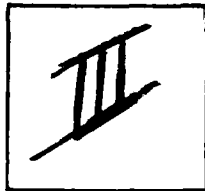


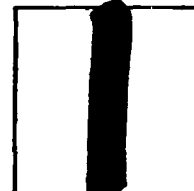
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INVENTORY

BDM/M-TR-0013-81, Appendix F

DOCUMENT IDENTIFICATION

Contract MDA903-81-C-0025

15 Jun '81

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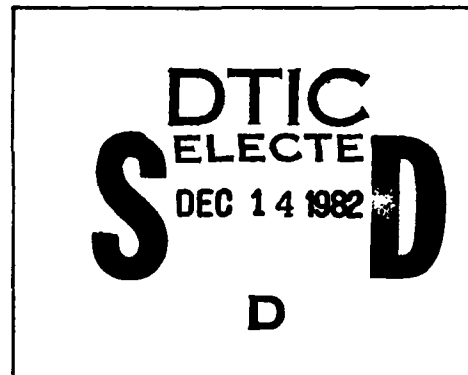
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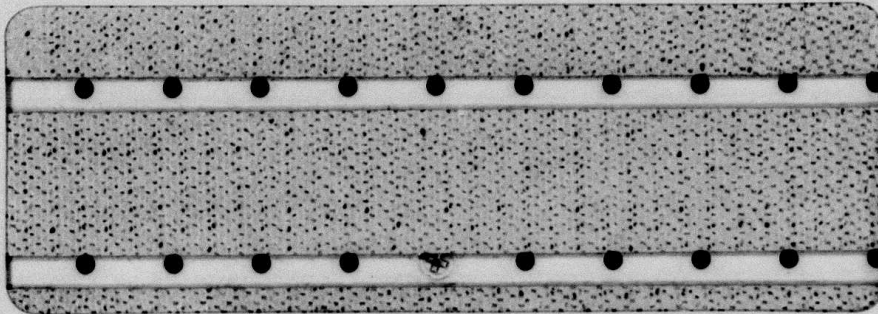
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BDM/M-TR-0013-81

DARPA ADVANCED CANNON PROPELLANT (ACP)
LIBRARY USER'S GUIDE
APPENDIX F
PATENTS DEALING WITH FLUID PROPELLANT TECHNOLOGY

ARPA Order Number: 4105
Contractor: The BDM Corporation, McLean, Virginia
Effective Date of Contract: January 14, 1981
Contract Expiration Date: January 29, 1982
Reporting Period: February 11, 1981 through June 30, 1981
Contract Number: MDA903-81-C-0025
Principal Investigator: Dr. Terrence P. Goddard
The BDM Corporation
P.O. Box 2019
Monterey, California 93940
Phone (408) 649-3880
Short Title of Work: ACP Library

The views, opinions, and findings contained in this report are those of the author(s) and should not be construed as an official Department of Defense position, policy, or decision, unless so designated by other official documentation.

FOREWORD

This Appendix is a compilation of patents that deal with liquid or fluid propellants, slurry explosives, geleation, or crosslinking methods and other technologies that might be of interest to propellant development tasks on the DARPA Advanced Cannon Propellant (ACP) Program. No claim is made on the utility of any of the materials or methods described herein, and this volume is intended for reference purposes only.

THE BDM CORPORATION

CONTENTS

U.S. ARMY PATENTS
U.S. NAVY PATENTS
THIOKOL CORPORATION PATENTS
OTHER U.S. FIRM PATENTS
FOREIGN FIRM PATENTS
UNASSIGNED PATENTS

THE BDM CORPORATION

U.S. ARMY PATENTS

Patent Number: 3,857,743

Author: Barry D. Allan, Huntsville, Alabama

Title: Thixotropic Metal-Containing Monomethylhydrazine Fuel and
Method of Preparing Same

