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Runge et al.

[11] **3,915,768**

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[54] **SENSITIZED NITROMETHANE**

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[52] **U.S. Cl.** **149/89**

[51] **Int. Cl.**[2] **C06B 25/36**

[58] **Field of Search** ..... 149/89, 91; 260/471 A, 260/404

[56] **References Cited**

UNITED STATES PATENTS

2,891,852	6/1959	Schaad	149/89
3,132,060	5/1964	Beegle	149/89
3,239,395	3/1966	Laurence	149/89
3,288,867	11/1966	Egly	149/89

Primary Examiner—Benjamin R. Padgett
Assistant Examiner—Donald P. Walsh
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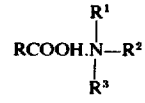
[57] **ABSTRACT**

A nitromethane composition sensitive to detonation by shock consisting essentially of nitromethane and a sensitizer represented by the formula



where R is hydrogen or an alkyl group of 1 to about 4 carbon atoms, R^1 and R^2 can be hydrogen or alkyl, e.g. alkyl of from 1–5 carbon atoms and can be the same or different, or R^2 plus R^3 can be $-(CH_2)_5-$, and R^3 can be alkyl, e.g. alkyl of 1–5 carbon atoms, or aryl, e.g. phenyl or benzyl.

10 Claims, No Drawings

SENSITIZED NITROMETHANE

BACKGROUND OF THE INVENTION

This invention relates to explosive compositions. In a particular aspect this invention relates to sensitized nitromethane compositions.

It is known from E. A. Laurence, U.S. Pat. No. 3,239,395 to sensitize nitromethane with 2–40% by vol. of substantially any organic amine. The mechanism of the sensitization was never satisfactorily understood, but it is known that nitromethane tautomerizes to the aci form, $CH_2{=}NO_2H$ which forms explosive salts with alkalis, so it was hypothesized that the amine reacted with the acid to form unstable compounds.

This method of sensitizing nitromethane has been quite successful, but several problems have arisen. Amines in general are corrosive to the skin and if not removed promptly by use of copious amounts of water, they can cause severe health problems. Explosives are frequently used in areas where little water is available, so there is substantial risk of the operator being exposed to the amine at the time it is added to the drum, but without adequate water supplies to flush away the amine. One of the outstanding advantages of using sensitized nitromethane is that, before sensitization, nitromethane can be subjected to rough treatment without risk of detonation, then, at the site, can be sensitized and detonated. Therefore it would be undesireable to sensitize the nitromethane before transporting it to the site of use. Furthermore, sensitized nitromethane deteriorates rather rapidly upon standing, so it should be used promply after sensitization. There is therefore a need for an improved method of sensitizing nitromethane.

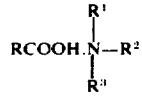
SUMMARY OF THE INVENTION

It is an object of this invention to provide an explosive composition.

It is another object of this invention to provide sensitized nitromethane compositions.

Other objects of the invention will be apparent to those skilled in the art from the disclosure herein.

It is the discovery of this invention to provide nitromethane compositions sensitive to detonation by strong shock consisting essentially of nitromethane and from about 1 to 20% based on the total weight of the composition of an amine salt sensitizer represented by the formula



where R is hydrogen or an alkyl group of 1 to about 4 carbon atoms; R^1 and R^2 can be hydrogen or alkyl of 1 to 5 carbon atoms, and can be the same or different, or R^2 and R^3 together can be the group $-(CH_2)_5-$; or R^3 can be an alkyl group, e.g. alkyl of 1 to about 5 carbon atoms or aryl, e.g. phenyl or benzyl.

DETAILED DISCUSSION

It was particularly surprising to discover that amine salts would sensitize nitromethane because of the belief that sensitization by amines was caused by formation of

an unstable reaction product of aci-nitromethane (methylnitronic acid) and the amine. Subsequent to this discovery, it has been determined by nuclear magnetic resonance studies that there is no evidence of molecular association between the amine and the nitromethane.

