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3,447,983

ACETONE TREATED NITROCELLULOSE-BASED PROPELLANT AND PROCESS

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10 Claims

ABSTRACT OF THE DISCLOSURE

A process for strengthening homogeneous nitrocellulose type propellants, made by the "solventless" process, which includes treating said homogeneous propellants with the vapors of a solvent of the type ordinarily used in the "solvent" process for dissolving and colloidizing nitrocellulose, such as acetone. A high strength solventless propellant prepared by the foregoing process.

BACKGROUND OF INVENTION

This invention relates generally to nitrocellulose type homogeneous propellants prepared by the "solventless" process and more specifically to a method for strengthening homogeneous propellants by contacting them with the vapor phase of a solvent of the type ordinarily used in the "solvent" process for dissolving and colloidizing nitrocellulose.

Solid propellants are generally classified as being either homogeneous or composite. The former refers to those types, usually containing nitrocellulose, which are considered true monopropellants, each molecule containing all the necessary fuel and oxygen for combustion. The composite type propellant, in contrast, consists of a physical mixture of a fuel and an oxidizer.

The homogeneous nitrocellulose propellants are further subclassified as being either single, or double base, depending on whether the composition contains nitrocellulose as the sole combustible or contains additional nitroxy compounds, such as nitroglycerin, as a second combustible.

At least two methods are presently available for producing these types of propellants; the "solvent" and the "solventless" techniques. In the "solvent" process, solvents such as acetone or ether-alcohol mixtures are used to dissolve and colloid nitrocellulose to form a viscous or doughy mass. The mass is granulated, usually by extrusion, and the volatile solvent is recovered as completely as possible. Although the "solvent" process produces a product of fair mechanical strength, difficulties are encountered in obtaining good ballistic properties. The "solventless" process avoids these limitations by eliminating entirely the need for volatile solvents to colloid the nitrocellulose. According to this process, nitrocellulose is slurried in a non-solvent to form a paste-like mixture which is dried and rolled on hot rolls. The resulting colloidized sheet is extruded or cut into the desired granulation. Although the product produced by the "solventless" process is generally characterized by good ballistic properties, it is nevertheless generally inadequate for those missile systems requiring a greater degree of mechanical strength. Previous attempts at strengthening "solventless" propellants have proved generally ineffective since they have concentrated on variations of ingredients and proportions which resulted in serious changes in ballistic parameters and workability. Moreover, although these prior art techniques were limitedly successful in increas-

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ing tensile strength, unfortunately they generally resulted in significant corresponding decreases in elongation.

SUMMARY OF INVENTION

It is therefore an object of this invention to provide a homogeneous nitrocellulose base propellant which is characterized by superior strength in both tensile characteristics and elongation characteristics.

It is further an object of this invention to provide a method for strengthening the mechanical properties of homogeneous nitrocellulose base propellants which have been prepared by the "solventless" technique.

These and other objects are accomplished according to this invention, by contacting a homogeneous nitrocellulose-containing propellant composition prepared by the "solventless" technique, with the vapor phase of an organic solvent of the type ordinarily used in the "solvent" process for dissolving and colloidizing nitrocellulose, for a time sufficient to cause absorption of the solvent by the propellant. The swelled propellant is dried for a period sufficient to cause substantial removal of the solvent resulting in an intermolecular rearrangement causing very substantial improvement in mechanical strength.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The homogeneous propellants strengthened by this invention are generally prepared by the "solventless" process which comprises slurring a quantity of nitrocellulose, with between 5 to 10 times its weight of a non-solvent, such as warm water, and adding necessary stabilizers, plasticizers, ballistic modifiers and secondary nitroxy combustibles.

While preferably the nitrocellulose used herein is a water wet soluble grade (12.6% N) nitrocellulose, those types possessing a nitrogen content as low as 11.5% or as high as 13.5% may also be used.

Various stabilizers may be added within the scope of this invention which include such art recognized derivatives of urea as ethyl centralite, also 2-nitrodiphenylamine N-methyl, paranitroaniline.

Among ballistic modifiers are included the copper and lead salts with aluminum, such as those disclosed by Camp et al. in U.S. Patent 3,138,499 issued June 23, 1964, which discloses the lead and copper salts of beta-resorcylic and salicylic acids.

Plasticizers may also be optionally included such as the high molecular weight esters of dimethyl-, diethyl- and dibutylphthalate, also tricresyl-phosphate, camphor, triacetin and castor oil.

