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PROCESS FOR MAKING NITROCELLULOSE PROPELLANT FORMULATIONS HAVING IMPROVED TENSILE STRENGTH AND BALLISTIC PROPERTIES

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The invention described herein may be manufactured and used by or for the Government of the United States of America for governmental purposes without the payment of any royalties thereon or therefor.

This invention relates to a process for making nitrocellulose-base propellant formulations having improved ballistic properties and increased strength.

It is now understood in the art of propellants that the term "double base propellant" means a nitrocellulose-nitroglycerin propellant. A mesa double base propellant is one which produces mesa characteristics upon burning; the mesa effect as well as mesa type double base propellants being fully disclosed in application Serial No. 352,312, Gas Producing Charge, by Albert T. Camp, filed in the U.S. Patent Office on April 30, 1953, and given a notice of allowability on February 17, 1955. As explained therein, an indicative factor of the effective operation of a double base rocket propellant is the slope n , or pressure exponent, of the curve produced by a logarithmic graph of the burning rate of the propellant plotted against pressure produced during burning. This factor is particularly important in the zone of useful rocket pressures, roughly, 700 to 3000 p.s.i. The relationship between the pressure at which a propellant burns and its burning rate is mathematically expressed as $r = cp^n$ or as $\log r = n \log p + \log c$, where r is the burning rate, p is the pressure at which the burning rate is measured, and c and n are constants characteristic of a given propellant. A plot of $\log r$ against $\log p$ for conventional propellants produces a straight line of slope n , that is, there is a progressive increase in burning rate for each increase in pressure. This characteristic is disadvantageous in propellants for jet actuated devices wherein it is highly desirable to have the value of n as low as possible and certainly below .7 in the zone of useful rocket pressures. For example, variations of performance due to changes in temperature, burning rates and operating pressures of prior propellants in the zone of useful rocket pressures necessitated expensive fire control apparatus designed to correct for these undesirable results. Further, heavy walled rocket motors were required to withstand the very high pressures developed at high temperatures of firing when prior art propellants were used, and the propellants were highly inefficient because of the low pressure and thrust developed with them at low temperatures of firing. Research developed that the addition of small amounts of additives such as certain lead compounds referred to as ballistic modifiers produced a "plateau" type propellant for which the value of the pressure exponent n is zero. Further research resulted in the mesa type propellant which is superior in performance in rocket motors to the plateau type propellant. Mesa type propellants are characterized by the fact that the slope n of the curve representing their pressure-burning rate relationship becomes zero at some point and then reaches a negative value thereafter in the region of useful rocket pressures, that is, the burning rate in this negative slope region actually decreases with increase in pressure.

A rocket propellant exhibiting mesa characteristics provides a number of highly desirable effects. For example, the negative pressure exponent serves as a safety valve in

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case of sudden large changes in burning surface during the operation of a rocket, such as that caused by cracking of the grain. With prior art propellants such a failure of the grain would ordinarily result in destruction of the rocket motor, but in the mesa type propellants only a small pressure increase results. Further, there is an inherent tendency for overlapping of rate-pressure relationships at various temperatures as illustrated by logarithmic graphs of the relationships, that is, in certain regions of pressure the burning rate of propellant for firings at low temperature may actually be higher than the burning rate for firings at high temperature. Also, the variation in performance with change in temperature for mesa type propellants is negligible and in some cases there is none at all. This advantage is particularly useful as respects fire control considerations in the design of aircraft rockets to be fired at moving targets. Further, the burning rate and energy content of the mesa propellants are higher than those of prior art propellants and can be controlled at will over rather wide limits.

A great deal of research is being directed to the development of improved stabilizers, plasticizers, ballistic modifiers and other components of mesa type propellants. A prime consideration in the development of such components is the fact that their addition to the final propellant composition must not vitiate the highly sensitive mesa effect of the propellant and, preferably, the presence of the additives should enhance the mesa effect.

A major difficulty in the development of nitrocellulose-base propellants is the production of a propellant grain possessing sufficient strength to withstand handling and long storage periods without cracking, and which will not crack or fissure during burning with resultant erratic rocket performance. It has long been recognized that the process by which the propellant is compounded can be a controlling factor in obtaining high-strength grains.

It is therefore an object of this invention to provide a process for the compounding of nitrocellulose-base propellant formulations of increased strength and enhanced ballistic properties.

The invention comprises homogeneously mixing the nitrocellulose-base propellant ingredients with an amount (about 80% of the nitrocellulose weight) of a mixture of acetone/ethyl alcohol in about 65/35 weight ratios, respectively, and adding diethyl ether in an amount equal to 25 to 100% of the weight of the nitrocellulose. The formulation is then extruded at ambient temperature and dried. A modification of the process by which the necessity for the addition of diethyl ether is eliminated consists of the extrusion of the propellant formulation at a temperature between 130 and 160° F.

