense study. Many investigators have studied, in detail, all aspects of nitrocellulose manufacture, properties and end use. Unfortunately, integration of these specific studies into a clear and concise picture of how nitrocellulose properties influence end product performance is absent. This is especially true in regard to manufacture of military gun propellants.

A plethora of literature can be cited that relates polymeric properties such as molecular weight (MW), molecular weight distribution (MWD), crystallinity, inter and intra-chain interactions and chemical properties to end product mechanical properties. It is not the intention of the author to reiterate these relationships, however, some key examples will be discussed and an attempt will be made to link some of the most important polymeric properties of nitrocellulose, using appropriate examples from the literature, to end product performance of modern gun propellants.



The first nitrocellulose, nitrated paper, was prepared by Theophile Jules Pelouze, a French chemist, in 1838. In 1845, a German chemist, Christian F. Schoenbein produced the first guncotton. Two years later in 1847, Schoenbein and another German, R. Boetter, obtained patents for preparation of guncotton. Approximately 40 years later, in 1884, smokeless gunpowder was invented by Paul Vieille of France (5).

The first plastic was produced by John Westely Hyatt in 1868 by mixing nitrocellulose and camphor (6). Since then, the use of nitrocellulose in commercial plastics has been largely discontinued due to its inherent flammability and the advent of higher performance materials (3). Nitrocellulose is still produced in large quantities for use in coatings and films.

Nitrocellulose has been a major component of military gun propellants and explosives for over 100 years (5). This longevity is a result of the desirable properties of nitrocellulose which include energetics, stability, mechanical properties and abundant, relatively cheap, raw materials. The raw material used in the production of nitrocellulose is cellulose.

To illustrate the complexity of nitrocellulose chemistry, the inherent difficulties of nitrocellulose characterization and how subtle changes in nitrocellulose properties may influence propellant properties, it is necessary to discuss, cellulose chemistry, cellulose purification, nitrocellulose manufacture and propellant processing. These factors will be discussed, only, in sufficient detail to convey the thrust of the current paper. Voluminous references are available on each of these areas.

Cellulose is the most abundant structural polysaccharide produced by plants. The empirical formula for cellulose is  $(C_6H_{10}O_5)_n$ . Cellulose is a linear polymer made up of repeat units of  $\alpha$ -D-glucopyranose, more commonly known as anhydroglucose, in the  $\beta$ -(1-4) linkage (7). The chemical structure of cellulose is shown in Figure 3.1. The  $-CH_2OH$  and  $-OH$  groups are in the equatorial positions relative to the plane of the anhydroglucose rings (8). The degree of polymerization (DP) of native and purified cellulose, as well as the resultant molecular weights are displayed in Table 3.1. Comparison of DP for native cellulose relative to purified chemical cotton or wood pulp clearly shows that the process used to purify cellulose causes chain scission.

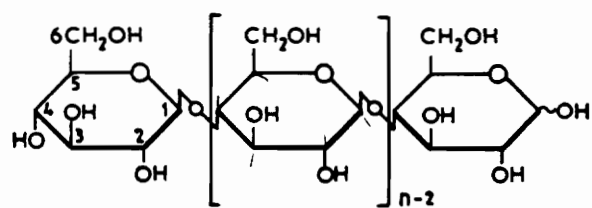


FIGURE 3.1  
Chemical Structure of Cellulose

TABLE 3.1

Molecular Weight and Degree of Polymerization Range  
for Cellulose

<u>Cellulose Type</u>	<u>MW Range (g/mole)</u>	<u>DP Range</u>	<u>Ref.</u>
Native cellulose	600,000 - 1,500,000	3,500 - 10,000	4
Chemical cottons	80,000 - 730,000	500 - 4,500	4
Wood pulps	80,000 - 340,000	500 - 2,100	4
Native cellulose	----	14,000	8
Purified cellulose	----	2,500	8

### 3.1 Microstructure of Cellulose

Cellulose is a semicrystalline material ,e.g., some areas of the cellulose fiber are crystalline in morphology and other areas are amorphous (9,10). Table 3.1.1 summarizes the approximate content of amorphous material in cellulose as determined by several different techniques. Values in Table 3.1.1 are approximate values taken from published literature (15). This data indicates that in all cases, regardless of the measurement technique, that cotton cellulose is more crystalline than wood pulp cellulose. Several investigators have explored the morphological properties of cellulose using X-ray diffraction (11,12,13,14). Prask and Choi (13) determined crystallinity of cellulose from several different sources of cotton and wood pulp using X-ray diffraction. Examination of the data in Table 3.1.2 reveals that cellulose crystallinity varies as a function of manufacturer and source, not only as a function of biological origin. Recent data published by Hofmann, et al, is in agreement with this idea of varying crystallinity as a function of cellulose source (14).

Prask and Choi also surmised that the degree of crystallinity of cellulose influences the nitratability, and subsequently the properties of the resultant nitrocellulose. This is in agreement with the postulate of Nevell and Zeronian (8), where the esterification (in this case nitration) of cellulose is a heterogeneous reaction for two reasons; solid cellulose is suspended in a liquid reaction medium, and cellulose itself is heterogeneous due to its semicrystalline nature. Nevell and Zeronian go on to say that this heterogeneous reaction mechanism results in a heterogeneous product with respect to the degree of substitution (DOS), especially since nitrocellulose is never produced, on a commercial scale, with a complete conversion of all hydroxyl functionality to nitrate ester groups. See Chapter 4 for explanation of DOS.

TABLE 3.1.1

Percentage of Amorphous Material in Various Celluloses (16)

<u>Technique</u>	<u>Cotton</u>	<u>Wood pulp</u>
X-ray diffraction	27	40
Density	36	50
Deuteration	42	55
Moisture regain (sorption)	42	49



TABLE 3.1.2

Percent Crystallinity of Cellulose from Several Different  
Sources as Measured by X-ray Diffraction (13)

<u>Cellulose type</u>	<u>Source</u>	<u>Percent Crystallinity</u>
cotton	Buckeye	49.1 +/- 2.0
cotton	Hercules	50.8 +/- 1.5
cotton	Hercules NS 70	44.1 +/- 1.6
wood pulp	Fortisan	35.1 +/- 2.2
wood pulp	Alaska	36.0 +/- 1.7
wood pulp	Ga.Pacific Puget 92	32.4 +/- 2.0
wood pulp	I. P. C. BH-C	35.4 +/- 1.9
wood pulp	Buckeye N-7	37.2 +/- 2.0
wood pulp	Buckeye N-5	32.3 +/- 2.1
wood pulp	Buckeye E-1	43.2 +/- 2.3
wood pulp	Buckeye V-12	26.7 +/- 3.3

### 3.2 Macrostructure of Cellulose

It is apparent from the previous discussion that there is diversity in the microscopic properties of cellulose. These microscopic properties, such as crystallinity, are important in determining the properties of nitrocellulose. To further appreciate the complexity of the characterization of nitrocellulose, one needs to address the macroscopic properties of cellulose. As earlier stated, cellulose is a product of biosynthesis in plants. Many references are available, mostly from the paper and textiles industry, that treat, in detail, the biochemistry of cellulose synthesis. Suffice to say that cellulose fiber architecture is quite complex and that each cellulose fiber is made up of many bundles of cellulose molecules. These bundles of cellulose molecules are usually referred to as fibrils. Figure 3.2.1 shows the basic structural features of both wood pulp and cotton fibers (17). References (7,8,9,10) discuss cellulose fiber structure in detail. The important point to consider about cellulose fiber structure is that in order to chemically modify cellulose, the reactants have to penetrate the fiber and the fibril networks to access the hydroxyl groups. This idea reinforces the notion that cellulose derivatives, nitrocellulose in particular, are heterogeneous with respect to the DOS.