For double or triple base compositions other nitric esters are added such as nitroglycerin, nitroguanidine, diethyleneglycol dinitrate, 1,2,4 - butanetriol trinitrate, 1,1,1 - trimethylol ethane trinitrate, pentaerythritol trinitrate, dinitroglycerin, and the like. If it is desired for reasons of safety to desensitize the nitrate ester prior to use, an ester may be added into the slurry in the form of an alcoholic solution.

Other additives which may advantageously be incorporated into the slurry include fine granular aluminum which tends to raise the heat of explosion of the mixture, carbon black as a darkening agent, and candelilla wax, which in minute quantities tends to enhance extrusion properties.

The slurry is filtered or centrifuged to remove most of the water, and the resulting paste aged from one to five days in heated air until the moisture level is from 8% to 15%. The dried paste is dumped into rotary drums where any water soluble salts, such as potassium sulphate, are optionally added and the mass is milled to a homogeneous colloidized sheet on heated differential rolls, ready for subsequent extrusion.

Vapor contact, for the purpose of strengthening the propellant, can be effected either at this point or subsequently, after extruding. For the purpose of vapor contact, any solvent ordinarily used in the corresponding "solvent" process for dissolving and colloiding nitrocellulose may be used herein. Among these solvents are included acetone, methyl acetate, ethyl acetate, methyl ethyl ketone, ethylene glycol monomethyl ether, ethylene glycol dimethyl ether, dimethyl formamide, mixtures of diethyl ether and ethanol in the weight ratio of 3:1 to 1:3, methyl propyl ketone, methyl isoketone, and the like, the various esters such as ethyl acetate, propyl acetate, butyl acetate, ethyl butyrate, isopropyl butyrate, ethyl propionate, β -ethoxyethyl acetate, benzene and the like and mixtures thereof. Preferred, however, are those solvents whose boiling points at normal pressures (760 mm.) are less than 350° F. to obtain maximum control in preventing undesirable gelatinization of the nitrocellulose. Most preferred however is acetone and the mixture of diethyl ether and ethanol.

Vapor contact may conveniently be obtained by suspending the propellant composition in a closed vessel containing a saturated atmosphere of the solvent. Optimum contact generally is determined for the specific solvent system and is dependent upon whether treatment is performed prior or subsequent to extrusion and propellant grain formation. It will be recognized by the skilled artisan that the rate of absorption is naturally affected by the physical features of the propellant such as grain configuration and shape as well as the physical properties, type and quality, of the nitrocellulose.

Alternative methods of obtaining vapor contact include blowing of an inert gas, saturated with solvent vapor past a suspended specimen of the propellant. Another more direct technique is to fit thin sheets of the propellant into a rocket casing and to blow the solvent vapor-saturated gas through the casing and swelling the propellant to fit the contours thereof.

Generally, vapor contact is maintained until the propellant composition begins to soften and swell. If contact is too short, the physical form of the nitrocellulose is left either unaltered or insufficiently altered, resulting in negligible strengthening. Unduly prolonged contact, conversely, causes undesirable gelatinization or actual dissolving of the nitrocellulose. Normally, sufficient contact is obtained after about 0.5 to about 36 hours at a temperature of about 60° F. to 250° F. at normal pressure. Hardening and strengthening of the propellant grains are subsequently achieved by removing the solvent either by boiling or by passing streams of air past the propellant. The drying operation is continued until approximately constant weight is obtained. Normally, this is achieved after about 20 minutes to 4 hours but by slower techniques may range up to 1 week.

While it is not known precisely why the technique results in mechanical improvements, it is generally believed that the organic solvent vapors soften and destroy the fibrous structure of the nitrocellulose within the propellant. It should be understood that the liquid phase of the solvent is generally ineffective for the purposes described herein, since it causes over gelatinization of the nitrocellulose particles which prevents the improved molecular rearrangement obtainable when the propellant composition is contacted with the vapor. Liquid solvent treatment generally results in mechanically weak products of varying diameters due to uneven solvent absorption and localized gelation and dissolution.

The general nature of the invention having been set forth, the following examples are presented as specific illustrations thereof. It will be understood that the invention is not limited to these examples but is susceptible to different modifications that will be recognized by one of ordinary skill of the art. The following formulations were prepared by the "solventless" process, parts and percentages are by weight unless otherwise designated.

