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EXPLOSIVE NITRATE-ALKYLAMINE COMPOSITION

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INTRODUCTION

This invention generally relates to novel blasting explosives and propellant compositions containing inorganic nitrates. More particularly, this invention relates to novel ammonium nitrate explosive compositions having improved properties.

BACKGROUND

The commercial plastic ammonium nitrate explosives usually comprise crystallized ammonium nitrate suspended in a liquid or a gel phase. Wood flour, aluminum, nitrohydrocarbons or other combustible ingredients are frequently added to plastic ammonium nitrate explosives in order to take care of the oxygen liberated from the nitrate upon detonation. The medium in which the ammonium nitrate is suspended commonly comprises an explosive mixture, such as nitroglycerin, nitroglycol or cellulose nitrate, but the medium can also be a non-explosive mixture such as cellulose nitrate dissolved in nitrobenzene. In order to produce a suitable propellant, the mixture is proportioned so as to achieve the property of speedy combustion without the property of detonation. Other inorganic nitrates, such as sodium nitrate, are often incorporated in such explosives to replace a part of the ammonium nitrate.

In manufacturing plastic ammonium nitrate explosives, the ingredients are usually kneaded together. The homogeneous product can be used directly, but is commonly extruded through an orifice and either provided with a wrapper or introduced into a suitable container.

It has long been a problem in the explosives industry to produce extrudable explosives having a high content of ammonium nitrate. Some prior art workers have heretofore attempted to solve this problem by adding substances which form low melting mixtures with the ammonium nitrate, for example, carbamide, or by adding compounds which improve the wetting of the ammonium nitrate by gelatin (the viscous phase), for example, paratertiary octylphenyldiethylphosphate. However, these procedures leave much to be desired.

Another undesirable property of plastic ammonium nitrate explosives is that they often show troublesome aging. To obtain a high velocity of detonation with aged explosives, a more powerful initiation, or better confinement or the use of explosives of larger diameter is required. The detonation transmission, i.e., the maximum distance over which the detonation is propagated from one cartridge to another is reduced. These drawbacks cause great disadvantages, particularly when blasting is carried out under low temperature conditions.

OBJECTS

It is therefore the primary object of this invention to produce an improved ammonium nitrate type of explosive having a higher detonation transmission range.

A further object of this invention is to produce an explosive having a better stability of detonation at low temperatures.

An additional object of this invention is to produce an improved ammonium nitrate type of explosive having a higher density and better storage properties.

Further objects and other advantages of the invention

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will be more apparent after reading the following detailed description and examples.

THE INVENTION BROADLY

This invention broadly encompasses the concept of a novel explosive and propellant composition of increased stability of propagation and increased detonation transmission comprising ammonium nitrate, said nitrate having a surface coating of an alkylamine having between 6 and 24 carbon atoms in the alkyl group in an amount of up to 1.5 grams of alkylamine with each 100 grams of nitrate.

THE AMMONIUM NITRATE

The ammonium nitrate used in accordance with this invention may consist of any type of ammonium nitrate which has been heretofore used for the manufacture of explosives. As those skilled in the explosive art will appreciate, this comprises ammonium nitrate of a wide range of particle sizes, density, water content, etc. The exact properties of the ammonium nitrate are not critical to the present invention.

THE LONG CHAIN ALKYLAMINE

The alkylamines which are useful in accordance with this invention are the long chain alkylamines having between 6 and 24 carbon atoms in the alkyl group. Alkylamines having between 12 and 20 carbon atoms in the alkyl group are particularly preferred, such as, for example, dodecylamine, hexadecylamine and octadecylamine. Alkylamines with alkyl groups having less than 6 carbon atoms have not been found to have the desired effect.

In the alkylamines a number of the methylene groups in the alkyl group may be substituted by an aryl group.

Primary amines are preferred because they are commercially available and comparatively inexpensive, but secondary and tertiary amines, such as stearyl dimethylamine may also be used.

