FIG. 1.

FIG. 2.

FIG. 5.

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FROZEN NITROGEN TETROXIDE-HYDROCARBON EXPLOSIVES

FIG. 3.

FIG. 4.

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This invention relates to convenient and safe means of handling N\textsubscript{2}O\textsubscript{4}-hydrocarbon explosive mixtures and more particularly to a composition comprising frozen N\textsubscript{2}O\textsubscript{4} and a hydrocarbon adapted for use as an explosive mixture.

Explosives most commonly used particularly for strip mining and quarry blasting are dynamite and blast gelatin. These explosives have the drawbacks of being dangerous in that they are sensitive to shock; have a relatively low explosive power—about 60% of TNT; are toxic to the person handling them; decrease in effectiveness at lower temperatures; and are relatively high in cost. Furthermore, the manufacture of these explosives requires the use of toluene or glycerine as raw material which are in short supply. Because of the low explosive power of dynamite and similar blasting powders, resort was had in a few instances to liquid oxygen explosives but these explosives have not been widely adopted in industry due to the cost of manufacturing and difficulties in handling.

One object of the present invention is to provide an N\textsubscript{2}O\textsubscript{4}-hydrocarbon explosive composition which is convenient and safe to use.

Another object is to provide an N\textsubscript{2}O\textsubscript{4}-hydrocarbon explosive composition which has practically zero impact sensitivity.

Another object is to provide an N\textsubscript{2}O\textsubscript{4}-hydrocarbon explosive composition which has an explosive power effectiveness many fold that of dynamite.

A further object is to provide an N\textsubscript{2}O\textsubscript{4}-hydrocarbon explosive composition which is non-toxic during handling by the explosive operator.

A still further object is to provide an N\textsubscript{2}O\textsubscript{4}-hydrocarbon explosive mixture which will not lose its explosive power effectiveness at low temperatures.

Another object is to provide an N\textsubscript{2}O\textsubscript{4}-hydrocarbon explosive composition which when detonated will not generate toxic gases.

Other objects are to provide safe means and methods, i.e., freedom from impact sensitivity and toxicity of the explosive compositions, for handling N\textsubscript{2}O\textsubscript{4}-hydrocarbon explosive compositions.

Further objects and advantages will be apparent from the description and accompanying drawings.

In general the present invention is directed to compositions containing frozen N\textsubscript{2}O\textsubscript{4} and hydrocarbons and the use of such compositions as explosive mixtures. More specifically, the present invention is directed to a composition adapted for use as an explosive mixture comprising frozen N\textsubscript{2}O\textsubscript{4} and a hydrocarbon in the liquid or solid state. The present invention also contemplates a composition comprising a mixture of N\textsubscript{2}O\textsubscript{4} and a hydrocarbon, both frozen to a solid state.

Explosive devices adapted for use in effecting explosions in accordance with the present invention comprise in combination a container, frozen nitrogen tetroxide disposed within the container, a hydrocarbon also disposed within the container and a detonator attached to said container adapted to cause explosion of the N\textsubscript{2}O\textsubscript{4}-hydrocarbon in the container.

In the preferred form of explosive device, the container will be in the shape of a hollow cylinder open at one end containing frozen nitrogen tetroxide in cylinder form and having a hollow cavity or core containing a hydrocarbon. A cap having a hollow cylinder extending therefrom for insertion into the cavity of the frozen nitrogen tetroxide closes the open end of the container, and a detonator adapted for causing explosion of the nitrogen tetroxide-hydrocarbon in the container, is disposed in the hollow cylinder attached to the cap.

In another form of explosive device the container may be loaded with alternate layers of frozen nitrogen tetroxide and frozen hydrocarbon in the form of cylinders or wafers. If it is desired to prevent intimate contact of frozen nitrogen tetroxide with frozen liquid hydrocarbons, the frozen constituents may be covered with reasonably impervious material, i.e., paper, wax or other protective coating. The covering should be of a type and applied to allow the constituents to mix readily when both become liquid.