Date: December 31, 1974

Patent Number: 4,039,360

Author: Barry D. Allan, Huntsville, Alabama

Title: Gelled Monomethylhydrazine Thixotropic Fuel

Date: August 2, 1977

Patent Number: 4,110,136

Author: Joseph Hershkowitz, West Caldwell, NJ; Irving B. Akst, Pampa, TX

Title: Explosives Containing Ammonium Nitrate and Nitrate Amines

Date: August 29, 1978

[54] THIXOTROPIC METAL-CONTAINING
MONOMETHYLHYDRAZINE FUEL AND
METHOD OF PREPARING THE SAME

[75] Inventor: Barry D. Allan, Huntsville, Ala.

[73] Assignee: The United States of America as
represented by the Secretary of the
Army, Washington, D.C.

[22] Filed: Jan. 3, 1966

[21] Appl. No.: 518,489

[52] U.S. Cl.: 149/28, 149/19.7, 149/21,
149/22, 149/36, 149/118

[51] Int. Cl.: C06b 19/04, C06c 1/02

[58] Field of Search: 149/36, 18, 20, 44, 19.7,
149/21, 22, 118

[56]

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3,164,505 1/1965 Hsieh et al. 149/36

FOREIGN PATENTS OR APPLICATIONS

978,105 12/1964 Great Britain 149/36

Primary Examiner—Leland A. Sebastian

Attorney, Agent, or Firm—Edward J. Kelly; Herbert
Berl; James T. Deaton

EXEMPLARY CLAIM

A composition consisting of gelled monomethylhydrazine containing dispersed therein up to 70 weight per cent finely divided metallic fuel particles and a cellulose or hydroxyalkyl-substituted cellulose gelling agent.