The term "sensitization" as used herein is intended to mean that the amine salt renders the nitromethane detonable by strong shock, but which is less than the shock required to detonate unsensitized nitromethane. The amine salt is useful in amounts of about 1 to about 30 percent based on the weight of the nitromethane, preferably about 5 to about 15 percent. Usually 5–10 percent will be preferred.

The nitromethane suitable for the practice of this invention is preferably the 95 percent grade of commerce. However, other materials to solubilize the amine salt can be present to as much as about 30–40 percent by wt. without interfering significantly with the sensitivity.

Amine salts generally exhibit poor solubility in nitromethane, so it is within the concept of the present invention to include sufficient solvent to provide complete solubility of the amine salt. The amount and character of the solvent will vary somewhat depending on the particular amine salt and the amount thereof, but it should be such as not to significantly counter the sensitizing action of the amine salt. Some materials act as stabilizers as disclosed by Egly et al., U.S. Pat. No. 3,288,867. Generally up to 30 percent by weight of a solvent based on the total weight of the composition can be tolerated, but preferably it should be less than 20 percent. Usually 5 percent or 5–10 percent will be satisfactory. Suitable solvents include the lower aliphatic alcohols, i.e., methanol, ethanol or propanol. Preferably the amine salt is dissolved in the solvent before adding to the nitromethane. The selection of the solvent and the amount thereof is well within the skill of the artisan.

The amine salts suitable for the practice of this invention include but are not limited to formic, acetic, propionic and butyric acid salts of such amines as methylamine, dimethylamine, trimethylamine, ethylamine, propylamine, butylamine, benzylamine, piperidine and aniline.

The use of amine salts to sensitize nitromethane is particularly advantageous because the salts and their solutions are relatively harmless if spilled on the skin and thus do not present a toxicity problem to workers handling the material. Another advantage is that nitromethane sensitized with amine salts has excellent shelf like and does not deteriorate as does amine-sensitized nitromethane. It is, of course, preferable that sensitized nitromethane be used promptly, yet circumstances occasionally arise which prevent its prompt use, so it is advantageous to have a stable composition.

The invention will be better understood with reference to the following examples. It is understood, however, that the examples are intended for illustration only and it is not intended that the invention be limited thereby.

EXAMPLE 1

Three nitromethane solutions sensitized with methylammonium acetate were prepared and were tested for explosibility in the card gap apparatus. In the card gap test, a series of plastic cards of 10 mil thickness are placed between a test sample and the initiator, which

can be a 25 g pellet of tetryl and a No. 8 blasting cap. The number of cards is increased or decreased in a series of trials until the distribution of detonations vs. failures indicate a "card gap" where statistically half of the trials will result in detonations and half in failures. The test is discussed in greater detail in "Nitroparaffins and Their Hazards," Research Report No. 12, pp 27–30, The national Board of Fire Underwriters, 85 John Street, New York, N.Y. 10038.

The composition and card gaps are as follows:

Nitromethane,%	100	90	77.5	70
Methanol,%	0	5	7.5	10
Sensitizer,%	0	5	15.0	20
Sensitizer based on nitromethane,%		5.5	19.4	28.6
Card gap	30	43	43	39
Change in gap	—	13	13	9

Although none of the above compositions would be expected to be detonated by a No. 8 blasting cap, a cap plus a small booster would initiate a satisfactory detonation in the sensitized compositions.

The 100% nitromethane used in this experiment was the regular commercial grade nitromethane.

EXAMPLE 2

The experiment of Example 1 was repeated in all essential details except that butylammonium acetate was substituted for methylammonium acetate as the sensitizer:

Nitromethane,%	100	92.5	88.75	85	85*	85	81.25
Methanol,%	0	2.5	3.75	5	6	7.5	6.25
Sensitizer,%	0	5.0	7.5	10	7.5	7.5	12.5
Sensitizer based on nitromethane		5.4	8.4	11.8	8.8	8.8	15.4
Card gap	30	44	45	47	45	42	46
Change in gap	—	14	15	17	15	12	16

*Also contained 1.6% water

These compositions are suitable for use as explosives in combination with a small booster.