In another form of explosive device the container may be loaded with an intimate mixture of nitrogen tetroxide and hydrocarbon, both frozen to a solid state.

Our preferred method for preparing and exploding composition of the present invention comprises disposing frozen N\textsubscript{2}O\textsubscript{4} and a hydrocarbon in a container, maintaining the N\textsubscript{2}O\textsubscript{4} in solid form until it is desired to explode the composition, thereafter melting the N\textsubscript{2}O\textsubscript{4} to allow it to mix with the hydrocarbon, and then detonating the mixture.

Although the use of mixtures composed of liquid nitrogen tetroxide and hydrocarbon for explosives were known for some time, nevertheless the commercial applications of such mixtures is practically nil. We have investigated the reasons for the noncommercial use of N\textsubscript{2}O\textsubscript{4}-hydrocarbon mixtures and found them to be primarily, difficulty in handling liquid nitrogen tetroxide explosive mixtures especially due to the effect of toxic gases resulting from vaporization of the liquid nitrogen tetroxide, and fear of detonation of mixtures of liquid nitrogen tetroxide and hydrocarbon. We have obviated these difficulties by employing nitrogen tetroxide in the frozen state thereby preventing any material escape of toxic gases. Furthermore, by separately freezing nitrogen tetroxide and maintaining it in solid state separate from the liquid hydrocarbon thereby preventing mixing of the two constituents during handling of the composition by the operating personnel, we have eradicated any apprehension on the part of all personnel handling the composition that a premature explosion may occur. These advantages combined with the lower cost and greater explosive power of our explosive compositions together with other advantages enumerated herein make for a practical, cheaper, safer explosive than hitherto known.

Figure 1 is a partial section of the preferred form of assembled explosive device showing the separate bodies of frozen nitrogen tetroxide and hydrocarbon contained therein.

Figure 2 is a partial section of an alternate form of explosive device showing the frozen nitrogen tetroxide in the container provided with a series of holes for distributing the hydrocarbon throughout the body of the frozen nitrogen tetroxide.

Figure 3 is another form of explosive device wherein wafers of frozen nitrogen tetroxide and frozen hydrocarbon are loaded interspersely in the container.

Figure 4 illustrates an explosive device loaded with an intimate mixture of N\textsubscript{2}O\textsubscript{4} and hydrocarbon frozen to a solid state.

Figure 5 illustrates one method of converting liquid nitrogen tetroxide as received in commercial ton containers into frozen forms for use in the explosive devices.
The hydrocarbon to be employed may be any hydrocarbon material such as derived from petroleum, coal carbonization and distillation of shale, preferably a hydrocarbon distillate which is liquid at normal temperature and pressure. Various hydrocarbons such as benzene, heptane and octane, as well as hydrocarbon distillate fractions such as the naphthas and kerosenes, have been employed with success. We have found petroleum distillate fractions boiling within the range of about 150°-600° F. to be most satisfactory as one of the constituents of the N₂O₅-hydrocarbon explosive mixture because of its lower impact sensitivity when admixed with nitrogen tetroxide, low volatility, availability and low cost. Other fuels such as methyl alcohol and ethyl alcohol while not as satisfactory may be employed as the "hydrocarbon" constituent of the N₂O₅-hydrocarbon composition. Methyl alcohol may be used as a fuel to be injected into a rocket motor containing frozen N₂O₅.

Referring to Fig. 1 of the drawing the explosive device shown therein is composed of a cylindrical rigid container 1 constructed of metal, paper, plastic or the like, enclosed at its open end by cap 2, which latter has a small hollow cylinder 3 for use as a detonator receptacle extending down into the container, and a plug 4 approximately the diameter of the hydrocarbon cavity in the frozen nitrogen tetroxide. It is not necessary to seal container 1 with cap 2 in such manner as to prevent any escape of gas. Desirably a small vent may be in the cap to allow any evolved vapor to escape. In case of misfire such a vent would permit release of N₂O₅ rendering the residual material in the container incapable of explosion. Disposed in container 1 is a solid cylinder 5 of frozen N₂O₅ having a hollow core 6 designated hydrocarbon cavity into which hydrocarbon is poured. A detonator 7 of any conventional type such as mercury fulminate having wires 10 attached thereto is inserted in detonator receptacle 3.