The alkylamines are ordinarily present in an amount ranging between about 0.001 and 1.5 grams for each 100 grams of ammonium nitrate, usually depending upon the size of the ammonium nitrate. When the ammonium nitrate crystals are less than about 0.1 mm. then the alkylamine should preferably be present in an amount more than about 0.005 gram per 100 grams of ammonium nitrate. With coarse ammonium nitrate, e.g., granulated ammonium nitrate, as little as 0.001 gram of alkylamine per 100 grams of ammonium nitrate can be suitably used. A preferred upper limit for the amount of alkylamine is 0.20 gram. Amounts in excess of 0.20 gram do not show enough improvement to warrant the increased cost.

The alkylamine can be added to the ammonium nitrate in a number of ways. The addition can be made to a minor portion of an entire bulk of ammonium nitrate which portion can subsequently be mixed with the remaining bulk of the ammonium nitrate. The best effect is achieved if the alkylamine is added to an already crystallized ammonium nitrate at a temperature higher than the melting point of the alkylamine, and the ammonium nitrate is then allowed to cool when stirred. The amine, however, may also be introduced into a solution or melt of ammonium nitrate previous to the crystallization or during the crystallization. It is also possible to use a salt of the alkylamine or a solution thereof, for example, hexadecyl ammonium chloride or acetate, instead of the alkylamine itself.

From a technical point of view it is most convenient to incorporate the alkylamine in the explosive composition by incorporating the alkylamine with the ammonium nitrate prior to the distribution of ammonium nitrate in the viscous phase of the explosive, because in this manner

the alkylamine is most easily handled and easiest to evenly distribute.

OTHER INGREDIENTS

The ammonium nitrate explosives made in accordance with the invention may also contain other ingredients, such as sensitizers, carbonaceous fuels and finely divided combustible metal powders. Examples of a sensitizer would be the explosive nitric esters, such as nitroglycerine and nitroglycol and nitrated hydrocarbons, such as trinitrotoluene. Examples of carbonaceous fuels would be coal and wood flour. The finely divided combustible metal powder may be powdered aluminum, silicon or ferrosilicon.

EXAMPLES IN GENERAL

The following examples are illustrative of preferred embodiments of the present invention. It should be understood that these examples are not intended to limit the invention and that obvious changes may be made by those skilled in the art without changing the essential characteristics and the basic concept of the invention. The parts and percentages are by weight, the temperature is room temperature and the pressure is atmospheric, unless otherwise indicated.

Example 1

A dynamite composition was prepared having the following components:

	Percent
Nitroglycerin	24.1
Nitroglycol	11.8
Ammonium nitrate treated with 0.16% of dodecylamine	54.4
Cyclic nitrohydrocarbons (trinitrotoluene)	6.0
Nitrocotton	1.4
Wood flour	2.1
Chalk	0.2

In extruding this dynamite at an average rate of shear of 8.27 sec.⁻¹ (cm./cm. sec.) a shear stress of only 2.3×10^4 dynes/cm.² was required. Essentially the same dynamite composition, but which contained no dodecylamine, required at the same rate of shear a shear stress of 2.8×10^4 dynes/cm.². After storage for 24 hours the dynamite with no dodecylamine was not extrudable in the extruder used, i.e., required a higher shear stress than 9.2×10^4 dynes/cm.², whereas the dynamite with dodecylamine required a shear stress of only 2.5×10^4 dynes/cm.² at a rate of shear 8.27 sec.⁻¹. This test clearly shows the advantage of using alkylamine in an explosive composition.

Example 2

A first dynamite composition was prepared having the following components:

	Percent
Nitroglycerin	24.1
Nitroglycol	11.8
Ammonium nitrate	54.4
Cyclic nitrohydrocarbon (trinitrotoluene)	6.0
Nitrocotton	1.4
Wood flour	2.1
Chalk	0.2

A second dynamite composition was prepared using the same component and amounts but with the difference that the ammonium nitrate was treated with 0.1% of octadecylamine. The two dynamites were compared in a laboratory extruder with an average rate of shear of 4.56 sec.⁻¹. 3 hours after manufacture the dynamite containing the octadecylamine only required a shear stress of 2.8×10^4 dynes/cm.², whereas the dynamite without octadecylamine required a shear stress of 4.1×10^4 dynes/cm.². 24 hours after manufacture the dynamite containing octadecylamine only required a shear stress of 3.0×10^4 dynes/cm.², whereas the dynamite without octadecylamine was not extrudable, i.e., required a higher shear stress than 9.2×10^4 dynes/cm.².