EXAMPLE 3

The experiment of Example 1 was repeated in all essential details except that piperidine acetate was employed as the sensitizer in the following composition:

Nitromethane,%	100	85
Sensitizer,%	0	10
Sensitizer based on nitromethane,%		11.8
Methanol,%	0	5
Card gap	30	43
Change in gap		13

The composition was determined to be suitable for use as an explosive in combination with a small booster.

EXAMPLE 4

The experiment of Example 3 was repeated in all essential details except that butylammonium formate was used as the sensitizer:

Nitromethane,%	100	85
Sensitizer,%	0	10
Sensitizer based on nitromethane,%		11.8
Methanol,%	0	5
Card gap	30	43
Change in gap	0	13

EXAMPLE 5

The experiment of Example 3 was repeated in all essential details except that dimethylammonium acetate was used as the sensitizer:

Nitromethane,%	100	90
Sensitizer,%	0	5
Sensitizer based on nitromethane,%		5.6
Methanol,%	0	5
Card gap	30	51
Change of gap	0	21

EXAMPLE 6

The experiment of Example 3 was repeated in all essential details except that trimethylammonium acetate was used as the sensitizer:

Nitromethane,%	100	90
Sensitizer,%	0	5
Sensitizer based on nitromethane,%		5.6
Methanol,%	0	5
Card gap	30	47
Change of gap	0	17

EXAMPLE 7

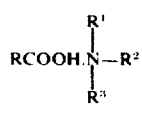
The experiment of Example 3 is repeated in all essential details except that benzylammonium propionate is used as the sensitizer. The card gap value of the mixture is significantly higher than that for nitromethane.

EXAMPLE 8

The experiment of Example 3 is repeated in all essential details except that aniline butyrate is used as the sensitizer. The card gap value of the mixture is significantly higher than that for nitromethane.

We claim:

1. A nitromethane composition sensitive to detonation by shock consisting essentially of nitromethane 70–95 percent and a sensitizer 1–30 percent, represented by the formula



where R is hydrogen, or an alkyl group of 1 to about 4 carbon atoms; R^1 and R^2 are hydrogen or alkyl of 1–5 carbon atoms and are the same or different; or R^2 or R^3 taken together are $—(CH_2)_5—$; or R^3 is an alkyl group of 1 to 5 carbon atoms, or phenyl or a benzyl group.

2. The composition of claim **1** wherein said sensitizer is methylammonium acetate.

3. The composition of claim **1** wherein said sensitizer is butylammonium acetate.

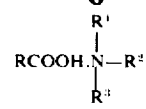
4. The composition of claim 1 wherein said sensitizer is piperidine acetate.

5. The composition of claim 1 wherein said sensitizer is butylammonium formate.

6. The composition of claim 1 wherein said sensitizer is benzylammonium propionate.

7. The composition of claim 1 wherein said sensitizer is aniline butyrate.

8. A method of sensitizing nitromethane comprising dissolving therein from 1 to about 30 percent, based on the weight of said nitromethane, of an amine salt corresponding to the formula



where R is hydrogen or an alkyl group of 1 to about 4 carbon atoms; R^1 and R^2 are hydrogen or alkyl of 1 to 5 carbon atoms and are the same or different; or R^2 and R^3 taken together are $-(CH_2)_5-$; or R^3 is an alkyl group of 1 to about 5 carbon atoms, a phenyl group, or a benzyl group, in the presence of an amount of an alkanol of 1 to 3 carbon atoms sufficient to provide a homogeneous solution of said amine salt.

9. The method of claim 8 wherein said amine salt is present in an amount of about 5 to about 15 percent.

10. The method of claim 8 wherein said amine salt is present in an amount of about 5–10 percent.

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