The proportion of hydrocarbon to N₂O₅ may vary from about 10-35% hydrocarbon to 90-65% N₂O₅ by weight depending to a large extent upon the nature of the hydrocarbon employed. For maximum efficiency it would appear desirable to employ the hydrocarbon-N₂O₅ in stoichiometric proportions. However, we have found that a hydrocarbon-N₂O₅ mixture is more sensitive to impact when in stoichiometric ratio. Further we found that when the amount of hydrocarbon is in excess of the stoichiometric amount required for combustion with N₂O₅, the gases formed as a result of an explosion of such mixture are contained carbon monoxide which is toxic in nature. Our experiments have shown that hydrocarbon-N₂O₅ compositions employing N₂O₅ in slight stoichiometric excess, roughly about 5%, have less impact sensitivity and generate gases when exploded consisting essentially of CO₂, N₂, and H₂O with practically negligible or zero amount of CO. In practice we have successfully exploded compositions of nitrogen tetroxide with the following hydrocarbons—octane, heptane, benzene, petroleum naphtha boiling in the range of 150° F. to 400° F., kerosene boiling within the range of 250° F. and 500° F., such compositions having the respective proportions of N₂O₅ to hydrocarbon by weight—84:16, 83.5:16.5, 83:17, 84:16, 84.5:15.5.

Figure 2 represents another form of explosive device consisting of container 8 sealed at its open end by cap 9 which latter has a detonator receptacle 11 extending from cap 9 into the body of container 8 for the purpose of holding detonator 12 having wires 13 attached thereto to initiate the explosion. Disposed in container 8 is a solid cylinder 14 of frozen tetroxide provided with a plurality of holes 15 in the frozen nitrogen tetroxide which will keep the liquid hydrocarbon poured therein separate until such time as the nitrogen tetroxide is permitted to melt thereby forming the explosive mixture. According to this invention involves freezing the nitrogen tetroxide and the hydrocarbon separately in the form of cylinders or wafers which can be loaded alternately to provide the proper ratio of hydrocarbon to oxidizer, which upon melting will properly blend into the desired explosive mixture. As shown in Fig. 3 layers 16 of frozen N₂O₅ are separated by layers 17 of frozen hydrocarbon in container 18. If desired intimate contact between the layers may be prevented by placing the N₂O₅-hydrocarbon in the frozen state by placing a protective coating 19, such as paper or wax, between layers 16 and 17, which layers 16 and 17 are desirably molded with a hollow core 21 to provide a cavity for the insertion of detonator receptacle 22 attached to cap 23 and also to allow the constituents to mix readily when both become liquid. The usual detonator 24 provided with wires 25 fits into detonator receptacle 22.

In the Arctic and Antarctic regions conventional types of explosives such as dynamite and nitroglycerine lose much of their explosive strength or fail completely at the low temperature conditions prevailing in these regions. Accidents have been known to occur due to an operator attempting to warm frozen dynamite prior to use. We have discovered that an intimate mixture of N₂O₅-hydrocarbon frozen to a solid state will explode when detonated without any noticeable loss in explosive power as compared with a mixture of liquid N₂O₅-hydrocarbon. Further the impact sensitivity of a frozen mixture of N₂O₅-hydrocarbon is low and may be safely handled by an operator.

Figure 4 illustrates an explosive device composed of container 26 into which is placed a solid cylinder 27 of a frozen intimate mixture of N₂O₅ and hydrocarbon with a hollow core in cylinder 27 adapted to receive detonator receptacle 28 attached to cap 29 sealing open end of container 26. Into detonator receptacle 28 is inserted detonator 30 having wires 31 attached thereto.

