Effect of Ultrasound on Single-Base Propellants for Pyrotechnic Purposes

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ABSTRACT

Investigations were conducted on the effect of ultrasound on single-base propellants. Changes in the average viscosimetric molecular weight of nitrocellulose in the solutions of propellants in acetone and in a mixture of ethyl alcohol-diethyl ether were studied. It has been established that, for at least 60 minutes, the molecular weight decreases exponentially. On-going degradation processes and the effect of cavitation during treatment of the propellants with ultrasound were analyzed. The change in nitrogen content and the heat released were also measured. The absorption coefficients and the sound velocities of the propellants were determined. Using these parameters, the dynamic modulus of elasticity was calculated. The results obtained are used in the processing of propellants for pyrotechnic purposes.

Keywords: single-base, propellants, ultrasound, degradation

Introduction

The use of ultrasound in characterization and treatment of propellants finds various applications. Reference 1 describes a technique for ultrasound measurement of propellant burning rate in a closed space. Using an ultrasound method developed in Reference 2, local regions in the propellants may be inspected to determine the defects in the composition of the individual components. Using an improved variant of the method, the inhomogeneity in the propellant elements may also be determined. Reference 3 examined changes in single-base propellants (SBP) during long term natural aging. Those same propellants were the subjects of examination after ultrasound treatment. The results obtained are to be used during their processing for pyrotechnic purposes.

The aim of the article proposed is to investigate the effect of ultrasound on propellant solutions and to determine the changes in acoustic properties of solid SBP.

Experimental

Single-base and other propellants: pyroxylin (NC), nitroglycerine (NG), and nitrodiglycol (ND or DEGN) (Arsenal, Bulgaria) with nitrogen (N_2) content of 13.05 and 12.47% were investigated. Solutions of the propellants with 3% concentration were prepared using the solvents acetone or ethyl alcohol-diethyl ether (A-E) in the ratio 1:2 (g/g). These solutions were treated with an ultrasound flaw detector USIP (Krautkrämer, Germany) with a frequency of 22 kHz and an intensity of 0.6 W/cm^2 for 60 min at 21 °C. The propellant solutions were put into open baths with distilled water without restricting the cavitation (i.e., under the conditions of an open system). Average viscosimetric molecular weight M_η was determined by drying samples of the solutions and, then, preparing new solutions with a concentration of 0.2 to 1 g per 100 cm^3. Using an Ostwald viscosimeter with a capillary diameter of 0.54 mm, the relative and specific viscosities were determined. From the relationship

$$[\eta] = \lim_{C \to 0} \frac{\eta_{sp}}{C},$$

the intrinsic viscosity $[\eta]$ was calculated. After its substitution into the Mark-Houwink equation[4] $[\eta] = KM^{\alpha}$, where K and α are the coefficient and exponent published in Reference 5, M_η was

calculated. The nitrogen content was determined using a G. Lunge nitrometer,[6] and a calorimeter was used to measure heat quantity. Each point of the graph is as an arithmetic mean of five measurements. The standard error of approximation was 0.07.

The coefficient of sound absorption was determined in propellant elements 25 to 30 mm in length and 8 mm in diameter. The specimens were fixed at both ends, using sensors for excitation and reception of elastic vibrations (Brüel-Kjær, Denmark). The same flaw detector with receptors in the frequency range from 1 to 10 MHz was used. The sound velocity in SBP was measured using a pulse method with non-detected signal. The scale of the ultrasound flaw detector was adjusted in time units, using steel standards with known velocity of sound transmission. Accuracy in reading the time was 0.25×10^{-2} s, and the relative error was 1.5%. The absolute error in measuring the signal amplitude was 0.5 dB.

Results and Discussion

Effect of Ultrasound on Degradation of SBP

The molecular weight is a major factor showing the on-going degradation processes in propellants treated with ultrasound, which, according to the classification published in Reference 7, belong to the homogeneous propellant group. Those processes change the molecular characteristics of nitrocellulose (NC), which is the main component in SBP. Molecules of NC are known to be spheroids that are characterized by increased skeletal hardness, and their size depends on the content of nitro and hydroxyl groups. The change of the average viscosimetric molecular weight M_η of NC in the solutions of SBP in acetone and in a mixture of ethyl alcohol-diethyl ether after treatment with ultrasound is shown in Figure 1.