6 Claims, 3 Drawing Figures

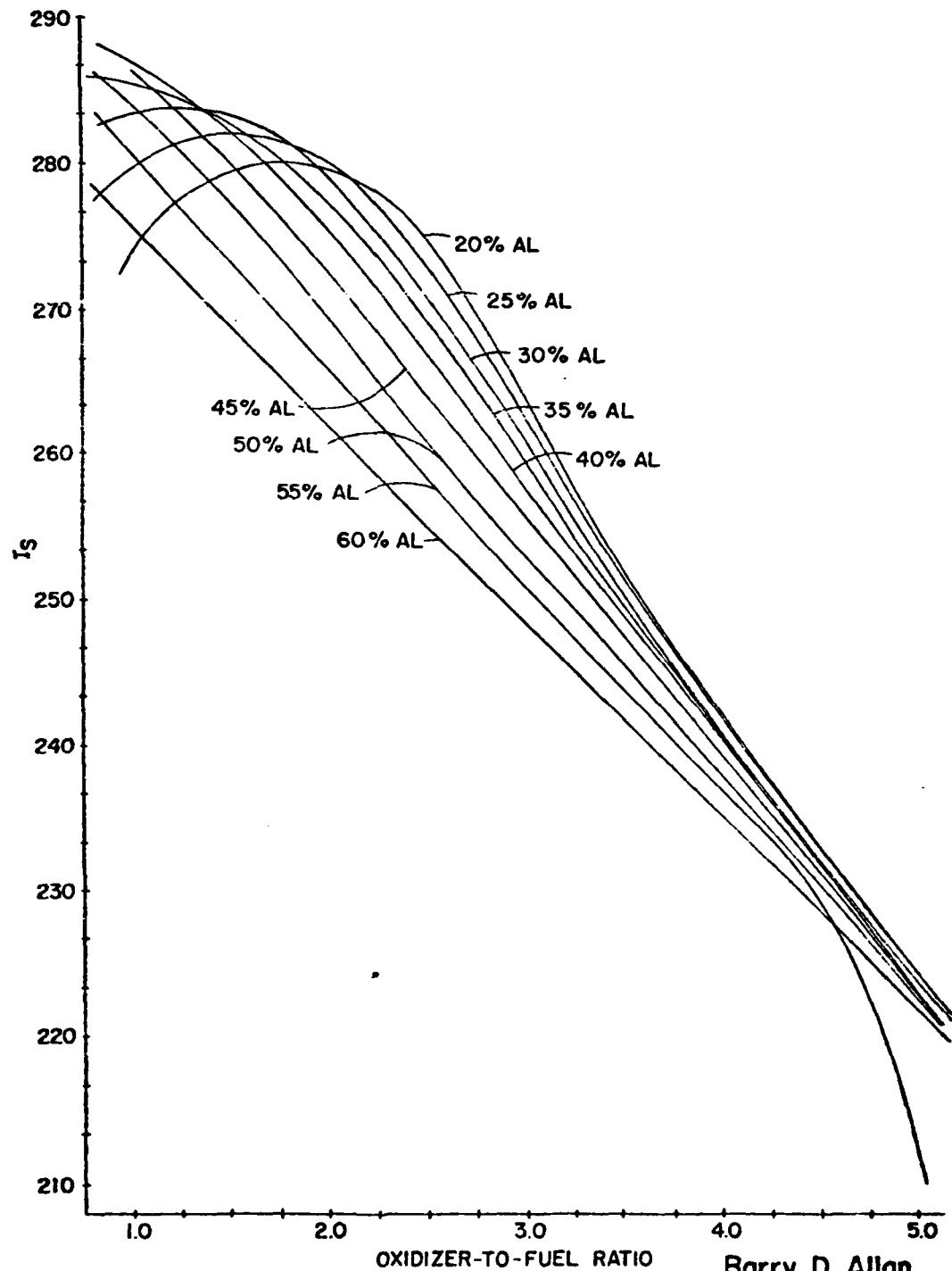


FIG. 1

Barry D. Allan,
INVENTOR

Harry M. Saragovitz