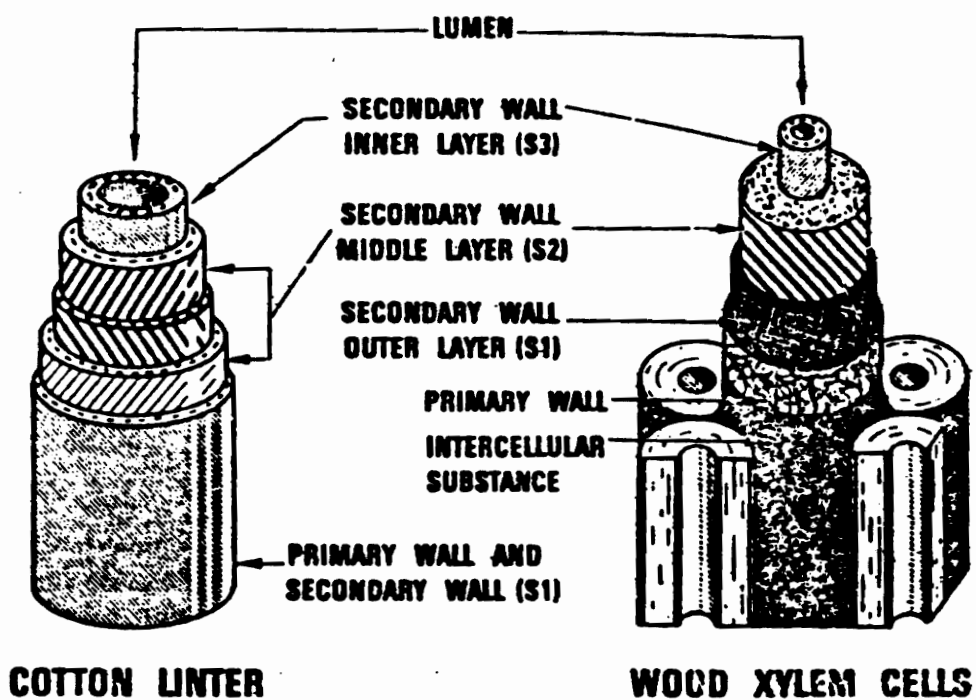


FIGURE 3.2.1

Model of Basic Cell Structures of Cotton and Wood Cellulose

(17)

### 3.3 Purification of Cellulose

Cellulose used in the manufacture of commercial materials and gun propellants is obtained from cotton linters and wood pulp. Both types of raw cellulose require some purification prior to nitration.

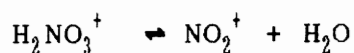
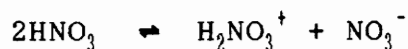
Purification of cotton linter cellulose begins with a mechanical cleaning operation to remove dirt and other contaminants. The cleaned linters are then pressure digested in dilute sodium hydroxide solution. This digestion step removes impurities such as waxes, proteins and other carbohydrates. Finally, the linters are bleached in a hypochlorite solution. Process control parameters such as temperature and solution strength are adjusted during both digestion and bleaching, to obtain the required viscosity or DP (18).

Cellulose from wood is subjected to a pulping mill for particle size reduction prior to the purification process. After pulping, the cellulose is digested in a cooking liquor, much like cotton cellulose, to remove impurities and reduce the DP. Two types of cooking liquors used to digest wood pulp are ; **sulfite**, which consists of a solution of sulphur dioxide and calcium bisulfite, and **sulfate**, which consists of a solution of sodium hydroxide, sodium sulfate and sodium

carbonate. The sulfate process is also known as the Kraft process. A bleaching step, similar to the cotton purification scheme, completes the wood pulp cellulose purification (19).

## Chapter 4      Manufacture of Nitrocellulose

Nitrocellulose is produced by the reaction of cellulose with mixtures of nitric acid, sulfuric acid and water in a reversible process, i.e.; if nitrocellulose with a high DOS is immersed in an acid mixture that would produce a lower DOS at equilibrium then the nitrocellulose will be denitrated to the equilibrium level (20,21). It has recently been determined by Munro, et al, that the nitrating species in nitrocellulose production is the nitronium ion  $\text{NO}_2^+$  (22). The nitronium ion is produced by the following scheme:



Extent of the reaction is gauged by the degree of substitution or as previously referred to, DOS. Complete substitution of all the hydroxyl groups on each anhydroglucose ring would result in a DOS of 3.0. Complete substitution is only accomplished under careful laboratory conditions (23). The relationship of DOS and weight percent nitrogen is portrayed graphically in Figure 4.1.

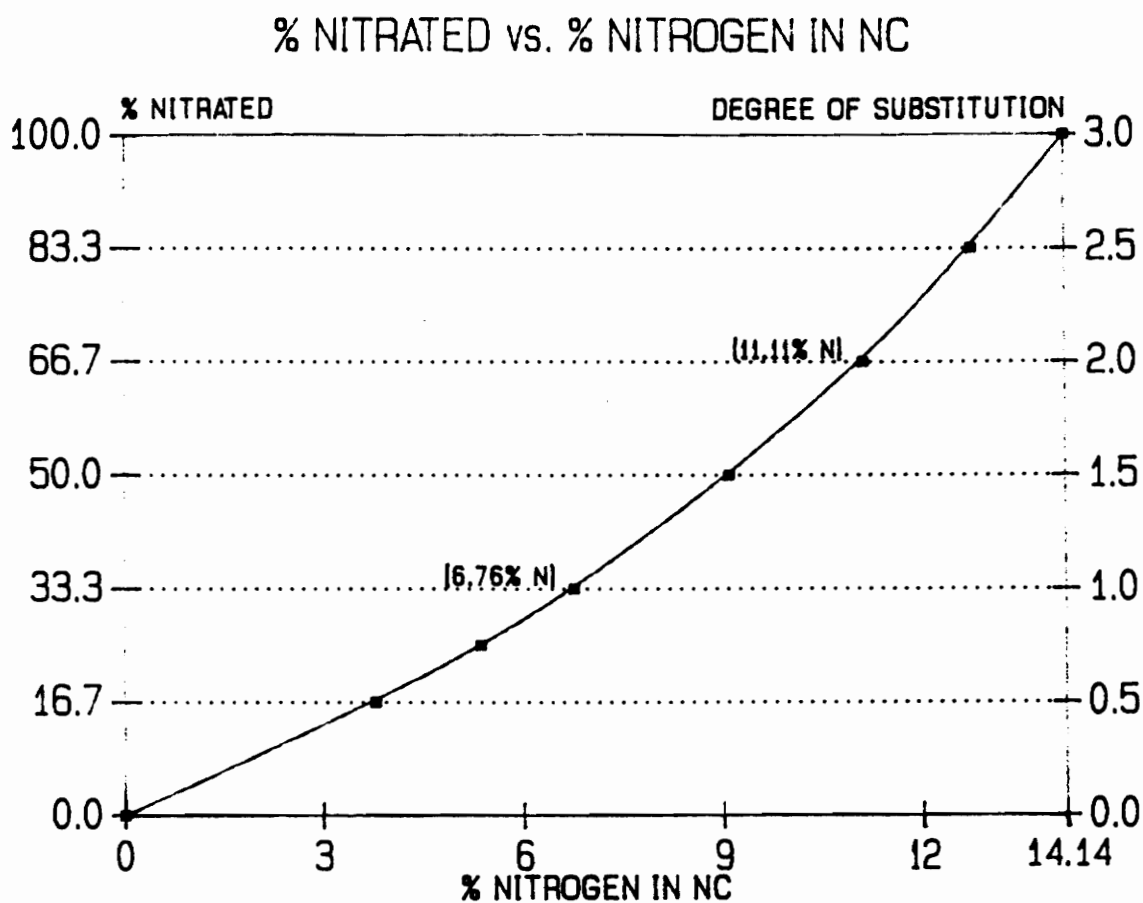


FIGURE 4.1  
Graphical Comparison of Degree of Substitution  
and Weight Percent Nitrogen (24)

Nitrocellulose used in the manufacture of gun propellants has a DOS range from 2.1 up to a maximum of 2.7. This corresponds to 11.4 to 13.5 percent nitrogen by weight (25). The useful DOS range for the production of lacquers and coatings is approximately 1.8 to 2.3, or 10.5 to 12.4 percent nitrogen by weight (26).