Figure 5 diagrammatically illustrates one practical method of preparing frozen nitrogen tetroxide or a form suitable for use in an explosive container at the sites of a coal mine or quarry where explosives are used. Liquid nitrogen tetroxide is shipped in commerce on railroad cars in large, strong metal vessels 32 termed in the industry as "ion containers." The liquid nitrogen tetroxide is withdrawn from ten container 33 through line 34 and valve 35 and discharged into enclosed cooling tank 36 wherein the temperature is maintained at about 10° C. by passing a refrigerant through refrigerating coil 37 immersed in the liquid N₂O₅ contained in cooling tank 35. When it is desired to prepare containers of frozen N₂O₅, liquid N₂O₅ is passed through line 37 and valve 38 into mold 39 of a form suitable to produce the desired shape of N₂O₅, suspended by means of bracket 41 on mold 35. Liquid refrigerant, such as freon, enters through line 42 and circulates around mold 34 thereby freezing the liquid nitrogen tetroxide contained therein, i.e. cools it to a temperature below about −10° C., and discharges from tank 42 through line 44. Although only a single mold 32 is shown in the drawing, obviously a plurality of molds may be employed in tank 42. The frozen cylinder 45 of N₂O₅ may be removed from mold 39 placed in a container similar to that shown in Figure 1 and then placed in a conventional storage refrigerator, not shown in the drawing, wherein a supply of containers with frozen liquid nitrogen tetroxide may be kept for use in a tank not shown in the drawing as the source of hydrocarbon supply for filling the hydrocarbon cavity in the explosive devices illustrated in Figures 1 and 2.

From the foregoing it will be evident that a large magazine of explosives such as dynamite with its attendant hazard is eliminated by the practice of this invention in that nitrogen tetroxide and hydrocarbon may be separately until shortly before use and then only placed together in very small quantities in the container. In this connection it should be noted that it is not uncommon for a single coal mine to consume about 200 tons of explosive per month.
In strip mining, a series of holes are drilled in the ground with the size of the holes depending upon the contour of the surface and the nature of the rock formation, and in these holes a conventional explosive such as dynamite is placed, which operation is called loading; the top of the hole plugged up with loose earth termed "stemming" and the dynamite then detonated to break up the surface overlaying the coal. Since dynamite or other conventional explosive powders used for the same purpose constitute a preformed mixture susceptible of explosion, it presents a real hazard during the handling of the dynamite to the hole into which it is to be placed and particularly during the loading period when the dynamite is dropped in the hole. In contrast the explosive device as illustrated in Figures 1, 2 and 3 contains a non-explosive composition during the carrying to and placing in the hole of the explosive device by the operator because the nitrogen tetroxide in frozen condition and in that form does not admix with the hydrocarbon in the container of the explosive device. After the explosive devices containing frozen N₂O₄-hydrocarbon are placed in the holes of the mine the operators move to a place of safety and after waiting for about 10 to 15 minutes to permit the frozen nitrogen tetroxide in the explosive device to melt due to the heat of the surrounding atmosphere and thereby cause it to blend with the hydrocarbon, the explosive is then detonated.

As pointed out previously the use of an explosive device containing frozen nitrogen tetroxide-hydrocarbon in accordance with the present invention has the advantages as compared to conventional explosives of greater safety, lower cost and reduced toxic effects with respect to both toxic effects resulting from handling the explosive and from the gases generated by explosion of the explosive. Perhaps, an even greater advantage in monetary terms results from the greater effectiveness of N₂O₄-hydrocarbon as compared with conventional explosives. In field tests one pound of dynamite was required to disrupt one cubic yard of rock overburden. In a similar test one pound N₂O₄-kerosene in accordance with the present invention disrupted 5 cubic yards of rock overburden. A very large item of expense in strip mining is the cost of drilling holes for loading with explosive. As is evident the number or size, or both, of such holes which need be drilled is materially reduced when employing N₂O₄-hydrocarbons as compared to use of conventional explosives thereby effecting a saving in money and speeding up of operation.