BY *Edward J. Kelly*
Herbert Berl
Joseph H. Beumer

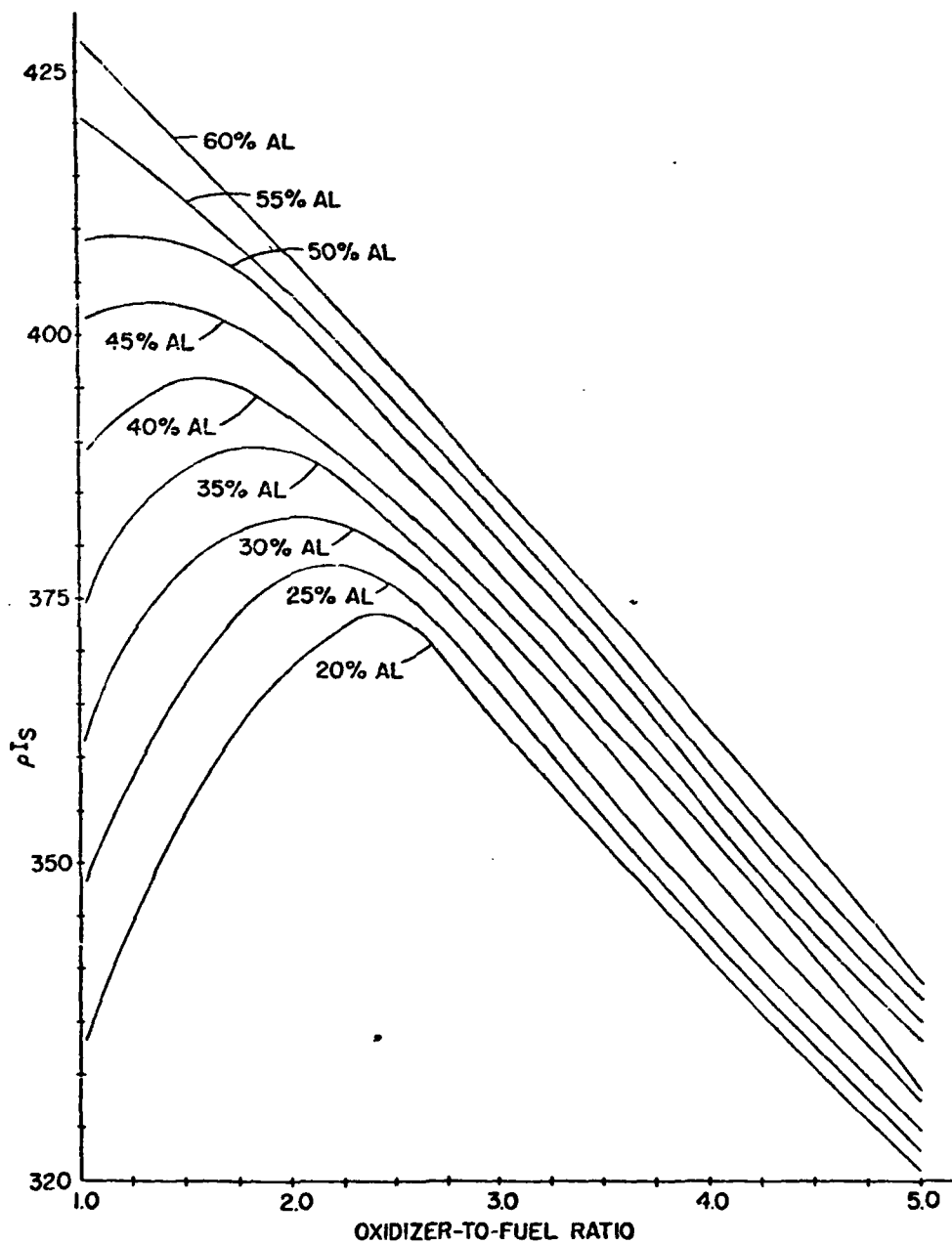


FIG. 2

Barry D. Allan,
INVENTOR.