Example 3

100 grams of dynamite composition according to Example 2 with 54.4% of ammonium nitrate and containing 0.1% of octadecylamine was admixed with additional ammonium nitrate containing 0.1% of octadecylamine until the same extrudability was achieved as with a dynamite of the same composition as Example 2 but without octadecylamine. For this purpose an addition of 7 g. of ammonium nitrate was required.

Example 4

A reference sample of 280 kg. of plastic explosive according to the first dynamite composition of Example 2 and containing 54.4% of ammonium nitrate was compared with a second sample of 292 kg. of an ammonium nitrate explosive comprising a mixture of 280 kg. of an explosive according to the second dynamite composition of Example 2 and 12 kg. of ammonium nitrate containing 0.1% of octadecylamine. In spite of the greater amount of ammonium nitrate in this second explosive sample, it required a somewhat lower effort to knead than the reference sample. In extruding at a rate of shear of 4.56 sec.⁻¹ the amine containing dynamite required a shear stress of only 3.5×10^4 dynes/cm.², whereas the reference sample required a shear stress of 4.1×10^4 dynes/cm.². The impact test (falling weight test), tearing sensibility, temperature of detonation, chemical stability and velocity of detonation were very similar for both samples. Detonation transmission from cartridge to cartridge (22 mm. diameter) was 10% higher for the second sample (containing octadecylamine) than for the reference sample, again demonstrating the advantages of incorporating alkylamines in ammonium nitrate explosive compositions.

Example 5

A quantity of ammonium nitrate which had been stored for one year was dried and ground. One half of the quantity was admixed with 0.1 oleylamine and the other half remained as a reference. Explosives with the same composition as stated in Example 1 were manufactured from these treated and untreated samples. The explosive containing the untreated sample was too viscous to be extruded into 25 mm. cartridges, whereas the explosive formed with amine treated ammonium nitrate gave a product which was almost too soft even for extrusion to 20 mm. cartridges. After storage for one week the detonation transmission from cartridge to cartridge (22 mm. diameter) was 425 mm. for the explosive containing amine treated ammonium nitrate, whereas the detonation transmission for the explosive formed with untreated ammonium nitrate was only 165 mm.

Example 6

Crystallized ammonium nitrate was admixed and stirred with 0.1% of isopropylaminelaurylsulphate dissolved in water to a concentration of 33%. This admixture was then dried at 30° C. in vacuum. 210 g. of the thus treated ammonium nitrate was kneaded together with 100 g. of a 4% solution of nitrocellulose in dibutylphthalate. In extruding the resulting product at a rate of shear of 4.56 sec.⁻¹ the plastic mass required a shear stress of only 2.8×10^4 dynes/cm.². A sample made in the same way but without isopropylaminelaurylsulphate required at the same rate of shear a shear stress of 6.5×10^4 dynes/cm.².

Example 7

A plastic explosive (A) was prepared having the following composition:

	Percent
Nitroglycerin-nitroglycol 70/30	35.9
Cyclic nitrohydrocarbons (trinitrotoluene)	6.0
Nitrocellulose	1.4
Ammonium nitrate	54.4
Wood flour	2.1
Chalk	0.2

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Another explosive (B) was prepared with the following composition with the same properties at extrusion:

	Percent
Nitroglycerin-nitroglycol 70/30	35.9
Trinitrotoluene	2.0
Nitrocellulose	1.4
Ammonium nitrate	58.4
Wood flour	2.1
Chalk	0.2
Hexadecylamine	0.02
Octadecylamine	0.02

The velocity of detonation and the detonation transmission (gap test) were determined for these two explosives.