Example 1

Into a cylindrical container as illustrated in Figure 1 having a diameter of about 2 inches and about 6 inches high was placed a solid cylinder of frozen N₂O₄ having approximately the same internal diameter and height of the container and having a hollow core, the cavity of which was equal to about 25% of the volume of frozen N₂O₄ cylinder. Kerosene is poured into the cavity and the container sealed with a cap which has a detonator receptacle extending into the core of the frozen N₂O₄. The amount of N₂O₄ in the container was approximately 8% in stoichiometric excess of the kerosene. A detonator was placed into the detonator receptacle and the explosive device permitted to stand for 15 minutes to allow the frozen N₂O₄ to melt and blend with the kerosene. An electric current was passed to the detonator which caused an immediate explosion.

Similar explosive devices employing benzene, heptane and octane as the hydrocarbon constituent were prepared and exploded in the same manner. Tests were made to determine the explosive power in accordance with the ballistic mortar test employed by the Bureau of Mines on these various compositions. The explosive mixtures tested were found to have 100 to 190% the explosive power of TNT as measured by the ballistic mortar method. When compared to dynamite which has only 60% of the explosive power of TNT, the N₂O₄-hydrocarbon mixtures were about three times as effective based on the ballistic mortar test.

The N₂O₄-hydrocarbon compositions were also subjected to impact sensitivity tests by dropping weights on compositions from varying heights. The results of these tests show the compositions to be insensitive to impact for all practical purposes.

Example 2

Liquid N₂O₄ and benzene in the proportion of 83.77% by weight were intimately mixed and frozen in the form of a solid cylinder and then placed in a container as shown in Figure 4. The frozen mixture upon detonation exploded immediately. The explosive force resulting from explosion of the frozen mixture was found to be substantially the same as a mixture of liquid N₂O₄-hydrocarbon in the same weight proportion.

Although certain preferred embodiments of the invention have been disclosed for purposes of illustration, it will be evident that various changes and modifications may be made therein without departing from the scope and spirit of the invention.

We claim:

1. A method of mine blasting which comprises boring a hole in the solid composite to be blasted, placing in said hole a device comprising an unpartitioned container containing a frozen body of nitrogen tetroxide and a separate body of hydrocarbon wherein upon melting of the nitrogen tetroxide the tetroxide will blend with the hydrocarbon, said device also having a detonator adapted to cause explosion of the nitrogen tetroxide-hydrocarbon in the container, thereafter melting the nitrogen tetroxide to allow it to mix with the hydrocarbon, and then detonating the mixture of nitrogen tetroxide and hydrocarbon.

2. A method of mine blasting which comprises boring a hole in the solid composite to be blasted, placing in said hole a device comprising an unpartitioned container containing a body of hydrocarbon and a separate frozen body of nitrogen tetroxide in slight stoichiometric excess wherein upon melting of the nitrogen tetroxide the nitrogen tetroxide will blend with the hydrocarbon, said device also having a detonator adapted to cause explosion of the nitrogen tetroxide-hydrocarbon in the container, thereafter melting the nitrogen tetroxide to allow it to mix with the hydrocarbon, and then detonating the mixture of nitrogen tetroxide and hydrocarbon.

3. A method of mine blasting which comprises boring a hole in the solid composite to be blasted, placing in said hole a device comprising an unpartitioned container containing an intimate mixture of frozen nitrogen tetroxide and a frozen normally liquid combustible fuel, said device also having a detonator adapted to cause explosion of the nitrogen tetroxide-hydrocarbon in the container, and then detonating the mixture of nitrogen tetroxide and combustible fuel.

4. A method of mine blasting which comprises boring a hole in the solid composite to be blasted, placing in said hole a device comprising an unpartitioned container containing an intimate mixture of frozen nitrogen tetroxide and a frozen hydrocarbon distillate boiling within the range of 150°-600° F., said device also having a detonator adapted to cause explosion of the nitrogen tetroxide-hydrocarbon in the container, and then detonating the mixture of nitrogen tetroxide and combustible fuel.

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