It is necessary to carefully remove all traces of acid from the nitrocellulose after nitration. This purification is accomplished in several steps which include, acid boil, fiber size and agglomerate reduction by further pulping or cutting, mild alkali boil, and finally, several washings in fresh water. The resultant purified nitrocellulose is then kept wet with water or alcohol (ethyl or isopropyl) as a safety precaution (27).



## **Chapter 5      Gun Propellant Manufacture and Mechanical Properties**

### **5.1          Background**

Nitrocellulose is the major constituent of modern gun propellants. Modern gun propellants can be divided into three different groups, referred to as single, double and triple-base propellants. Single-base propellants consist of nitrocellulose and a small fraction of stabilizer plus an inert, non-energetic plasticizer. Double-base propellants contain all ingredients of single-base with the addition of nitroglycerine as an energetic plasticizer. Finally, triple-base propellants contain all the ingredients of double-base with the addition of a solid energetic oxidizer (28).

### **5.2      Gun Propellant Manufacture**

Propellants are manufactured by two different processes. The most common process is called the solvent process. In the solvent process, nitrocellulose is partially dissolved or gelled by volatile solvents, usually mixtures of ethanol and diethyl ether or ethanol and acetone. Some European manufacturers use a mixture of acetone and water as the solvent system. The other process is known as the

solventless process. In the solventless process the nitrocellulose is plasticized by heat and mechanical work, i.e., in the solventless process, the material is treated as a thermoplastic (29). In both processes the propellant is ultimately extruded into the desired geometry for particular applications. The extrudate is commonly referred to as grains. During the extrusion process, significant molecular and supramolecular alignment occur which causes the grains to be anisotropic. For brevity, propellant properties discussed in the remainder of this paper will be confined to those propellants manufactured using the solvent process.

### 5.3 Gun Propellant Mechanical Properties

Since nitrocellulose is the only polymeric material in the majority of modern gun propellants, the properties of nitrocellulose determine, to a large extent, the mechanical properties of these propellants. It is well known in the industry that nitrocellulose in propellants exists in a semicrystalline state (17). A significant portion of the nitrocellulose in any given propellant formulation is fibrous which serves to reinforce the grain structure. This can easily be determined by microtoming a propellant grain and examining the resultant cross-section under the optical

microscope. Dissolved or amorphous nitrocellulose, which in most cases is plasticized, fills the space between the fibers and is often referred to as the glue or adhesive that holds the fibers together. Nitrocellulose based propellants are, therefore, heterogeneous on the microscopic scale and could more accurately be classified as fiber reinforced composites. This fact leads the author to believe that most of the classical methods of polymer characterization that have been applied to nitrocellulose, although of great academic interest, are of little practical utility to the propellant manufacturing industry for prediction of mechanical behavior of propellants. It would be a much simpler task to predict propellant mechanical properties if propellants were isotropic homogeneous glasses.

Two unanswered problems confront the propellant processing community, simply stated these problems are; under normal established operating conditions, some of the propellants intermittently fail to mix and extrude well, and even though the propellants may have processed well, they may fail to retain their shape or physical integrity under the mechanical stresses of gun firing.

Propellant mechanical failures usually occur when the propellants are conditioned at low temperature, approximately

-40°C, prior to gun firing. Reported glass transition temperatures ( $T_g$ )s for nitrocellulose range from 53 to 66°C (30). Balcells (31) used dynamic mechanical thermal analysis (DMTA) to measure the mechanical properties of various nitrocellulose and polymer blends in an attempt to identify plasticizers that might broaden and lower the  $T_g$  of nitrocellulose plasticizer blends and hence improve the low temperature mechanical properties, especially the fracture toughness of propellants.

The role of plasticizers is to increase the free volume of the polymer system and thus, in simple terms, allow the polymer chain segments more room for motion, which dissipates mechanical energy (32). Balcells used the dampening factor, also known as  $\tan \delta$ , to estimate the location and breadth of the  $T_g$  region.  $\tan \delta$  is a measure of the ratio of the mechanical energy that is dissipated by heat to the mechanical energy that is stored in the material in a dynamic mechanical experiment (33). Thus,  $\tan \delta$  is a method of measuring the ability of the material to dissipate mechanical energy. The temperature at maximum  $\tan \delta$  is usually taken to be the  $T_g$ . Profound changes in the mechanical response of materials occur at the  $T_g$  (34). Typical results of Balcells' DMTA experiments on nitrocellulose and plasticizer blends are displayed in

Figure 5.3.1. The instrumental frequency of each of the reported mechanical spectra was 1 Hz. From this work, it can be concluded that the  $T_g$ , even at relatively high plasticizer levels, is much higher than the low temperature extreme for gun testing.

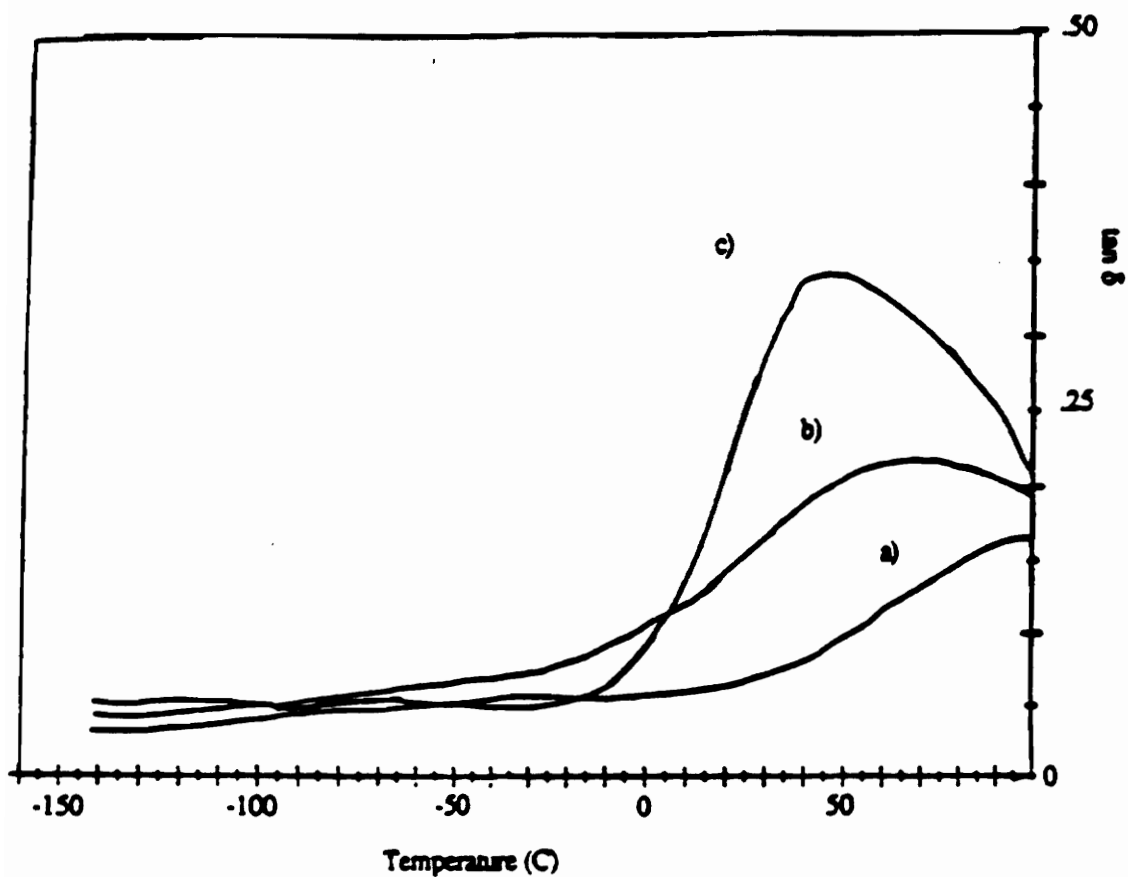


FIGURE 5.3.1

Tan  $\delta$  verses Temperature Plot for Blended Nitrocellulose Films with (a). 5 wt/wt % Plasticizer (b). 15 wt/wt % Plasticizer (c). 40 wt/wt % Plasticizer (31)

