Patented Sept. 21, 1943 2,330,112

UNITED STATES PATENT OFFICE

2,330,112

NITROETHYL NITRATE DERIVATIVE

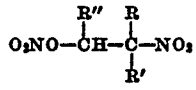
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No Drawing. Application October 2, 1940, Serial No. 359,361

6 Claims. (Cl. 52—11)

This invention relates to new explosive compounds and more particularly to neutral derivatives of nitroethyl nitrate.

More specifically the invention relates to nitroisobutyl nitrate and compounds corresponding to the general formula—



When ethylene is nitrated there is obtained an explosive admixture which comprises about 40 parts of nitroglycol and 60 parts of beta-nitroethyl nitrate. This admixture is not of commercial value because it is instable and has a tendency to decompose with the evolution of oxides of nitrogen. The instability of the explosive has been attributed to the nitroethyl nitrate because of its acidic group $=CHNO_2$. The prior art has proposed various methods of destroying the nitroethyl nitrate in order to make use of the nitroglycol, which in itself is a stable explosive. However, no method of commercially using the nitroethyl nitrate has been proposed.

The instability of explosives due to decomposition with the formation of acidity is known in the art, and antacids such as chalk or magnesiumcarbonate are employed to remedy this condition but nitroethyl nitrate has not been successfully used in explosive compositions, even when antacids are present.

This invention has as an object the production of a neutral stable explosive oil.

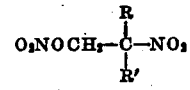
A further object of this invention is the production of neutral derivatives of nitroethyl nitrate.

A further object of this invention is the production of explosive compounds containing neutral derivatives of nitroethyl nitrate.

A still further object of this invention is the production of nitrates of nitroalcohols which have relatively greater stability than nitroethyl nitrate.

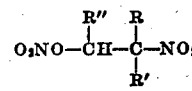
Other and further objects will appear hereinafter.

The objects of this invention have in general been accomplished by substituting neutral lower alkyl radicals for the hydrogen atoms attached to the carbon atom holding the nitro radical in nitroethyl nitrate. For example, nitroethyl nitrate has the formula



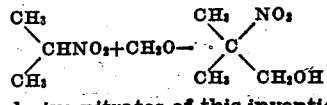
in which R and R′ are hydrogen atoms and in accordance with this invention these hydrogen atoms have been replaced by either methyl or ethyl groups, thereby forming a neutral derivative. When methyl groups are substituted for each hydrogen atom there is formed the compound nitroisobutyl alcohol nitrate which is neutral and is a very useful explosive.

In addition to the formation of the above neutral derivatives it is to be understood that in accordance with this invention other substituted nitroethyl nitrates may be prepared. Thus I have found that in the general formula



I may form neutral derivatives by substituting for the R and R′ lower alkyl radicals, for example, the methyl and ethyl radicals, and for the R″ I may substitute either hydrogen or lower alkyl radicals, for example, methyl and ethyl radicals. Compounds with the above type substitutes are neutral, are explosive, and are very useful in explosive compositions as they do not tend to decompose and set up dangerous conditions in the composition.

In order to produce the neutral derivatives of nitroethyl nitrate I may first prepare substituted nitroethyl alcohols, for example, by condensing secondary nitro compounds such as the secondary nitroparaffins with formaldehyde in the presence of an alkaline catalyst. To illustrate this condensation reaction the following equation in which secondary nitropropane and formaldehyde are condensed is given:



The explosive nitrates of this invention may be produced by nitration of substituted nitroethyl alcohols prepared as illustrated above by treating them with mixed acid in the manner described by

the following example in which all parts are by weight:

Example I

Nitroisobutyl alcohol is nitrated by adding it to mixed acid containing approximately 50% HNO_3 and 50% H_2SO_4. The reaction is carried out in the same type of nitrator as used for nitrating glycerin, the procedure being as follows: Place 500 pts. of mixed acid in the nitrator and cool to about 35° F. Then gradually add with agitation 200 parts of nitroisobutyl alcohol at such a rate as to maintain the temperature of nitration at about 45° F. After nitration is complete, the charge is drowned to get the nitrated material out of the spent acid, by running it into cold water under agitation. The amount of water should be approximately five times the volume of the charge.

After the charge is completely drowned the agitation is stopped and the nitrated product allowed to settle. It is then drawn into an equal volume of water and agitated at about 105° F. for ten minutes and then allowed to settle. The charge is then neutralized by washing it with an equal volume of about 5% soda ash solution at 105° F.

The nitroisobutyl nitrate prepared in this manner analyzed 13.3% nitrate nitrogen in the nitrometer and had a pH of 7.2 which is indicative of its neutrality. The pH was determined by testing 10 cc. of neutral water after it had been shaken with 2 cc. of the explosive oil.