In Figure 1 the values of M_η are seen to decrease in both solvents with the duration of ultrasonic treatment. The observed exponential decrease of the molecular weight is connected with the beginning of ultrasonic degradation. This is explained by ultrasound causing equalization of the lengths of molecule fragments. Therefore,

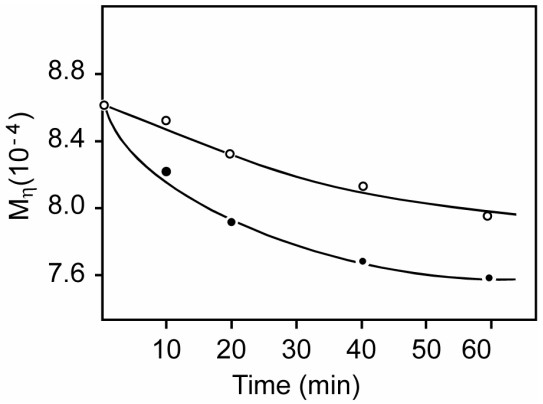

Figure 1. Dependence of molecular weight M_η on time of treatment with ultrasound of solutions of SBP in a mixture of ethyl alcohol-diethyl ether 1:2 (-○-○-) and acetone (-●-●-).

this type of degradation cannot be assigned to oxidation reactions.

It is also necessary to note the effect of cavitation on ultrasonic degradation of solutions of SBP. Because of this, the degradation processes can take place not only mechanically, but also as oxidative degradation with a chain-radical mechanism. An initial elementary step in this process is connected with tearing NO_2 from the molecules (i.e., with dissociation of the RO–NO_2 bond). This assumption is warranted by the low values of the activation energy in degradation, which is 38 kcal/mol,[8] and the dissociation energy in RO–NO_2, which is 51.7 kcal/mol.[9] Observations showed cavitation could be limited to a considerable extent by degassing or increasing pressure before treatment of the solutions with ultrasound. By doing this, air bubbles serving as centers of cavitation were removed from the solutions.

The effects of the solvents used should also be taken into consideration. Hydroxyl and ether groups have a stronger ability to form hydrogen bonds with NC than the carbonyl groups. A portion of the ultrasonic energy is spent for destruction of the polymer-solvent associates. This portion is larger in the A-E solvent mixture than in the acetone mixture due to formation of a higher number of hydrogen bonds.

To investigate the effect of ultrasound on SBP, changes in nitrogen content N_2 and released heat Q were studied. From the exhaustion of N_2

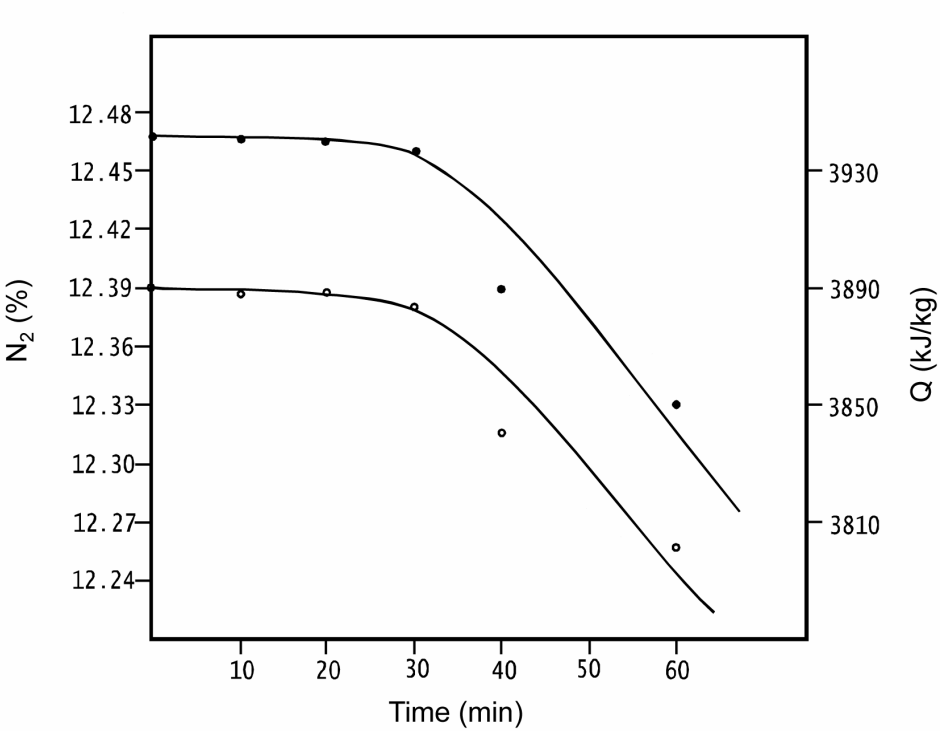

Figure 2. Dependence of N_2 (-●-●-) and Q (-○-○-) on time of treatment of SBP with ultrasound.

and changes in *Q* shown in Figure 2, one may make judgments about the degradation processes in the macromolecules of NC from the propellants.

