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DETONATABLE COMPOSITIONS COMPRISING METAL NITRATES AND MONONITROPARAFFINS**Edwin M. Scott, Jr., Box 323, Tujunga, Calif. 91042**
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This application is a continuation-in-part of my co-pending application Serial No. 92,161, now Patent No. 3,178,325, filed February 28, 1961.

The present invention relates to detonatable compositions comprising metal nitrates and certain mononitroparaffins, together with additional components, all as more fully described below.

Some years ago, the commonly used blasting material for general industrial and commercial use, such as quarrying or earth-work blasting, or the like, was dynamite. In recent years, the latter has been largely displaced by relatively simple mixtures of ammonium nitrate with sensitizers such as diesel oil. While the latter has met with wide acceptance, the commonly used mixtures are not without some disadvantages. Ammonium nitrate itself, even before admixture with the diesel oil or sensitizer, is not entirely free of explosive hazard, as the Texas City disaster showed. It is accordingly desirable to be able to use a nitrate which is not of itself explosive, such as the metal nitrates, including sodium nitrate, calcium nitrate, and potassium nitrate. Heretofore, however, compositions utilizing these metal nitrates have included other materials or combinations of materials which in themselves form detonatable compositions. Thus, blasting mixtures have been proposed which comprise sodium nitrate and nitromethane, the latter being explosive in its own right.

An object of the present invention is to provide a detonatable composition consisting essentially of a non-explosive metallic nitrate together with a nonexplosive mononitroparaffin, together with a third nonexplosive component in order to provide a composition of great blasting effectiveness and one capable of propagation in relatively narrow cylinders.

Other objects of the invention will appear as the description thereof proceeds.

Generally speaking and in accordance with illustrative embodiments of my invention, I prepare a detonatable composition by mixing together a mononitroparaffin selected from the class consisting of mononitropropane and mononitrobutane and mixtures thereof; from $3\frac{1}{2}$ to 5 parts of a metallic nitrate chosen from the class consisting of sodium nitrate, potassium nitrate, and calcium nitrate, and mixtures thereof; and $\frac{1}{3}$ to $\frac{1}{2}$ part of a comminuted material chosen from the group consisting of starch, starch flour, cellulose, and lignocellulose, and mixtures thereof, the relative proportions of the three being such as to result in an overall oxygen balance for the composition of substantially zero, viz., within the approximate limits of minus 3% to plus 3%.

The two mononitroparaffins which I may use in my mixture are, as already stated, mononitropropane and mononitrobutane. These have very low oxygen balances of -134.6% and -163% respectively. I do not use nitromethane or nitroethane as a source of mononitroparaffin, inasmuch as these are explosive in their own right; it may also be observed that they have relatively low oxygen balances of -39.3% and -96% respectively.

On the relative detonatability of the mononitroparaffins, attention may be called to Research Report No. 12 of the National Board of Fire Underwriters, "Nitropar-

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affins and Their Hazards" (New York, 1959), which states on page 23:

"Shock may affect nitroparaffins, however, only nitromethane and nitroethane have been reported to detonate and then not by the most commonly used explosive evaluation tests."

The report gives details of the disastrous explosions of tank cars of nitromethane at Niagara Falls, New York, and Mount Pulaski, Illinois.

As regards nitromethane, I have exploded 1500 grams of pure mononitroethane with a Composition B booster. The nitroethane was placed in a container at the bottom of a $1\frac{1}{2}$ -foot deep drill hole in a flat clay bed. A crater having a ten-foot diameter was produced.

The matter of oxygen balance is well known to those skilled in the art, and a simple formula for computing it is given in the paper by Lothrop and Hendrick appearing in Chemical Reviews, vol. 44, pages 419-445 (1949) at page 421. Oxygen balance is also discussed and used in Research Report No. 12 just cited.

The comminuted material which I use, as already stated, may be starch, a starchy flour, cellulose or lignocellulose, and, of course, mixtures of any or all of these. Cellulose includes cellulosic materials generally, such as cotton, cellulose pulp derived from woody materials, and the like. The term "lignocellulose" refers to woody materials generally, and this includes sawdust, wood flour, ground cork, ground almond shells, and the like. All of these materials, when used in the mixtures in accordance with the invention, are effectively porous and act to retain the nitroparaffin within the interstices of the mixture.