Since plasticized nitrocellulose systems (propellants) are known to be viscoelastic in nature (35), it is necessary to examine the mechanical response at strain rates that are expected in the end use. Fong, at el, applied high rate strains using a modified Hopkinson bar to cast double-base propellant samples. The propellant composition was 42:46 weight percent nitrocellulose - nitroglycerine. It is assumed that the remainder of the formulation is stabilizer and an inert plasticizer. The impact velocity of the bar was between 12 to 14 m/sec. The mechanical response of the propellant is depicted in Figure 5.3.2. It can easily be seen that the propellant response to the applied load changes dramatically with temperature. As expected, the propellant displays a relatively high modulus, brittle response at low temperatures, and dissipates more of the applied load at the higher test temperatures. There appears to be a large change in the propellant response between  $-40$  and  $-20^{\circ}\text{C}$  which may be indicative of a  $T_g$  at this strain rate.

Fong, at el, also employed dynamic mechanical analysis (DMA) to determine the temperatures where relaxations occur in double-base propellant. Three relaxation temperatures were reported,  $T_a$ ,  $T_b$  and  $T_c$ . The highest relaxation temperature,  $T_a$ , is associated with the  $T_g$  while the other two are called

secondary loss peaks. Since they did not report a frequency for the DMA tests, it is assumed that their work was at a relatively low frequency, 60 to 1 Hz. as reported by others applying DMA to double-base propellants. The reported  $T_g$  from DMA is  $11^\circ\text{C}$ . Since the DMA experiments were conducted at a lower strain rate, or in this case frequency, than the Hopkinson bar test, the  $T_g$  would be expected to be higher. Therefore, the earlier estimation of the  $T_g$  from the Hopkinson bar test is probably in the correct range.

Warren and Townend (36) studied the relaxations in double-base propellants that had a nitroglycerine content of 10, 35 and 60 weight percent. They also found three thermal relaxations using DMA. Thermal relaxation temperatures for double-base propellants are displayed in Table 5.3.1. The  $T_g$  data reported by Fong, et al, is not in good agreement with the data of Warren and Townend. This discrepancy may be a result of sample history, since Warren and Townend experimented with extruded samples and Fong, et al, used cast samples.

Warren and Townend believe that the low temperature  $\gamma$  relaxation at about  $-80^\circ\text{C}$ , which is only found in pure nitrocellulose or low nitroglycerine content propellants, is due to motion of the pendent nitrate groups. They also



surmise that the  $\beta$  relaxation, which is also a function of the nitroglycerine content, is due to motion of segments of the nitrocellulose chains which are associated with nitroglycerine. The  $\alpha$  relaxation was also dependent on the nitroglycerine content. However, during further experimentation using differential scanning calorimetry (DSC) and thermal mechanical analysis (TMA), they were unable to detect a change in heat capacity or thermal expansion coefficient at  $T_g$ . The expected discontinuities in the expansion coefficient and heat capacity were measurable for the  $\gamma$  and the  $\beta$  relaxations. Warren and Townend did not speculate on the process responsible for the  $\alpha$  relaxation.

Baker, et al, (37) determined that nitrocellulose morphology does influence the processibility and end product mechanical properties of double-base propellants. In the work of Baker, et al, nitrocellulose derived from wood pulp and cotton linters was used to produce several different lots of double-base propellant. Interestingly, the nitrocellulose from wood pulp had a molecular weight of 220,000, while the cotton linter nitrocellulose was lower at 167,000 g/mole. Molecular weights were determined by viscosity measurements. In process, rheological measurements were used to address processibility. The significance of this work to the present discussions is the DMA of the resultant propellants.

Baker, et al, found that the extruded double-base propellants had two relaxation processes which correspond with the temperature range of the previously discussed  $\alpha$  and  $\beta$  peaks. Since they did not observe the low temperature  $\gamma$  peak, it is assumed that the propellants contained a significant portion of nitroglycerine, which would agree with the findings of Warren and Townend (36), see Table 5.3.1. Baker and coworkers found that the position and amplitude of the  $\alpha$  peak was influenced by nitrocellulose type and rate of extrusion, while the  $\beta$  was not affected by these variables. They also found that annealing the propellant at 80°C prior to DMA irreversibly altered the  $\alpha$  process. It was concluded that the  $\alpha$  process is a function of the remaining nitrocellulose fibers in the extruded propellants and that the changes associated with annealing occur from molecular relaxations of stress fields created during extrusion.

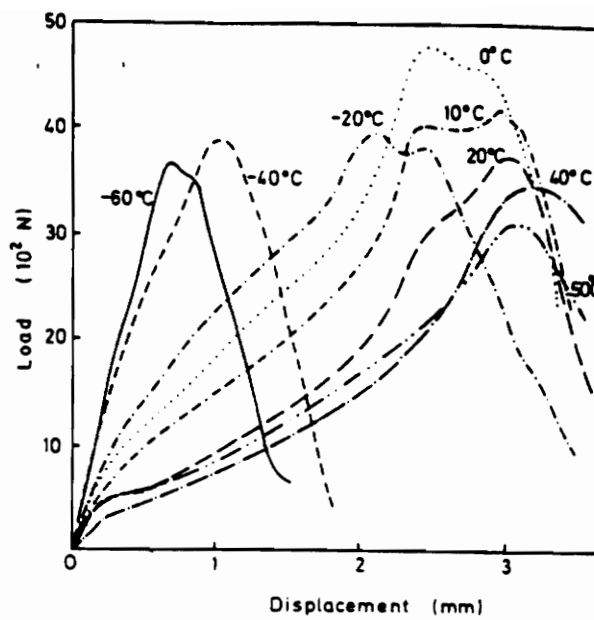


FIGURE 5.3.2

Mechanical Response of Double-Base Propellant  
Under High Strain Rate (35)

TABLE 5.3.1  
Results From Dynamic Mechanical Analysis of  
Double-Base Propellant

Thermal Transitions for Double-base Propellant				
Nitroglycerine	Thermal Relaxation Temperature			
Content	Range °C			
<u>weight percent</u>	$T_{\alpha}$	$T_{\beta}$	$T_{\gamma}$	<u>Ref.</u>
0	140	0	-80	36
10	110	-15	---	36
35	90	-23	---	36
46	11	-35	-100	35
60	55	-33	---	36

Many references are available that correlate the relaxation properties of simple isotropic amorphous polymeric materials with mechanical properties and fracture toughness. Generally, the position and magnitude of the  $\beta$  relaxation as measured by  $\tan \delta$  is related to fracture toughness. Unfortunately, nitrocellulose propellants are rather complicated in morphology and sufficient data to correlate dynamic mechanical properties with fracture toughness and subsequently ballistic performance is lacking. It is the opinion of the author that the morphological complexity and different molecular relaxation mechanisms of plasticized nitrocellulose propellants cause the system to be thermorheologically complex which will disallow application of simple time temperature superposition principles. This means that mechanical testing of propellants needs to be performed at the high strain rates that would be expected in the end use environment. This complexity is most likely the reason that no references are available that show the complete relationship of dynamic mechanical properties of propellants to propellant ballistic performance.