The values obtained for velocity of detonation, m./sec. by a column of explosive 25 mm. in diameter initiated by a Standard No. 8 detonator were as follow:

After storage for—	m./sec. for Explosive	
	(A)	(B)
24 hours, confined	6,410	6,605
24 hours, nonconfined	6,110	6,535
1 week, nonconfined	3,735	6,225
1 month, nonconfined	3,305	5,810
3 months, nonconfined	3,605	5,930
6 months, nonconfined	3,065	6,190

The values obtained for the gap test, mm. by a column of explosive 22 mm. diameter were as follows:

After storage for—	Temperature, ° C.	mm. for Explosive	
		(A)	(B)
24 hours	17	200-210	480-490
1 week	17	200-210	500-510
1 month	17	200-210	460-470
3 months	17	200-210	400-410
6 months	18	200-210	430-440

After storage for—	Temperature, ° C.	mm. for Explosive	
		(A)	(B)
72 hours	-20	50-60	430-440
216 hours	-20	30-40	200-210
1 month	-20	50-60	260-270
3 months	-20	70-80	250-260
6 months	-20	70-80	320-330

This example illustrates the superiority of the present compositions at low temperature.

Example 8

A dynamite was prepared with the following composition:

	Percent
Nitroglycerin-nitroglycol, 50/50	35.9
Trinitrotoluene	6.0
Nitrocellulose	1.4
Wood flour	2.1
Ammonium nitrate	54.5
Chalk	0.05
Iron oxide (red pigment)	0.05

Said dynamite was admixed with increasing amounts of stearyl amine. The extrudability was determined at a rate of shear of 4.56 sec.⁻¹ after 3 hours' storage.

G. stearyl amine/g. dynamite:	Shear stress, dynes/cm. ²
0	4.00×10 ⁴
0.0004	2.70×10 ⁴
0.0032	2.55×10 ⁴

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Example 9

A mixture was prepared containing:

	G.
Ammonium nitrate	20
A 4% solution of nitrocellulose in dibutylphthalate	10

This mixture was admixed with increasing amounts of stearyl amine. The extrudability was determined at a rate of shear of 4.56 sec.⁻¹.

Percent stearyl amine:	Shear stress, dynes/cm. ²
0.00	Not extrudable
0.008	9.8
0.03	3.29
0.07	3.26
0.09	2.88
0.70	2.23

Example 10

A pulverous explosive composition was prepared from the following components:

	Percent
Nitroglycerin-nitroglycol (60/40)	6.3
Ammonium nitrate treated with 0.05% of stearyl amine	76.1
Trinitrotoluene	11.5
Silicon	2.0
Kieselguhr	1.2
Wood flour	2.7
Paraffin	0.2

This explosive confined in an iron tube gave a velocity of detonation of 5,400 m./sec. The detonation transmission (gap test) of explosive 22 mm. diameter, was 230-240 mm. A corresponding explosive without stearyl amine gave a detonation transmission of only 150-160 mm.

Example 11

A pulverous explosive composition was prepared from the following components:

	Percent
Nitroglycerin	6
Wood flour	5
Aluminium	4
Ammonium nitrate treated with 0.1% of stearyl amine	85

The explosive had a density of 1.25 g. per cm.³. Corresponding explosive without stearyl amine had a density of only 1.14 g. per cm.³. The velocity of detonation in a paper cylinder 25 mm. diameter was 2,800 m./sec. and the detonation transmission 60-70 mm. A corresponding explosive without stearyl amine gave a velocity of detonation of 2,500 m./sec. and a detonation transmission of only 50-60 mm.

Example 12

A pulverous ammonium nitrate explosive was prepared in our plant with the following composition:

	Percent
Nitroglycerin-nitroglycol (60/40)	6.0
Ammonium nitrate treated with 0.08% of stearyl amine	85.3
Silicon	3.0
Wood flour	2.8
Paraffin	2.9

A sample thereof showed a detonation transmission of 40-70 mm. at 20° C., 25 mm. diameter, but a sample without stearyl amine showed a detonation transmission of only 0-20 mm. under the same conditions.

Example 13

A pulverous explosive was prepared with the following composition:

	Percent
Nitroglycerin-nitroglycol (60/40) -----	6
Wood flour -----	2
Paraffin -----	3
Silicon -----	2
Ammonium nitrate treated with 0.08% of stearyl amine -----	87

The detonation transmission by a column of explosive 22 mm. diameter initiated by a Standard No. 8 detonator at 20° C. was 40–70 mm. and the figure of the transmission was only slightly lower at lower temperatures. The detonation transmission of the same explosive without stearyl amine at 20° C. was only 0–30 mm.