The stability of nitroisobutyl nitrate as shown by the standard KI test was in the range required of commercial nitroglycerin for use in dynamite, that is, a KI test of over 10 minutes was obtained.

The sensitivity of the nitroisobutyl nitrate to impact was satisfactory as the drop of a 2 kilogram weight from a height of 100 cm. would cause no detonation. This relative insensitivity and its high negative oxygen balance (—68%) puts nitroisobutyl nitrate in a class with trinitrotoluene. Because of its relative insensitivity and high negative oxygen balance, nitroisobutyl nitrate is especially suited for sensitization of safety explosives containing no ingredients which are classed as of the type of nitroglycerin consisting chiefly of ammonium nitrate and other salts of high positive oxygen balance.

The explosives produced in accordance with this invention are also adaptable for use in the nitroglycerin type of explosives, and they may be added directly to the nitroglycerin or they may be prepared by nitrating the substituted nitroethyl alcohols in conjunction with the substances being used for the preparation of nitroglycerin.

The following example illustrates the preparation of a nitroglycerin type of explosive in which there is included an explosive in accordance with this invention. All parts are by weight.

Example II

An admixture of 20 parts nitroisobutyl alcohol, 20 parts sugar, 30 parts glycerin and 30 parts glycol are dissolved by warming to 50° C. After cooling, the mixture of alcohols is added gradually with agitation to 500 parts cold mixed acid consisting of equal parts by weight of nitric acid and sulfuric acid. The addition is carried out at such a rate that a temperature of approximately 45° F. is maintained. When the nitration is complete the charge is run into a separator where it is allowed to stand and separate due to difference in specific gravity of the acid and nitrated product.

After separation is complete the charge is washed by agitating it at 105° F. with a volume of H_2O equal to about 1½ times the volume of nitrated material. It is then neutralized as outlined in Example I.

Nitroisobutyl alcohol nitrate in admixture with nitroglycerin and/or its equivalents may be used in manufacture of dynamites. For example, the following compositions gave satisfactory results in standard tests.

Example III

	Per cent
75% nitroglycerin 25% nitroisobutyl alcohol nitrate	40.0
$NaNO_3$	48.0
Wood pulp	11.0
Chalk	1.0

Example IV

	Parts by weight
Nitration product of: 20 parts by weight nitroisobutyl alcohol 20 parts by weight sugar 30 parts by weight glycerin 30 parts by weight glycol	17
NH_4NO_3	60.5
$NaNO_3$	12.7
Wood pulp	0.5
Manioc flour	5.8
Sulfur	3.0
Chalk	0.5

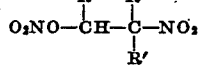
Where in the above examples and specification I have used the term nitroglycerin, I wish it to be understood that I mean the term as used by the art, that is, nitroglycerin includes the compound by itself or with the addition or partial substitution of any of the commercially used freezing point depressants such, for example, as ethylene glycol dinitrate, nitrated polymerized glycerin, nitrated sugars, nitrated chlorohydrins, etc.

The new explosive compounds which have been produced in accordance with this invention have been found to be useful as sensitizers for safety explosives and as substitutes for various compounds used in conjunction with nitroglycerin. The explosive compounds have been proven to be stable, reliable, and sensitive, and for this reason have proven highly desirable in explosive compositions.

It will be understood that the details and examples hereinbefore set forth are illustrative only and that the invention as broadly described and claimed is in no way limited thereby.

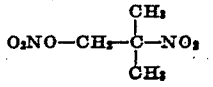
What I claim and desire to protect by Letters Patent is:

1. A substitution product of nitroethyl alcohol nitrate having the following general formula:

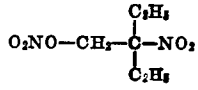


in which R and R′ are alkyl radicals having not more than two carbon atoms and R″ is a radical from the group consisting of H, CH_3, and C_2H_5.

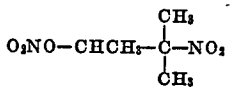
2. A compound of the following chemical formula:



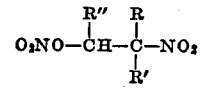
3. A compound of the following chemical formula:



4. A compound of the following chemical formula:

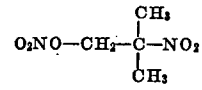


5. A safety explosive composition comprising a major proportion of ammonium nitrate and as a sensitizer a compound of the following general formula:



in which R and R' are alkyl radicals having not more than two carbon atoms and R'' is a radical from the group consisting of H, CH_3, and C_2H_5.

6. A safety explosive composition comprising a major proportion of ammonium nitrate and as a sensitizer a compound of the following chemical formula:



RICHARD F. B. COX.