The metallic nitrate, as already noted, may be sodium nitrate, potassium nitrate, calcium nitrate, or mixtures of any of these, in any of their common commercial forms. They are available in general either as relatively crystalline granular materials or as prills. Any and all of these forms may be used in accordance with my invention.

The actual compounding of my inventive composition requires no special discussion; I merely mix the separate ingredients together, taking reasonable care to obtain a relatively homogeneous mixture. In small quantities, this can be done by simple stirring, by using a wooden paddle in a suitable container. For larger quantities, tumbling mixers of the cement mixer type may be used, or ribbon blenders such as are common in the chemical process industries.

The compositions are detonated in any desired fashion, most commonly with a Composition B initiator, this being a standard term in the explosive art.

A remarkable property of my inventive compositions is that they are able to propagate even in a small diameter drill hole, such as, for example, three inches in diameter. Many commercially used blasting compositions, such as may be produced from ammonium nitrates and diesel oil mixtures perform well in the mass and will propagate in a large diameter drill hole, such as six inches or larger, but fail to propagate at three inches or four inches diameter. This is particularly true when explosive compositions of high density, such as those of the present invention, are compared. By propagation of course is meant the ability of the detonation to continue along a cylinder of the blasting composition of indefinite length. For practical purposes, if propagation in a three-inch or six-inch pipe is obtained for as much as six feet, then in practice it will be found to propagate indefinitely, for example, for hundreds of feet.

Some working examples in accordance with my invention will now be given.

EXAMPLE 1

Ordinary commercial Chilean sodium nitrate having a grain size of about -20 mesh was mixed with 2-nitro-

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propane and sawdust, the latter being ordinary hardwood sawdust of about -40 mesh, in the proportions by weight of 74.38% sodium nitrate, 19.4% 2-nitropropane, and 6.22% sawdust. This mixture had an oxygen balance of about zero. It was packed in two open-ended, 3-inch diameter steel pipes which were laid end-to-end; a Composition B booster was fired adjacent one of the exposed ends of the pipe. Detonation was complete, with propagation throughout.

EXAMPLE 2

The same ingredients as in Example 1 were mixed in the weight proportions 74.41; 17.25; 8.34, to give an oxygen balance of about zero. The same experimental arrangement was used and again detonation and propagation were complete.

EXAMPLE 3

The test of Example 1 was repeated except that 2-nitrobutane was substituted for the 2-nitropropane, and the weight proportions were 76.93:16.85:6.22, to give an oxygen balance of about zero. Again, detonation and propagation were complete.

EXAMPLE 4

A composition quite similar to that of Example 1 was made up, except that wood flour of about -100 mesh was substituted for the sawdust, and the weight proportions were the same. This was tested by boring an 18-inch deep hole in a uniform, moist playa deposit in the Mojave Desert in east central California, this particular deposit being widely used for explosive tests of this nature. The holes were loaded with 1500 grams of the explosive mixture and half a stick of dynamite. The holes were thoroughly back-filled and tamped, and the dynamite detonated. A crater was formed having a diameter of 11 feet, 8 inches.

EXAMPLE 5

The test of Example 4 was carried out except that the following composition was used: sodium nitrate, 76.03%; ordinary corn starch, 7.1%; 2-nitrobutane, 16.87%. This mixture had oxygen balance of about zero. The crater diameter was 12 feet, 10 inches.

EXAMPLES 6 through 14

Compositions in accordance with the invention were prepared, variously, with 2-nitropropane and 2-nitrobutane; with calcium nitrate, potassium nitrate, and sodium nitrate; with starch and sawdust. The potassium and sodium nitrates were the commercial anhydrous, fine-granular varieties, while the calcium nitrate was in the form of fine prills; the sawdust was hardwood sawdust of about -40 mesh; and the starch was ordinary corn starch. These all propagated indefinitely, as already described, when detonated using a Composition B booster. The table below gives the compositions for the various mixtures of these experiments. The oxygen balances for all of these were within the range minus 3% to plus 3%, and thus were substantially zero.