Example 14

93 g. of crystallized ammonium nitrate were mixed at 60° C. with 4 g. of wood flour and 0.1 g. of laurylamine. After cooling, 3 g. of fuel oil were introduced and the product packed in paper cylinders to form cartridges. The density of the packed material was 10% greater than could be achieved by packing with an ammonium nitrate which did not contain an alkylamine.

Example 15

A 4% solution of nitrocellulose in dibutylphthalate was prepared. One part by weight of said gel was admixed with two parts by weight of ammonium nitrate, which was treated with 0.0003 mole/100 g. ammonium nitrate of an amine compound listed in the table below. The shear stress was determined at a rate of shear of 2.28 sec.⁻¹.

Additive:	Shear stress, dynes/cm. ²
-----	9.40 × 10 ⁴
Stearyl amine -----	3.41 × 10 ⁴
Stearyl amine acetate -----	3.76 × 10 ⁴
Stearyl dimethylamine -----	5.65 × 10 ⁴
C ₁₈ H ₃₇ NH(CH ₂) ₃ NH ₂ (N-stearyl propylene diamine) -----	3.76 × 10 ⁴

ADVANTAGES OF THE PRESENT NOVEL COMPOSITION

The composition of the present invention has a number of advantages which can be summarized as follows:

(1) The wetting of the ammonium nitrate surfaces by the liquid phase is reduced and hence air bubbles of suitable dimensions are retained on the salt crystals even after storage for a long period of time.

(2) The sensibility of the stored explosive will be retained for a long time.

(3) The freshly prepared explosive will have a higher detonation transmission range.

(4) The explosive will have a better stability of detonation also at low temperatures.

(5) The improved properties resulting from the addition of alkylamines are not limited to the plastic explosives but are also obtained for ammonium nitrate explosives in pulverant form, which latter explosives have also a higher density and a better storage property.

(6) The plastic viscosity and the flow limit of the explosive mixtures are reduced and accordingly the power acquired for the kneading operation is diminishing and the extrusion of the mixture can be made at a lower pressure or at a higher velocity.

(7) The maximum amount of solid substances in the mixture can be increased.

Unless otherwise specified the terms used in this specification have the meaning set forth in the most recent edition of Hackh's Chemical Dictionary.

Those skilled in the chemical arts, and particularly in the art to which this invention pertains, will readily appreciate that many modifications of the basic invention set forth here are possible. For example, it is quite possible that other closely related compounds might work as well as the herein specifically described compounds and there would certainly be no invention involved in trying such closely related compounds, in view of the present broad disclosure. All of these modifications are considered to be within the scope of the present claims by virtue of the well-established "doctrine of equivalents."

What is claimed is:

1. A novel explosive and propellant composition of increased stability of propagation and increased detonation transmission comprises ammonium nitrate, said nitrate having a surface coating of an alkyl amine having between 6 and 24 carbon atoms in the alkyl group in an amount of up to 1.5 grams of alkyl amine with each 100 grams of nitrate.

2. A novel explosive according to claim 1 wherein said nitrate is ammonium nitrate.

3. A novel explosive according to claim 1 wherein said alkyl amine is an alkyl amine having between 12 and 18 carbon atoms in the alkyl group.

4. A novel explosive according to claim 3, wherein said amine is an amine selected from the group consisting of stearyl amine, dodecyl amine, hexadecyl amine and octadecyl amine.

5. A novel explosive according to claim 3 which additionally contains a combustible material.

6. A novel explosive according to claim 3 which additionally contains a combustible material and an explosive sensitizer.

7. A novel explosive according to claim 1 with improved extrudability which additionally contains a liquid carbonaceous material.

8. As a new product ammonium nitrate consisting essentially of between about 0.001 and 0.20 grams of an alkyl amine for each 100 grams of ammonium nitrate, said alkyl group of said alkyl amine having between 12 and 18 carbon atoms.

References Cited in the file of this patent

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