Since mechanical investigations of nitrocellulose propellants have not resulted in satisfactory explanations of why some propellants fail ballistically, many investigators have attempted to address these problems through rigorous characterization of nitrocellulose. The next chapter will introduce the best of the nitrocellulose characterization efforts and an attempt will be made to integrate the findings in order to better understand how nitrocellulose properties may cause propellant failures.

## Chapter 6 Nitrocellulose Characterization

### 6.1 Background

Literally hundreds of attempts to characterize nitrocellulose are present in the literature. Perhaps the oldest method of characterization, which is still used today, is solubility. Nitrocellulose solubility data is used to predict, subjectively, the ratio of fibrous to amorphous nitrocellulose content in finished propellant grains. Viscosity of nitrocellulose in solution is probably the second oldest characterization method. These viscosity measurements are used to estimate, again subjectively, the molecular weight of the nitrocellulose and therefore hint at processibility and end product mechanical properties. More modern methods of polymer characterization, such as gel permeation chromatography and low angle laser light scattering have recently been brought to bear on this complex problem. The author will attempt to explain the basis of how each of these techniques contribute to the overall problem of nitrocellulose characterization.

## 6.2 Solubility Studies of Nitrocellulose

Many general references are available that describe the solubility characteristics of nitrocellulose in the preferred solvents for propellant manufacture. It is well accepted that the solubility is a function of the molecular weight and DOS of the particular nitrocellulose samples (38).

Nitrocellulose with an average nitrogen content less than approximately 10.5 percent is only slightly soluble in a mixture of diethyl ether and ethanol (2 to 1 by volume). If the average nitrogen content is in the range of 10.5 to 12.8 percent, under the same conditions it is completely soluble. At the extreme of high nitrogen content, above 12.8 percent, the nitrocellulose becomes only sparingly soluble. Pure ethanol can only dissolve nitrocellulose with an average nitrogen content of less than 11.0 percent nitrogen. Likewise, acetone alone can only dissolve nitrocellulose of average nitrogen content of greater than 10.0 percent nitrogen (39).

Hammond and Warren (40) conducted experiments to address the solubility differences between nitrocellulose made from wood and cotton cellulose. They claim that there are solubility differences as a result of different fibrous and crystalline properties between the two starting materials.



They also claim that the original fibrous structure of cellulose is not destroyed during the nitration reaction. This is in agreement with the findings of Herzog and Londberg (41) [taken from Urbanski (20)]. Herzog and Londberg found that a carefully nitrated and subsequently denitrated nitrocellulose resulted in cellulose of roughly the same crystalline properties as the starting material. This was determined by X-ray diffraction measurements. Results from the two previously discussed references (40,41) support the importance of the macro and microstructural features of cellulose. Attempts will be made in a later chapter to show how these findings correlate with results from viscosity and molecular weight determination studies. Also, the influence of cellulose and nitrocellulose morphology on gun propellant performance properties will be clarified.

As further evidence for the chemical heterogeneity of nitrocellulose, Abadie (38) fractionally precipitated nitrocellulose from solution and determined the average nitrogen content of each fraction. Results from Abadie's work are graphically displayed in Figures 6.2.1 , 6.2.2 and 6.2.3. These figures show that nitrocellulose from sulfite treated wood pulp has a wider distribution of nitrogen substitution than nitrocellulose from wood pulp purified using

the sulfate process and finally that nitrocellulose from cotton cellulose has a very narrow distribution of nitrogen substitution. These results are not in complete agreement with the ranking of breadth of nitrogen substitution that might be expected from the X-ray diffraction data from Prask and Choi (13). They reported that wood cellulose from the sulfate process has a much more variable degree of crystallinity than pulp from the sulfite process.

It appears to be the opinion of most researchers that the easier diffusion of the nitrating agents in the more loosely packed amorphous areas may lead to locally high percentages of nitrogen and likewise, the more crystalline areas would be of generally of lower nitrogen substitution. Using this logic, one would think that cellulose with a wider distribution of percent crystallinity would display a broader distribution of nitrogen substitution. The only reasonable disagreement with the idea of heterogeneous DOS in the nitration reaction being caused by differences in the ability of the nitronium ion to diffuse in the crystalline verses the amorphous regions is the work of Clark (42). Clark used electronic spectroscopy for chemical analysis (ESCA) to interrogate the surface of nitrocellulose during nitration. He first concluded that the nitronium ion diffuses into the bulk very quickly and effects

a nearly homogeneous reaction. However, realizing that the nitration reaction in mixed acid (nitric, sulfuric acid) requires that the sulfuric acid also diffuse, he monitored the diffusion of the larger sulfate ion, indirectly, by measuring the concentration of the sulfate ester on the surface versus the bulk. He found that the larger sulfate ion does not diffuse into the bulk as easily as the smaller nitronium ion, and that this difference may be the cause for heterogeneous DOS in nitrocellulose.

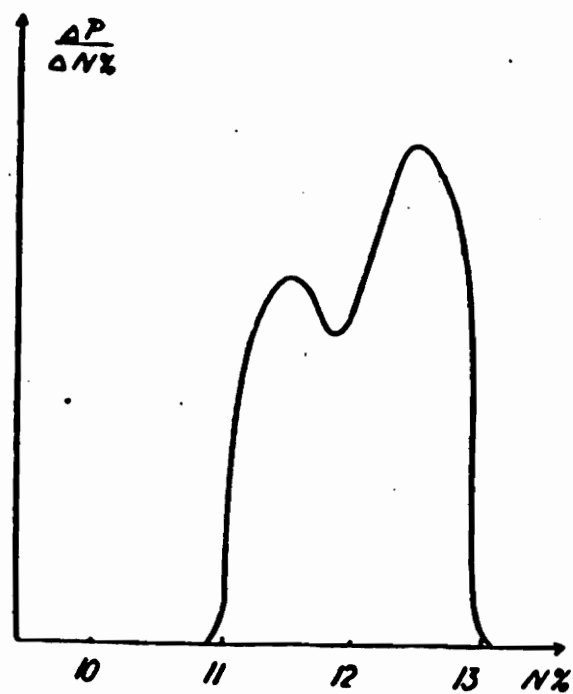


FIGURE 6.2.1  
Nitrogen Distribution for Nitrocellulose  
from Sulfate Pulp (38)

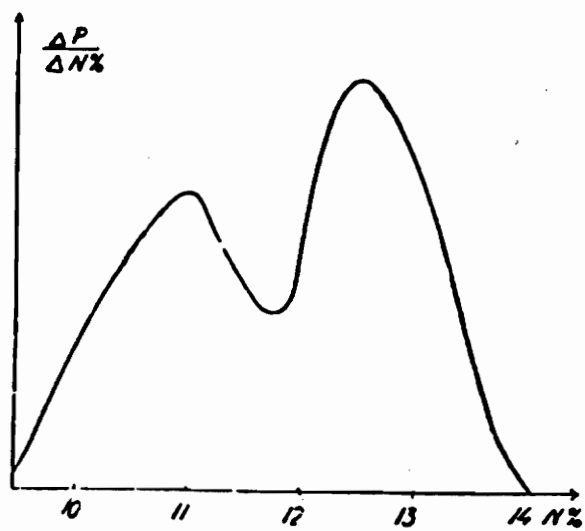


FIGURE 6.2.2  
Nitrogen Distribution for Nitrocellulose  
from Sulfite Pulp (38)

