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PROPELLANT AND EXPLOSIVE COMPOSITION

Ralph F. Preckel, Cumberland, Md., assignor, by mesne assignments, to the United States of America as represented by the Secretary of the Navy

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This invention relates to propellent compositions, more particularly, it relates to double base propellent compositions.

It is an objective of this invention to provide a substitute in double base propellants for nitroglycerin, the explosive plasticizer for nitrocellulose in propellants which imparts to them properties of high impact sensitivity and high heat sensitivity which makes handling of the propellants extremely hazardous.

It has been found that satisfactory propellent and explosive compositions are produced by the substitution in double base propellants and explosives containing nitrocellulose, of hydroxyethyl glycerol trinitrate for nitroglycerin in approximately analogous amounts. The compositions are made by methods analogous to those used for compounding conventional double base propellants and explosives containing nitrocellulose, such methods being well known in the art. Propellent grains may be made from them by the conventional solventless process, casting, or otherwise.

Hydroxyethyl glycerol trinitrate was found to have a lower vapor pressure than nitroglycerin and to be markedly less sensitive to impact than nitroglycerin. Its sensitivity to heat is also appreciably less than that of nitroglycerin. The compound may be obtained in about 50 percent yield by the addition of ethylene glycol to epichlorohydrin followed by hydrolysis. The resulting ether is then nitrated to form the nitrate.

Hydroxyethyl glycerol was prepared as follows: 1,120 grams of technical ethylene glycol were added to a 3-necked flask equipped with an efficient stirrer, thermometer and dropping funnel. 9.0 cc. of conc. H_2SO_4 were added as a catalyst. 610 grams of epichlorhydrin (technical) were added dropwise, over a period of four hours controlling the temperature to 50° C. After the addition, the reaction mixture was heated to 95° C. for two hours to assure complete reaction. Then, technical soda ash was added to neutralize the H_2SO_4. The excess ethylene glycol was distilled off at 100–135° C./15–22 mm. Most of this came off at 115°/16 mm. Then 370 grams of tech. sodium carbonate, dissolved in 1100 ml. of distilled water were added to the residue in the flask. The mixture was hydrolyzed at 100° C. for 24 hours. The water was distilled off until the deposition of salt crystals caused too much "bumping." The salt was filtered out and the salt washed with 50 ml. of methyl alcohol. This was necessary once more, and then the methyl alcohol extract was added to the main portion, and the alcohol and remaining water stripped off under reduced pressure (up to 150° C. at 10 mm.). 588 grams of product were distilled between 151–180° at ca. 1 mm. with 160 grams of residue. 588 grams corresponds to a 65.4% yield of hydroxyethyl glycerol.

Hydroxyethylglycerol trinitrate was prepared as follows: 450 grams hydroxyethylglycerol was treated with

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1500 grams nitrating mixed acid having the following composition:

	Percent
Total nitric	46.13
Total sulfuric	53.95
Moisture	.74
DVS	4.36

The temperature was maintained at 4–6° F. during nitration. The crude hydroxyethylglycerol trinitrate was separated in the usual way and washed with a total of 1800 grams of wash water to give a total of 791 grams of hydroxyethylglycerol trinitrate of the following analysis: KI test—20 minutes, nitrogen content—15.35%, moisture—2.45%. The 832 grams of spent acid obtained analyzed as follows:

	Percent
Total nitric	8.31
Total sulfuric	75.54
Actual nitric	5.14
Total oxidizables	4.54
Nitrogen oxides	.74
Hydroxyethylglycerol trinitrate	3.80

The wash waters analyzed 0.17% hydroxyethylglycerol trinitrate.

Tables I to IV, below, set forth data illustrating the invention and its operability for the expressed purpose. In Table I there is presented the percentage composition of eight propellent formulations (Examples 1, 2, 3, 5, 7, 8, 10 and 12), incorporating hydroxyethyl glycerol trinitrate as the explosive plasticizer for nitrocellulose. For comparative purposes Examples 4, 6, 11 and 13, incorporating nitroglycerin as the explosive plasticizer, and Example 9, incorporating equal amounts of nitroglycerin and hydroxyethyl glycerol trinitrate as the explosive plasticizer, are given. Table I also presents a comparison of important ballistic properties of the propellent compositions based on actual tests. Table II presents comparisons of other ballistic properties of the two types of propellants based on the examples given in Table I. Table III presents comparative physical properties of formulations incorporating nitroglycerin and those incorporating hydroxyethyl glycerol trinitrate, based on four of the examples given in Table I. Table IV gives a comparative showing of the Taliani stability of the two type formulations, obtained using the compositions of the examples of Table I.