Table

Example.....	Percent								
	6	7	8	9	10	11	12	13	14
2-nitropropane.....	19.40	17.06	12.13	17.06	12.13	20.03	17.25	20.02	17.25
2-nitrobutane.....	73.	77.44	82.37	76.77	81.60	73.52	76.3	72.71	75.48
Sodium nitrate.....	73.	77.44	82.37	76.77	81.60	73.52	76.3	72.71	75.48
Potassium nitrate.....	73.	77.44	82.37	76.77	81.60	73.52	76.3	72.71	75.48
Calcium nitrate.....	73.	77.44	82.37	76.77	81.60	73.52	76.3	72.71	75.48
Sawdust.....	7.1	5.5	5.5	6.27	6.27	6.45	6.45	7.27	7.27
Cornstarch.....	7.1	5.5	5.5	6.27	6.27	6.45	6.45	7.27	7.27

In accordance with a further aspect of my invention, I have found that the inventive compositions already described hereinabove and which as stated have oxygen bal-

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ances of approximately zero, may be admired with up to an equal weight of a second type of composition prepared from a metallic nitrate chosen from the class consisting of sodium nitrate, potassium nitrate, calcium nitrate, and mixtures thereof, as before; and with from about 10% to about 20% of a liquid hydrocarbon and of a woody, cellulosic, or starchy material as before, so as to give to this second mixture an oxygen balance within the range of minus 3% to plus 3%, viz., substantially zero. The liquid hydrocarbons which I may use in this second type of mixture comprise those corresponding to this term and include paraffinic and aromatic hydrocarbons such as kerosene, diesel oil, mineral spirits, toluene, xylene, and the like. As those skilled in the art may readily compute, the oxygen balance of sodium nitrate, calcium nitrate, and potassium nitrate are respectively plus 47.1%, 48.8%, and 39.6%. The oxygen balance of average wood is about -140%, while that of starch and cellulose is about -118.5%. The oxygen balance of diesel oil, a typical relatively paraffinic hydrocarbon, is about -348%; while that of benzene is about -307%. Thus, compositions of the second type may be readily made up within the limits specified and using the components mentioned so as to give an overall oxygen balance of substantially zero.

Mixtures of this second type, that is, those made of the woody, cellulosic, or starchy material, the metallic nitrate, and the liquid hydrocarbon, will not propagate when detonated by themselves in a 3-inch diameter pipe, but, as just mentioned, when admixed with my inventive compositions as already set forth, the composite mixtures may be detonated with a Composition B booster, and the detonation will be propagated indefinitely even at a 3-inch diameter. When these two types of composition are admixed, as by simple stirring together, the liquid hydrocarbon is retained by the overall mixture by virtue of the wood flour, starch, or the like, contained therein.

An example of such a composite mixture is as follows:

EXAMPLE 15

A first mixture was made of sodium nitrate, 76.91%; sawdust, 6.22%; and 2-nitrobutane, 16.87% to give an oxygen balance of substantially zero. A second composition was made up containing 83% sodium nitrate, 6.22% sawdust, and 9.9% benzene. This likewise had an oxygen balance of substantially zero. Equal weights of these two compositions were then mixed together. The composition was detonated with a Composition B booster, and the detonation propagated indefinitely in a 3-inch diameter pipe.

It will be understood that my invention is a broad one, and although I have described it with the aid of numerous examples, nevertheless, may variations are possible within the broad scope of the invention in components, proportions, and the like, all as delineated by the claims which follow.

Having described my invention, I claim:

1. A detonatable composition consisting essentially of

a mononitroparaffin selected from the class consisting of mononitropropane, mononitrobutane, and mixtures thereof; from 3½ to 5 parts by weight for each part of said

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nitroparaffin of a metallic nitrate chosen from the class consisting of sodium nitrate, potassium nitrate, calcium nitrate, and mixtures thereof; and from about $\frac{1}{8}$ to about $\frac{1}{2}$ part by weight, per one part of said nitroparaffin, of a comminuted material chosen from the group consisting of starch, starchy flours, cellulose, and lignocellulose, and mixtures thereof, the relative proportions of the several components within the said limits being chosen to result in an overall oxygen balance of from within about minus 3% to about plus 3%.

2. A detonatable composition consisting of a mixture of a composition in accordance with claim 1 together with not more than an equal weight of a composition consisting essentially of a metallic nitrate chosen from the class consisting of sodium nitrate, potassium nitrate, calcium nitrate, and mixtures thereof, with from about 10% to

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about 20% by weight of said second composition of a liquid hydrocarbon and of a comminuted material chosen from the group consisting of starch, starchy flours, cellulose, lignocellulose, and mixtures thereof, the relative proportions of said liquid hydrocarbons and said comminuted material being selected within the aforesaid limits so as to result in an oxygen balance of said composition with the range of about minus 3% to about plus 3%.

3. A composition in accordance with claim 2 in which said liquid hydrocarbon is diesel oil.

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