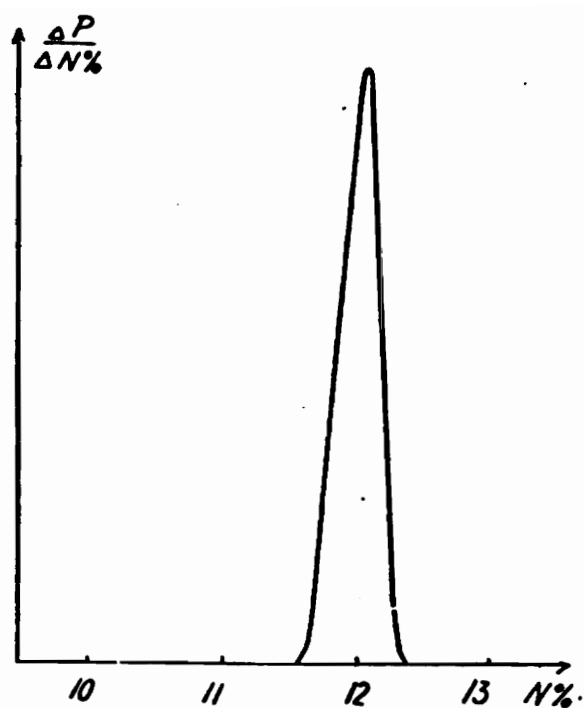


FIGURE 6.2.3  
Nitrogen Distribution for Nitrocellulose  
from Cotton Cellulose (38)

Data presented in this section further corroborates the idea of chemical (DOS) as well as molecular weight heterogeneity within nitrocellulose samples. Arguments will be presented in a later chapter on how these heterogeneities contribute to the complexity of nitrocellulose characterization and manufacture of acceptable gun propellants.

### 6.3 Viscosity Studies of Nitrocellulose

Viscosity is a measure of resistance that a fluid offers to an applied shearing force. The normal representation for viscosity is  $\eta$  (eta). A more specialized type of viscosity measurement is called intrinsic or limiting viscosity, represented as  $[\eta]$ . Intrinsic viscosity measurements require that several specific viscosity measurements be made on a series of low concentration solutions. The resultant specific viscosities are then plotted as a function of concentration. In the limit of low concentration the plot yields a linear relationship. Intrinsic viscosity is then obtained by extrapolation to zero concentration of the solute. This relationship is shown mathematically below (43).

$$[\eta] = \lim_{c \rightarrow 0} \frac{1}{C} \frac{(\eta - \eta_0)}{\eta_0}$$

Equation 6.3.1

Intrinsic viscosity can be related to the molecular weight of polymers through the Mark-Houwink-Sakurada (MHS) equation, shown below, where K and a are constants that depend on the polymer type and polymer solvent interaction.  $M_v$  is known as the viscosity average molecular weight which is generally taken to be close to the weight average molecular weight,  $M_w$ .

$$[\eta] = K \overline{M_v^a}$$

Equation 6.3.2

It is well accepted that polymer solutions are non-Newtonian. This means that the viscosity is not constant



as a function of the shear rate, but decreases as shear rate increases. To compensate for this shear rate dependence, researchers generally measure the intrinsic viscosity at several different shear rates and then extrapolate these values to zero shear rate. This is shown mathematically below.

$$[\eta] = \left( \frac{\eta_{sp}}{C} \right) \lim_{C \rightarrow 0, \dot{\gamma} \rightarrow 0}$$

Equation 6.3.3

Marx-Figini and Gonzalez recently published work on intrinsic viscosity measurements on nitrocellulose (44). They performed a series of rheological measurements to determine the dependence of the intrinsic viscosity of nitrocellulose in ethyl acetate at constant DOS on; concentration of nitrocellulose, DP of nitrocellulose and shear rate. Data from (44) is reproduced in Figures 6.3.1 below. These plots show that in order to obtain linear experimental results during intrinsic viscosity measurements on nitrocellulose, one would need to perform experiments at low shear rates and concentrations, especially if the subject nitrocellulose is of high DP.

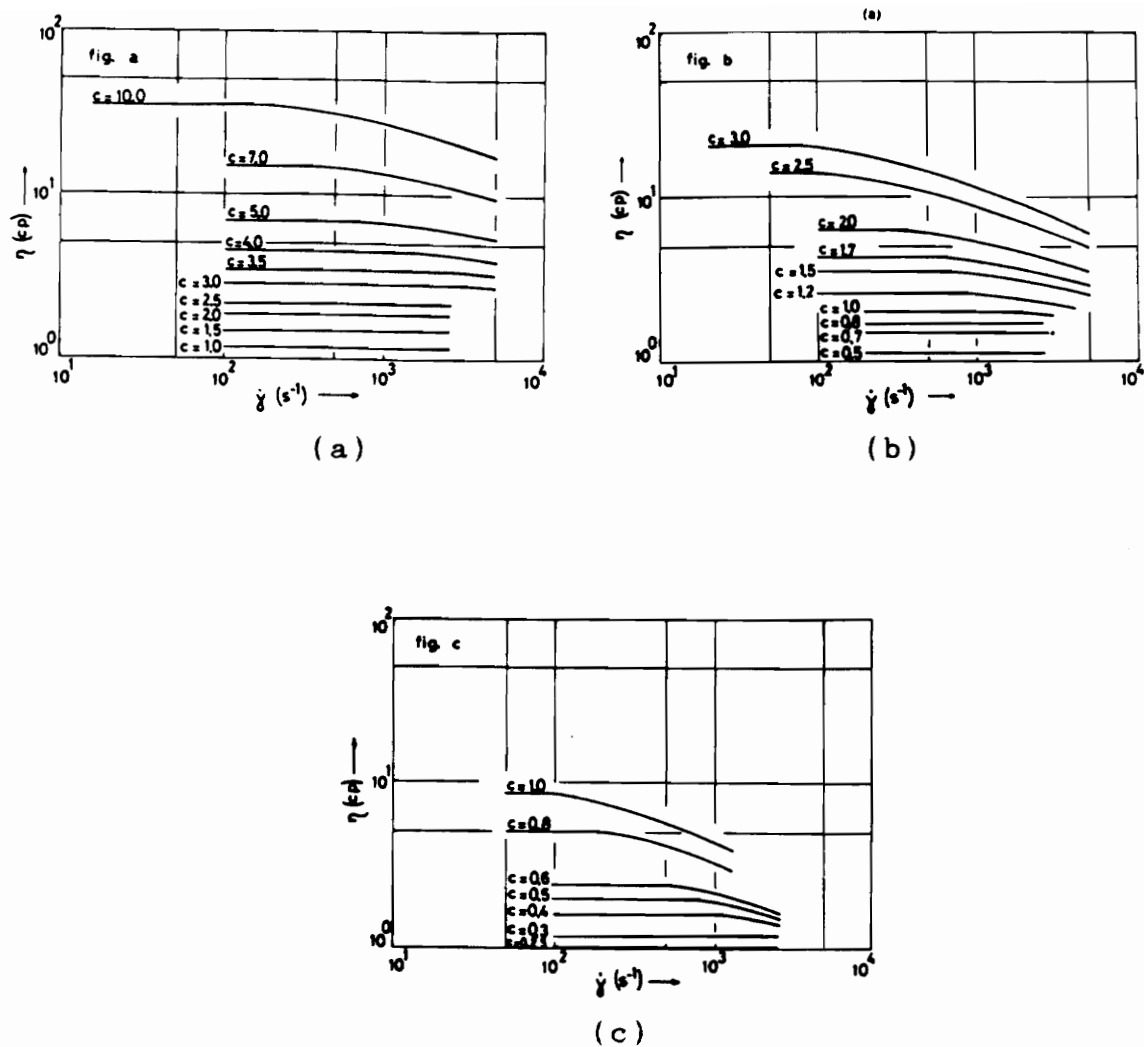


FIGURE 6.3.1

Intrinsic Viscosity versus Shear Rate for Nitrocellulose in Ethylacetate [ $C$  given in (g/mL)  $\times 10^3$ ]. (a).  $DP_n = 734$ ; (b).  $DP_n = 1874$ ; (c).  $DP_n = 5400$  (44)

Viscosity measurements are used in the propellant manufacturing industry as a process control parameter. Generally, process control viscosity measurements are performed on relatively concentrated solutions, approximately 10 percent nitrocellulose by weight, using the falling ball method. Nitrocellulose used in propellant manufacture is generally of higher viscosity than nitrocellulose for lacquer and coating applications.