Figure 2 shows that the nitrogen content curve has two sections. In the first section, the nitrogen content has a constant value until about the 25th minute. During this time, it can be assumed that the diphenylamine stabilizer was able to inhibit the initial oxidation processes caused by the ultrasonic degradation. In the second section, after the 25th minute, nitrogen content decreases rapidly with continued ultrasound treatment. It follows from this that the hydroxyl groups increase at the expense of NO_2 groups. The free radicals or nitrogen oxides formed by ultrasonic degradation interact with the diphenylamine and form slightly active or inactive diphenyl nitrogen oxides. The processes are of a pulsing nature due to catalytic action of released nitrogen oxides. The above-mentioned assumptions are also confirmed in Figure 2 by the graphed released heat *Q*, which correlates with that for nitrogen content N_2.

The initial elementary act of ultrasonic degradation of propellants is the breaking of the bonds between the glucose rings at $C^{(1)}$ or $C^{(4)}$ in the main chains of the macromolecules of NC in accordance with the diagram shown in Figure 3.

The proposed diagram (Figure 3) for the degradation of NC of propellants shows the formation of new molecule fragments, thereby increasing the structural disorder. The disorderly areas have more developed segmental movement, and the orderly formations have lower molecular mobility. Degradation of the super-molecular structures of propellants by the ultrasound also leads to formation of areas with various molecular mobility and duration of existence.

It may be summarized that, with ultrasonic treatment, there are two different mechanisms of degradation of SBP. Mechanical degradation begins with the breaking of bonds between the glucose rings at $C^{(1)}$ and $C^{(4)}$, and oxidative degradation occurs with the dissociation of RO–NO_2. Usually, neither mechanism acts separately and is not easily explained independently. They always act together or complement each other,

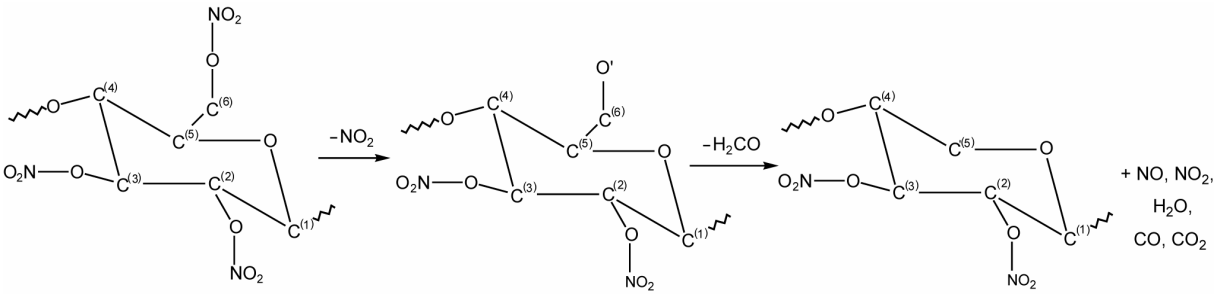

Figure 3. Probable diagram of ultrasonic degradation.

making it difficult to differentiate the action of either type of degradation.

Acoustic Properties of SBP

To obtain a fuller picture of on-going processes in SBP during treatment with ultrasound, the sound velocity C and the coefficient of sound absorption α were determined. Using these parameters, the dynamic elasticity modulus E' was determined, from which conclusions may be drawn about physicomechanical parameters and the structure of propellants used for pyrotechnic purposes.

The sound velocity C in SBP was determined using the formula:

$$C = \frac{l_2 - l_1}{t_2 - t_1} \text{ [m/s]},$$

where l_1, l_2 are the acoustic paths through the specimen examined [m]; and t_1, t_2 are the times for passing of the ultrasonic pulse through the specimen [s].