Example 1

	Parts by wt.
Nitrocellulose (12.6% N) -----	50.0
Nitroglycerine -----	39.8
Di-n-propyl adipate -----	3.1
2-nitrodiphenylamine -----	2.0
Candelilla wax -----	0.1
Ballistic modifiers -----	4.5
	100.0

Example 2

Nitrocellulose (12.6% N) -----	48.0
Nitroglycerine -----	41.3
Di-n-propyl adipate -----	3.6
2-nitrodiphenylamine -----	2.0
Candelilla wax -----	0.1
Ballistic modifiers -----	4.5
	100.0

EXAMPLE 3

Nitrocellulose (12.6% N) -----	42.0
Nitroglycerin -----	40.5
Triacetin -----	5.4
2-nitrodiphenylamine -----	2.0
Ballistic modifiers -----	5.0
Aluminum, atomized -----	5.0
Candelilla wax -----	0.1
	100.0

The propellant compositions were formed into sheets of about 20 inches square and 0.11 inch thick. Five gallons of acetone were placed in a stainless steel vessel (enough acetone to form a one- or two-inch layer to cover the entire vessel bottom), a screen was placed over the acetone and a sample placed on the screen. The vessel was covered to permit acetone vapor build-up and contact was maintained for 24 hours at about 85° F. The propellant was observed to become soft and flexible, picking up the imprint of the screen. The vessel was uncovered and the acetone drained. Treated specimens were left in the tank to dry at temperatures of between 70 and 100° F. for approximately one week. The specimens were periodically weighed and removed after achieving approximately constant weight. The specimens were then tested for tensile strength at varying temperatures. The following results were obtained:

TABLE

Propellant	Hours contact time	Temperature of testing, ° F.	Tensile strength (p.s.i.)	Percent elongation
Example 1-----	0	77	637	12.38
	24	77	3,230	73.19
Example 2-----	0	130	289	12.30
	6	130	759	84.15
	24	130	1,028	76.92
Example 3-----	0	130	254	-----
	7	130	412	-----
	0	77	712	13.83
	6	77	2,727	57.70

The preceding table presents data comparing the tensile strength and toughness of corresponding treated and untreated propellants prepared by the "solventless" process. This data indicates that substantial improvements in tensile strength and toughness are obtained by the herein disclosed solvent vapor treatment. By prior art techniques, the increase in tensile strength is generally accompanied by either elongation decreases or constant elongation. By the methods of this invention however, not only is there a substantial increase in tensile strength but also a corresponding increase in toughness is obtained. There are no adverse effects on strand burning rates, stability or sensitivity of the propellant.

Since modifications of the invention will be apparent to those skilled in the art, it is intended that the scope of the invention be limited only by the appended claims.

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What is claimed and desired to be protected by Letters Patent is:

1. A process for preparing high strength solventless propellants which comprises:

(a) preparing a propellant composition by the solventless process comprising:

- (1) forming a slurry of single, double, or triple base propellant ingredients in a non-solvent,
- (2) drying said slurry, and
- (3) rolling said dried slurry on hot rolls so as to obtain said propellant composition

(b) contacting said propellant composition with the vapor phase of a solvent used for dissolving and colloidizing nitrocellulose for a sufficient time to cause absorption of the solvent vapors, and

(c) substantially drying said propellant composition for a time sufficient to cause shrinkage thereof.

2. The process of claim 1 wherein said solvent is characterized by a boiling point at normal pressure of less than 350° F.

3. The process of claim 2 wherein the propellant composition is contacted with the solvent vapor for a time sufficient to cause absorption of the solvent vapors and at least from 0.5 to 36 hours at a temperature of from about 60° F. to 250° F.

4. The process of claim 1 wherein contact of the propellant composition with the vapor phase of the solvent is obtained by suspending said propellant composition in an atmosphere saturated with solvent vapor at a temperature of from about 60° F. to 250° F. at normal pressure.

5. The process of claim 1 wherein contact of the propellant composition with the vapor phase of the solvent is obtained by blowing the solvent vapors into proximity with the propellant composition for a time sufficient to cause absorption of said solvent vapors.

6. The process of claim 1 wherein the solvent is acetone.

7. The process of claim 1 wherein the solvent is a mixture of from about 3:1 to 1:3 parts by weight diethyl ether with ethanol.

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8. The process of claim 1 wherein the propellant composition is a double base propellant composition comprising essentially 40-65 percent nitrocellulose, 20-45 percent nitroglycerin, and 0-10 percent plasticizer.

9. A high strength solventless propellant prepared by the method of claim 1.

10. A process for preparing high strength solventless propellants which comprises:

(a) preparing a propellant composition by the solventless process comprising:

- (1) forming a mixture comprising single, double or triple base propellant ingredients,
- (2) rolling said mixture on hot rolls so as to obtain said propellant composition,

(b) contacting said propellant composition with the vapor phase of a solvent used for dissolving and colloidizing nitrocellulose for a sufficient time to cause absorption of the solvent vapors, and

(c) substantially drying said propellant composition.

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