Low viscosity nitrocellulose is used in lacquer formulations to maximize the solids loading and minimize the volatile solvents necessary for spray applications. Low viscosity nitrocellulose is produced by digestion after nitration (4,26).

## **6.4 Molecular Weight Determination**

### **6.4.1 Methodology**

Gel permeation chromatography (GPC) is the method of choice for determination of molecular weight (MW) and molecular weight distribution (MWD) of polymeric materials. GPC is generally less time consuming and labor intensive than other methods.

Viscosity MW determinations of nitrocellulose were

discussed in the previous section. It is clear from the data presented that viscosity MW determinations are time consuming and subject to experimental error. Also, viscosity methods only determine the  $M_v$  and give no information on MWD.

Low angle laser light scattering (LALLS) is also used to determine the  $M_v$  of polymers as well as information about the molecular conformation in solution (45,46,47). Here again, no information is obtained about the MWD. Several investigators have applied LALLS to the characterization of nitrocellulose. The most notable of this work was reported by Holt, et al, (45). Holt and co-workers used LALLS, fractionation, infra-red spectroscopy, membrane osmometry and ultracentrifuge measurements to study the molecular configuration of nitrocellulose in solution. Pertinent results from their work will be discussed in section 6.4.2.

Membrane osmometry measures colligative properties of the solution; i.e., the number of molecules of solute, therefore measuring the number average molecular weight ( $M_n$ ). Membrane osmometry is difficult to perform on nitrocellulose due to the relatively high molecular weights of nitrocellulose and resultant high concentrations required to obtain a large number of molecules in solution. The following equation illustrates the technique used to obtain  $M_n$  from osmometry.

$$\lim_{C \rightarrow 0} \frac{\pi}{C} = \frac{RT}{M_n}$$

$$\pi = \rho hg$$

Equation 6.4.1

It can easily be seen from equation 6.4.1, where  $\pi$  is the osmotic pressure, that low solute concentrations would yield small differences in column height (h) for measurement.

Fractionation is probably the oldest and most time consuming method of determining MW and MWD. Two general methods of polymer fractionation may be applicable to nitrocellulose. These two methods are fractional precipitation and fractional solution. Fractional precipitation is accomplished by dissolving the polymer in a good solvent and reducing the solvent power by 1. adding a nonsolvent to the system, 2. changing the temperature to reduce the solvent power, or 3. evaporating the solvent until precipitation occurs. In this method, the fraction with the highest molecular weight precipitates first (48).

Fractional solution is accomplished in the reverse of this process. In fractional solution, the finely divided solid polymer is subjected to relatively weak solvent systems first, so that only the lowest molecular weight fraction is dissolved. After removal of the lowest molecular weight fraction, a more powerful solvent system is applied and higher molecular weight fractions dissolve. A more convenient method to accomplish this type of fractionation is to apply the solid polymer to the top of a column packed with an inert filler and add a progressively more powerful solvent system while collecting fractions (49).

Since nitrocellulose is a semicrystalline polymer and the crystallites would be much slower to dissolve than the amorphous areas, fractional precipitation would probably give a much cleaner separation.

In either case, fractionation must be done in a very slow and time consuming fashion so that equilibrium is established at each step (48). A more problematic attribute of fractionation is the fact that polymers are separated on the basis of solubility, which in the case of heterogeneous polymers, such as nitrocellulose, is a function of distribution of DOS as well as molecular weight.

#### 6.4.2 Molecular Weight Determination of Nitrocellulose

Realizing the limitations and problems associated with the previously discussed methods of molecular weight determination, it becomes even more clear that GPC is the method of choice for nitrocellulose molecular weight analysis.

GPC separates polymers on the basis of hydrodynamic volume. In the GPC experiment, the polymer to be analyzed is dissolved in a suitable solvent system and applied to a column packed with an inert porous gel. These porous gels are highly cross-linked polymers that reproducibly swell in the solvents used in the GPC experiments. The solvent used to dissolve the sample is also used to elute the column. The principal of separation is that the solvent and smaller of the solute molecules are able to freely diffuse in and out of the gel pores while the larger of the solute molecules are excluded from most of the pores and thus spend more time in the moving solvent stream (50). Therefore, in the GPC experiment, the larger of the solute molecules elute first and the smallest molecules elute after a longer period of time.

The use of GPC for molecular weight determination has been a very active area of research for some time and literally thousands of references are available that deal with

a wide range of polymers. Many researchers have applied GPC to nitrocellulose as a way to address the molecular weight properties of cellulose. This is because cellulose is only soluble in exotic solvent systems that form metal chelates and therefore are not compatible with most GPC hardware. Solutions of dimethyl acetamide (DMAC) and 2 % LiCl have been used to dissolve and elute wood pulp cellulose samples in GPC (51) with reasonable results. It is doubtful, however, that this technique could be applied to higher molecular weight cotton cellulose.

There are several examples of application of GPC to nitrocellulose to explore propellant processing problems. Unfortunately, the bulk of available molecular weight data for nitrocellulose is only relative and no good correlations have been made with propellant processing or mechanical properties.

The majority of the investigators attempting to measure nitrocellulose molecular weight using GPC have relied on multiple detectors to interrogate eluting polymer fractions (52,53,54,55,56,57,58). Some of the more rigorous attempts to determine nitrocellulose molecular weight report statically determined molecular weight properties to confirm their GPC results.



All the GPC references listed above made use of some type of concentration measuring detector. The differential refractive index (DRI) detector appeared to be the most prominent method for concentration determinations. Ultra violet or infrared detectors were the second choice. In most cases, the fractions were eluted from the GPC columns into the DRI detector system and then through one of the spectroscopic detectors mentioned above. Variations of the infrared detectors appear to enjoy the widest use in the case of nitrocellulose since the asymmetric nitrate stretching region falls within the infrared frequency range. Thus, using an infrared detector, one can monitor the elution of nitrocellulose fractions based on the nitrate group concentration.

The concentration sensitive DRI and spectroscopic detectors depend on calibration of the GPC column with narrow molecular weight standards to yield a standard curve of molecular weight verses elution time or volume. The polymeric standards used for calibration are usually narrow molecular weight distribution polystyrenes. There is a fundamental problem with application of this universal standard concept, namely, that one assumes that the hydrodynamic volume of the standard polymer at a given

molecular weight is the same as the polymer being analyzed (59). Huang and Barth (57) have applied a mass detector to the GPC analysis of nitrocellulose. The mass detector relies on light scattering of the eluted particles after the eluting solvent is evaporated. The mass detector suffers from the same calibration problem as the concentration sensitive detectors.

Realizing the calibration problems inherent to GPC analysis of nitrocellulose, several investigators have applied a second detector in series with the concentration sensitive detectors that can determine the average molecular weight of the polymer in the eluting fractions. Wirsen (52) used GPC with a LALLS detector to measure the absolute molecular weight of nitrocellulose. Using the concentration of the polymer in each GPC fraction, as measured by the concentration sensitive detector, and determining the average molecular weight of the same fractions by LALLS, Wirsen was able to construct absolute molecular weight distribution curves for nitrocellulose.