In propellants, the quantity C depends to a considerable extent on the angle between the direction traveled by the ultrasound and the axis of manufacturing of propellant elements. That is why the sound velocity in axial C_{ax} and radial C_r directions of the specimens was measured. The anisotropy index I_A was determined from the C_{ax}/C_r ratio. In Table 1, C is given for SBP, nitroglycerine (NG) and nitrodiglycol (ND) propellants.

The sound velocity and the anisotropy index data in Table 1 are explained by different mechanisms of transmission of ultrasonic vibrations depending on the angle between the direction of the ultrasound and the axis of the segments of the macromolecules. When the direction of ultrasound is parallel to the segments of the macromolecules, the propagation of ultrasonic vibrations is at the expense of intramolecular interaction energy. When the direction of ultrasound is perpendicular to the segments of the macromolecules, the ultrasonic vibrations propagate at the expense of the energy of intermolecular interaction. Because the energy of intramolecular interaction is considerably higher than the energy of intermolecular interaction, C_{ax} is greater than C_r.

Table 1. Sound Velocity C and Anisotropy Index I_A of SBP, NG and ND.

No.	Propellant	C_{ax} [m/s]	C_r [m/s]	I_A
1	SBP	2.493	2.228	1.12
2	NG	2.223	2.096	1.06
3	ND	2.306	2.268	1.02

The coefficient of sound absorption α was determined using:

$$\alpha = \frac{A_1 - A_2}{l_2 - l_1} \text{ [dB/cm]}$$

where A_1, A_2 are the amplitudes of signals that have passed though the specimens, read from the attenuator [dB]; and l_1, l_2 are the lengths of the specimens [cm].

A pulse method of measurement was used to compare the amplitudes of signals passing through the specimens with frequency f of the ultrasound. The results are shown in Figure 4.

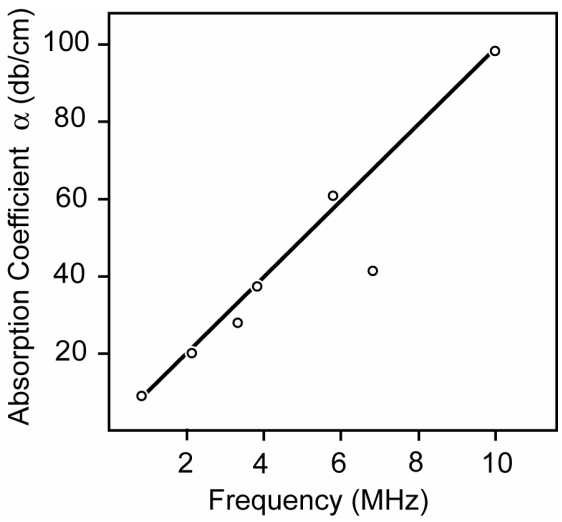

Figure 4. Determination of the absorption coefficient, α, of SBP versus the frequency, f, of the ultrasound.

Figure 4 shows that α may be plotted as a straight line with a certain slope. From it, a conclusion may be drawn about the acoustic state of the propellants, taking into account on-going relaxation processes. It is also necessary to note the special case when $\alpha = 0$ (i.e., the sound waves propagate in an ideally elastic body).

A major index characterizing mechanical behavior of the propellants during ultrasonic treatment is the dynamic modulus of elasticity *E′*. It is the ratio of the applied stress coinciding in phase with the strain, to the value of this strain.

After determining α and *C*, the modulus of elasticity is calculated using the formula:

$$E' = \frac{48\pi^2}{a_n^4} \rho \frac{l^4}{d^4} f^2 \ [\mathrm{N/m^2}],$$

where ρ is the density [kg/m^3]; l is the length of unfixed part of the specimen examined [m]; d is the diameter of the specimen examined [m]; a_n is a coefficient depending on the frequency of the ultrasound; and f is the resonance frequency [Hz].

The elasticity coefficient, *E′* for SBP, equals 10^9 N/m^2. This value falls between highly elastic polymers at 10^5 to 10^6 N/m^2 and harder polymers at 10^{11} N/m^2. This is one of the characteristics that allows for successful use and processing to obtain propellant elements with good mechanical properties for pyrotechnic purposes. The dynamic modulus *E′*, *α*, and *C* allows obtaining two types of information: about mechanical properties and about structure, constitution, and condition of the propellants. From these, conclusions may be drawn about acoustic and physicomechanical properties of the propellants.

The results obtained are of substantial importance. Ultrasonic treatment of the propellants is of interest in terms of their practical application in various pyrotechnic products. A necessary requirement is that they have trouble-free operation under conditions of large loads and vibrations.

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