The following examples of propellant formulations were processed by a well established slurry process of the prior art and by the process of the invention. The slurry process is the one used for making N-5 propellant and is as follows: The nitrocellulose is mixed to a thin slurry in about 10 times its weight of warm water and finely ground 2-nitrodiphenylamine added slowly. A solution of lead 2-ethylhexoate in 2-3 times its weight of warm diethyl phthalate is admixed with the slurry. A solution of the nitroglycerin in the remaining diethyl phthalate to be used is slowly added to the slurry. Thereafter, the slurry is filtered or centrifuged to remove most of the water and the resulting paste is aged for a period of 1 to 5 days or more at a temperature of about 130° F. It is then dried to a moisture level of from 8 to 15 percent, the lead salicylate added to the partially dried paste and the mixture milled to a homogeneous colloid on a heated differential rolling mill. The method of mixing is not critical, provided distribution of all ingredients is uniform and no losses of ingredients occur

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which are not otherwise accounted for. The sheet propellant formed may be extruded into strands or other forms in a warm press. The mixing operation may also be done by a damp process in conventional Schroeder bowl or Sigma blade, or Talley mixers. In this case the lead salicylate is preferably added to the damp nitrocellulose before the other ingredients. The object is to achieve optimum homogeneity. Slightly modified procedures are equivalent provided they do not cause maldistribution of any ingredients. Comparative strength tests made on strands of propellant processed by the two methods are given. In making the formulations by the process of the invention, the propellant ingredients were thoroughly mixed with an amount (about 80% of the nitrocellulose weight) of a mixture of acetone-ethyl alcohol in about 65/35 weight ratios, respectively. To the formed mixture was added diethyl ether in an amount equal to 25 to 100 percent of the weight of the nitrocellulose. The formulation was extruded at ambient temperature into strands 1/16-inch in diameter and the strands allowed to dry. The examples are intended to be illustrative of the invention but not limiting thereof. 40 and 200 gram batches were made up having the following percentage compositions:

	Examples, Weight Percent			
	I	II	III	IV
Nitrocellulose (12.6% N).....	50.0	50.0	55.0	55.0
Nitroglycerin.....	35.4	35.4	30.4	30.4
Diethyl Phthalate.....	10.0	-----	10.0	-----
Adiponitrile.....	-----	10.0	-----	10.0
2-Nitro Diphenylamine.....	2.0	2.0	2.0	2.0
Lead Salicylate.....	1.2	1.2	1.2	1.2
Lead 2-Ethyl Hexoate.....	1.2	1.2	1.2	1.2
Candelilla Wax.....	0.2	0.2	0.2	0.2

The strands were tested with a standard tensile strength testing machine.

Typical strength values for the above compositions are as follows:

STRANDS MADE BY THE SLURRY PROCESS FOR MAKING N-5 PROPELLANT

	I	II	III	IV
Tensile Strength (p.s.i.).....	600	600	800	800

STRANDS MADE BY THE PROCESS OF THE INVENTION

Tensile Strength (p.s.i.).....	1,000	2,500	1,500	4,000
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It is to be noted that all of the formulations give increased strength values when processed by the process of the invention. However, the most surprising result was obtained with formulations containing adiponitrile. The process is equally effective on formulations containing other dinitriles, such as, succinic, pimelo and sebaco-dinitriles which were tested by the process of the invention and the modification thereof. Dinitriles, as a class,

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display a high solvating action on nitrocellulose. When formulations containing dinitriles are processed by the present process the propellant matrix is translucent rather than opaque. There is some evidence that the dinitrile plasticizer complexes with the nitrocellulose and nitroglycerin. The results also show that the effect is more pronounced when higher percentages of nitrocellulose are used in the formulations.

Equally striking comparative results were obtained when the above referred-to modification of the process was used; that is, when the step of adding diethyl ether was omitted and the propellant formulation was extruded at a temperature between 130 and 150° F. In compounding formulations by the modification of the process the compositions of Examples 1 through 4, inclusive, were used.

In addition to the production of higher strength formulations it was found that a double-base propellant is produced by the new process having sharper and more pronounced mesa burning characteristics.

Obviously, many modifications and variations of the present invention are possible in the light of the above teachings. It is therefore to be understood that within the scope of the appended claims the invention may be practiced otherwise than as specifically described.

What is claimed is:

1. A process for making double-base propellant grains which contain from about 40% to about 65% nitrocellulose and from about 30-45% nitroglycerin and at least 5% of a dinitrile containing up to ten carbon atoms which consists essentially of thoroughly mixing the propellant ingredients with an amount equal to about 80% of the weight of the nitrocellulose, of a mixture of about 65 parts of acetone and about 35 parts of ethyl alcohol, by weight, adding diethyl ether to the formed mixture in an amount equal to about 25 to about 100% of the weight of the nitrocellulose, extruding the resulting formulation into the desired shape, and drying the extruded product.

2. The process of claim 1 in which the step of adding diethyl ether is omitted and the mixture extruded at a temperature from about 130° to about 160° F.

3. The process of claim 1 in which the propellant to be extruded contains, in addition to the ingredients enumerated, about 2% 2-nitrodiphenylamine, about 1.2% lead salicylate, and about 1.2% lead 2-ethylhexoate.

4. The process of claim 2 in which the propellant to be extruded contains, in addition to the ingredients enumerated, about 2% 2-nitrodiphenylamine, about 1.2% lead salicylate, and about 1.2% lead 2-ethylhexoate.

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