During the same time period, Siochi (58) recognized that the science of molecular weight determination of nitrocellulose had many inconsistencies, especially in the area of GPC analysis. She proceeded to perform the most thorough study of molecular weight determination of

nitrocellulose to date. In addition to developing a new method to determine the absolute molecular weight distribution of nitrocellulose, she was able to determine the major reason for previous inconsistencies in GPC analysis.

Siochi performed a series of molecular weight distribution determinations using GPC with a new differential viscometer detector [GPC-DV] (60,61,62) in series with a DRI detector that, like GPC-LALLS, can determine the absolute molecular weight distribution for nitrocellulose. She found that the molecular weight of nitrocellulose was time dependent, e.g., generally the longer the nitrocellulose solutions were stored, up to a characteristic time, the lower the molecular weight. Siochi confirmed the time dependence of nitrocellulose molecular weight using static LALLS and solution viscosity determinations. Figure 6.4.2.1 (58) shows the time dependence of nitrocellulose molecular weight as determined by GPC-DV. She found, generally, good agreement between the trends in molecular weight dependence on time using GPC-DV, LALLS and solution viscosity measurements.

The theories developed on the basis of Siochi's experiments are that nitrocellulose is very difficult to completely dissolve, even in very dilute solutions. This is in agreement with other investigators that suggest that the

morphological properties of cellulose are retained in nitrocellulose, which result in strong polymer-polymer interactions that are very difficult to overcome with solvents. Holt, et al, (45) attributed the persistence of gel-like particles in nitrocellulose solutions to heterogeneous DOS properties of nitrocellulose and that the gel-like particles result from relatively low DOS material that has sufficient hydroxyl functionality remaining for effective hydrogen bonding.

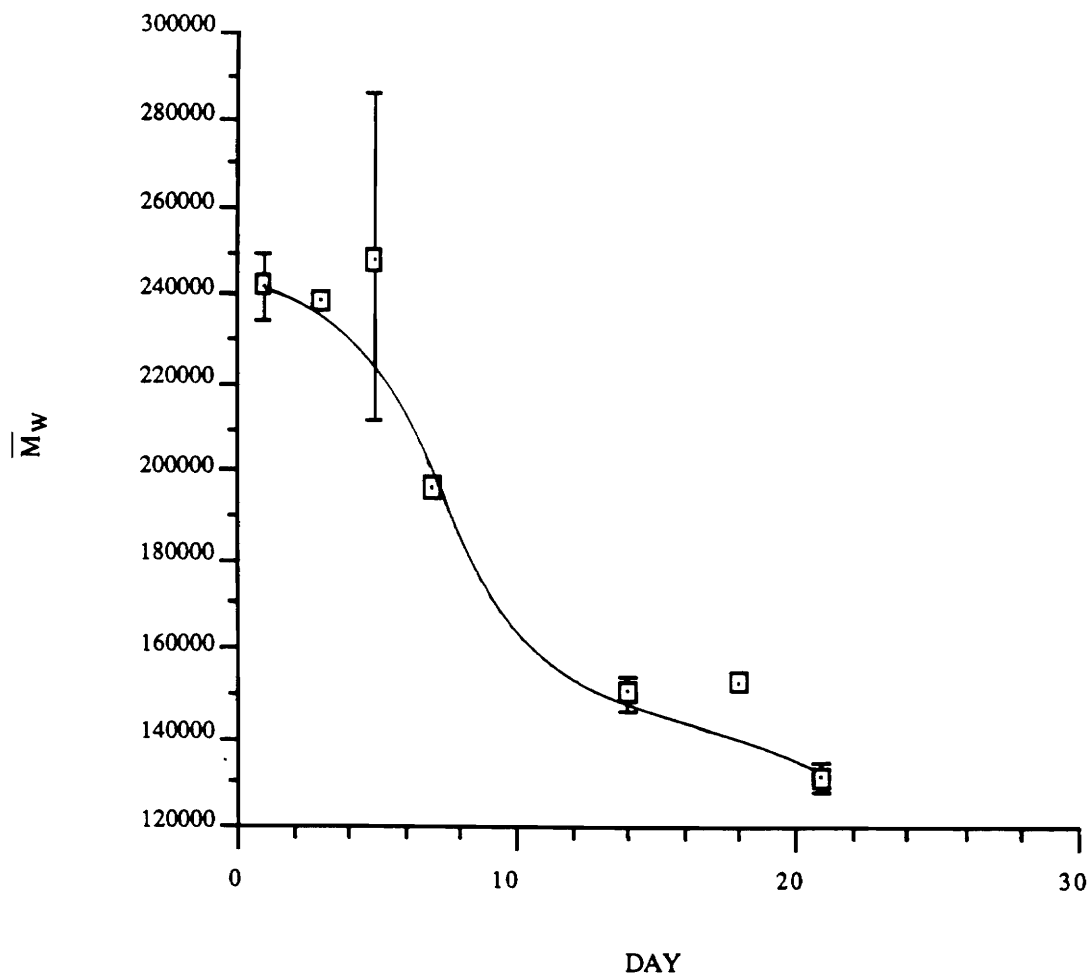


FIGURE 6.4.2.1  
(a) Time Dependence of Average Molecular Weight Determined by  
GPC of 12.58% N Nitrocellulose (58)

## Chapter 7      Conclusions and Recommendations for Further Study

### 7.1              Conclusions

Clearly, nitrocellulose characterization is a difficult task. However, previous investigators have developed the required methodology for application to new studies. Solution properties of nitrocellulose are especially complex, depending on solvent properties, temperature, nitrocellulose molecular weight characteristics and nitrocellulose DOS homogeneity. The realization of the time dependence of these properties has added to the complexity.

Mechanical characterization of nitrocellulose propellants appears to be an emerging technology. The morphological intricacy of nitrocellulose propellants in addition to the chemical complexity of nitrocellulose has hampered direct correlation of the polymeric properties of nitrocellulose with propellant mechanical behavior and subsequently ballistic performance.

Solubility properties of nitrocellulose depend on nitrocellulose morphology. These solubility properties become quite complex when a distribution of DOS is superimposed on a molecular weight distribution. These solubility properties also control the relative amounts of

amorphous versus fibrous nitrocellulose in gun propellants. The kinetics or ease of nitrocellulose solubility and molecular weight, influences the rheological properties of in-process propellant and therefore, controls the morphology of finished propellant grains. Mechanical and ballistic properties of gun propellants are, thus, directly affected by micro and macroscopic properties of cellulose.

## **7.2 Recommendations for Further Study**

### **7.2.1 Nitrocellulose Characterization**

The chemical heterogeneity of nitrocellulose requires further study. Elucidation of how distribution of DOS along the nitrocellulose chains and distribution of DOS within the entire sample effects the solution properties, especially the hydrodynamic volume, is a key element in the characterization of nitrocellulose.

Careful laboratory nitrations of cellulose with a range of well defined morphological characteristics and subsequent analysis, may help explain how cellulose properties influence nitrocellulose properties.

Exploratory work should be performed to attempt fractionation of nitrocellulose based on molecular weight or

DOS properties, but not based on both as is currently the case. Saunders, et al, (63,64) have taken the lead in this area with fractionation of nitrocellulose by GPC with subsequent determination of DOS by FT-IR spectroscopy.

#### **7.2.2      Integration of Nitrocellulose Characteristics With                  Propellant Mechanical Properties                  and Ballistic Performance**

Gun propellants should be manufactured under strictly controlled conditions using fully characterized nitrocellulose. The resultant propellants should be subjected to DMA and high rate mechanical testing to determine how nitrocellulose characteristics affect propellant mechanical properties.

Finally, the well characterized propellants should be gun tested under controlled conditions to determine ballistic properties.



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