It will be noted from Table I that the use of hydroxyethyl glycerol trinitrate as an explosive plasticizer in double base propellants produces a propellant having platonic ballistics. The temperature coefficient of equilibrium pressure in the plateau range for solventless and cast formulations is good. Other ballistic properties are quite acceptable. As illustrated by Table I, operable percentage ranges for nitrocellulose, hydroxyethyl glycerol trinitrate and lead stearate are 55–61, 23.5–39 and 1–2, respectively. As stated previously, hydroxyethyl glycerol trinitrate may be substituted in propellent compositions in amount equal to the nitroglycerin content. This, of course, includes propellants incorporating other lead compound ballistic modifiers, such as lead, 2-ethyl hexoate and lead salicylate.

TABLE I

Compositions and Ballistics of Hydroxyethyl Glycerol Trinitrate and Nitroglycerin Propellants

Example No.	1	2	3	4	5	6	7
Nitrocellulose (12.6% N)	58.5	60.0	60.0	60.0	60.0	60.0	60.0
Nitroglycerin				39.0		29.5	
Hydroxyethyl glycerol trinitrate	27.5	33.0	39.0		30.0		23.5
Dimethylphthalate					9.0	9.5	15.5
2-dinitrophenylamine				1.0	1.0	1.0	1.0
Ethyl centralite	3.0	1.0	1.0				
Triacetin	8.5	6.0					
Dinitrotoluene	2.5						
Diglycol diacetate							
Carbon black (add)							
Lead stearate (add)	1.0	2.0	2.0	2.0	1.0	1.0	1.0
Heat of explosion (cal./g.)	697	824	972	1,190	764	910	587
Plateau n [1]	0.0	0.12	0.24	0.67	0.0	0.53	0.22
Plateau pressure region (p.s.i.)	1,400-2,000	550-1,000	300-720	340-1,200	1,500-1,900	300-1,050	2,000-2,850
Temp. coeff. of equil. pressure, percent/° C	0.3	0.6	0.5	1.3	0.4	1.2	0.6
Burning rates, p.s.i. (in./sec.):							
25° C.:							
1,000	0.20	0.21	0.29	.44	0.23	.24	0.15
1,500	.26	.28	.39	.61	.31	.34	.22
2,000	.26	.34	.48	.78	.33	.44	.28
50° C.:							
1,000	.23	.24	.33	.49	.27	.27	.17
1,500	.29	.31	.44	.67	.34	.39	.25
2,000	.31	.39	.54	.86	.36	.51	.33

Example No.	8	9	10	11	12	13
Nitrocellulose (12.6% N)	60.0	60.0	55.0	55.0	60.7	59.5
Nitroglycerin		13.0		30.0		28.1
Hydroxyethyl glycerol trinitrate	30.0	13.0	30.0		27.2	
Dimethylphthalate	9.0	13.0				
2-dinitrophenylamine	1.0	1.0	1.0	1.0	1.0	1.0
Ethyl centralite						
Triacetin						
Dinitrotoluene						
Diglycol diacetate			12.0	12.0	9.2	9.5
Carbon black (add)	0.5		0.2	0.2		
Lead stearate (add)	2.0	1.0	[2] 2.0	[2] 2.0	[2] 1.9	[2] 1.9
Heat of explosion (cal./g.)	742	726	667	832	735	885
Plateau n [1]	0.25	0.34	0.0	0.12	0.0	0.27
Plateau pressure region (p.s.i.)	2,000-4,000	1,000-1,800	1,800-3,000	1,500-3,400	1,100-1,750	350-1,050
Temp. coeff. of equil. pressure, percent/° C	0.5	0.6	0.3	0.2	0.2	
Burning rates, p.s.i. (in./sec.):						
25° C.:						
1,000	0.31	[3] 0.23	[3] 0.30	[3] .37	0.29	0.26
1,500	.41	.27	.38	.49	.31	.34
2,000	.50	.32	.43	.51	.34	.41
50° C.:						
1,000	.34	[4] .26	[4] .34	[4] .41	.34	
1,500	.45	.30	.44	.54	.34	
2,000	.55	.35	.45	.56	.39	

[1] Defined in Table II. [2] Not added. [3] 70° F. [4] 125° F.

TABLE II

Slopes From Log n[1]–Log P[2] Graphs for Hydroxyethyl Glycerol Trinitrate and Nitroglycerin Propellants (25° C. Data)

Example No.													
1		2		3		4		5		6		7	
n	P range	n	P range	n	P range	n	P range	n	P range	n	P range	n	P range
0.86	300-1,400	0.49	300- 550	0.75	160- 300	0.67	340-1,200	0.82	350-1,500	0.53	300-1,050	0.66	350- 750
.0	1,400-2,000	.12	550-1,000	.24	300- 720	0.86	1,200-4,000	.0	1,500-1,900	.88	1,050-4,000	.93	750-2,000
0.95	2,000-4,000	.65	1,000-4,000	.67	720-1,800			.83	1,900-4,000			.22	2,000-2,850
				.96	1,800-4,000							1.0	2,850-4,000

Example No.											
8		9		10 (70° F)		11		12		13	
n	P range	n	P range	n	P range	n	P range	n	P range	n	P range
0.85	300- 740	0.83	300-1,000	0.58	500-1,800	0.68	500-1,500	0.76	600-1,100	0.70	160- 350
.68	740-2,000	.34	1,000-1,800	.0	1,800-3,000	0.12	1,500-3,400	.0	1,100-1,750	0.27	350-1,050
.25	2,000-4,000	.82	1,800-4,000			0.80	3,400-4,000	.63	1,750-2,900	.70	1,050-3,450

[1] The slope of the line resulting from a logarithmic plot of burning rate against the pressure at which burning rate is measured.
[2] The pressure at which burning rate is measured.

TABLE III

Physical Properties of Hydroxyethyl Glycerol Trinitrate and Nitroglycerin Propellants

	Ex. 10		Ex. 11	Ex. 12	Ex. 13
Tensile strength (p.s.i.)	320		341	--------	627
Elongation (percent)	11.0		7.7	--------	24
Work to failure (in. lb./cu. in.)	2.2		1.6	--------	11.7
Compressive strength (p.s.i.)	[1] 880	[2] 2,900	[1] 687	[2] 8,500	[1] 4,020
Compression (percent)	50	50	50	43	53
Work to failure (ft. lb./cu. in.)	18.7	68	[3] 17.1	123	81
Impact strength (in. lb./in. notch), ° C.:					
25	11.9	--------	8.9	--------	17.6
6–8	4.9	--------	2.4	--------	6.0
−10	2.4	--------	2.1	--------	3.3
−25	1.1	--------	0.6	--------	2.0
−40	0.4	--------	0.5	--------	0.7

[1] For constant deformation rate of 0.1 in./in./sec.
[2] At high rate of loading of 10,000 p.s.i./sec.
[3] At 50 percent.

The data in the above table indicates that the physical properties of the compositions incorporating hydroxyethyl glycerol trinitrate as the explosive plasticizer are of approximate equivalence of those incorporating nitroglycerin.

TABLE IV

Taliani Stability of Hydroxyethyl Glycerol Trinitrate and Nitroglycerin Propellants (110° C., N_2 Atmosphere)

Example No.	Time to 100 mm. (min.)	Slope at 100 mm.	Slope at 100 mm.
1	138	0.69	------------
2	166	0.61	0.60
3	188	0.51	0.50
4 (NG)	182	0.61	0.60
5	256	0.40	0.40
6 (NG)	311	0.44	0.45
7	216	0.46	0.45
8	253	0.40	0.40
9	221	0.45	0.45
10	258	0.45	0.45
11 (NG)	129	0.74	0.75
12	211	0.46	0.50
13 (NG)	183	0.52	0.50

The above table shows that heat stability as measured by the Taliani test is satisfactory for all of the compositions incorporating hydroxyethyl glycerol trinitrate, and in fact, there is indication that their stability is measurably better than that obtained using nitroglycerin.

The percentage composition range of the examples and the range of components given, together with the test results thereon, establish the operativeness in general of hydroxyethyl glycerol trinitrate as an explosive plasticizer in double base propellants utilizing nitrocellulose.

From the above data it is seen that the invention provides a substitute for nitroglycerin in propellants and explosives which provides compositions having satisfactory propellant and explosive properties, and which are less sensitive to impact and heat than compositions incorporating nitroglycerin, thus making them safer to handle than conventional propellants and explosives.

This is a continuation-in-part application of my application Serial No. 517,109, filed in the U.S. Patent Office on June 21, 1955, now abandoned, for Propellant and Explosive Composition.

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 double base propellant composition, consisting essentially of from about 50 to about 55 percent of nitrocellulose and from about 20 to about 45 percent of hydroxyethyl glycerol trinitrate.

2. A double base propellent composition consisting essentially of from about 55 to about 61 percent nitrocellulose, from about 23 to about 33 percent of hydroxyethyl glycerol trinitrate, and from about 1 to about 2 percent of lead stearate.

No references cited.