Harry M. Sragovitz
BY Edward J. Kelly
Herbert Berl
Joseph H. Bunker

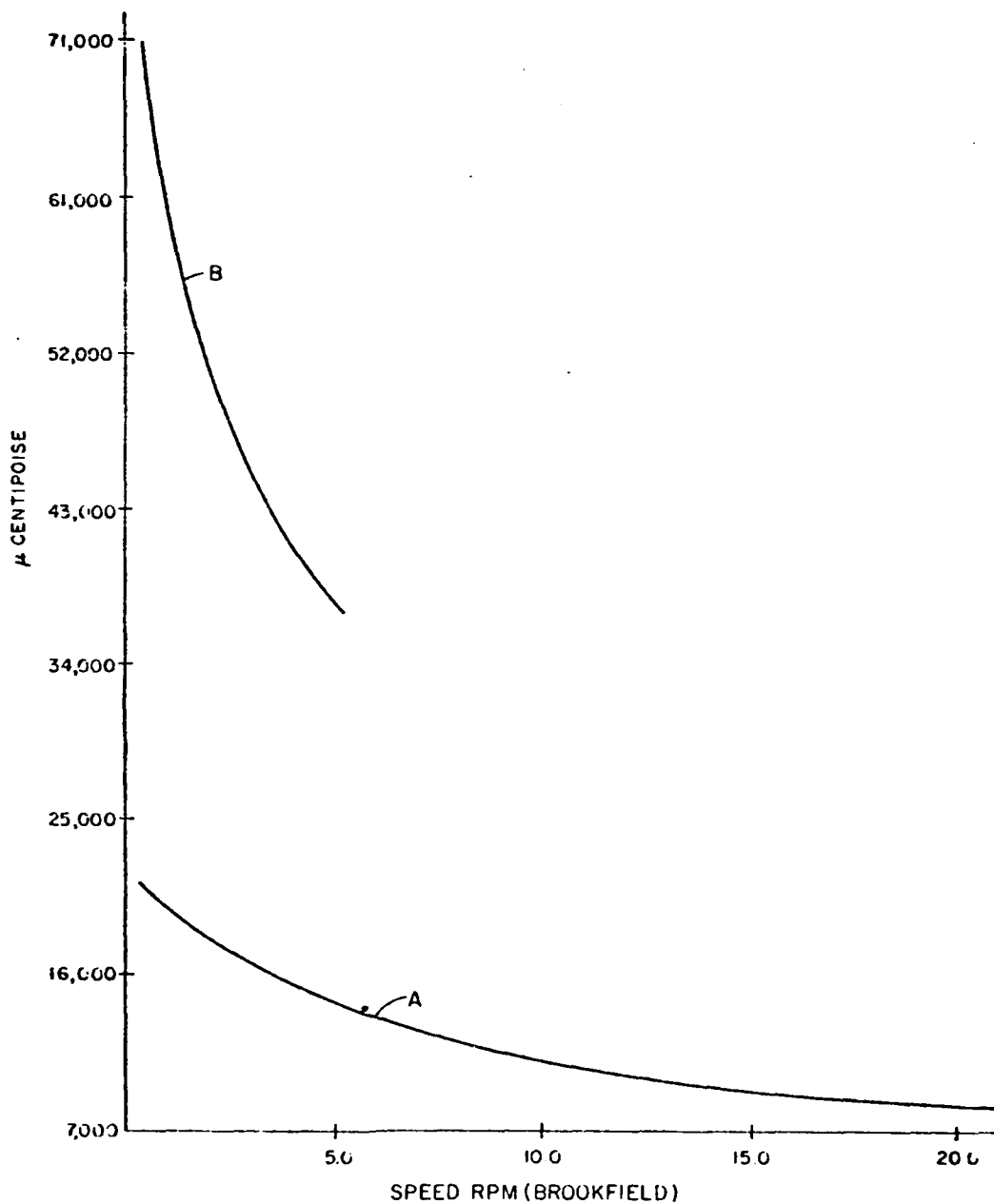


FIG. 3

Barry D. Allan,
INVENTOR.

BY *Harry M. Saragovitz*
Edward J. Kelly
Herbert Beil
Joseph H. Brunner

THIXOTROPIC METAL-CONTAINING MONOMETHYLHYDRAZINE FUEL AND METHOD OF PREPARING THE SAME

The invention described herein may be manufactured and used by or for the Government for governmental purposes without the payment of any royalty thereon.

This invention relates to rocket fuels and more particularly to gelled monomethylhydrazine containing metallic particles.

Monomethylhydrazine, commonly referred to as MMH, is useful as a liquid fuel for rocket motors. This material exhibits favorable combustion properties when reacted with an oxidizer such as nitric acid, a specific impulse, I_s , of 278 seconds (1,000—14 psia) being obtained. For applications where fuel-tank volume is limited, it is desired to increase the density of MMH while maintaining a high specific impulse. The effectiveness of the fuel in this regard is expressed in terms of specific impulse-density, ρI_s , the product of density and specific impulse values. The specific impulse-density value for MMH — nitric acid is 355.8.

One means of increasing the specific impulse-density of MMH fuel is to provide finely divided particles of a metal such as aluminum in the MMH, this measure having been employed previously for solid propellants. Such an approach has not been practical for liquids such as MMH, however, owing to the difficulty of maintaining the particles in suspension. The fuel is normally stored in a tank on board the rocket for an extended period prior to firing, and the metal particles settle to the bottom of the liquid. The resulting inhomogeneity could not be tolerated in operation of the rocket motor. Stability of the metal-containing fuel is also adversely effected by vibration and acceleration forces encountered in flight of the rocket.

In order to maintain the metal particles in suspension and yet allow pumping of the fuel as a liquid the metal-containing MMH should be provided in the form of a thixotropic gel, which behaves as a stable solid until disturbed, but flows as a liquid when force is applied.

Provision of metal-containing MMH in the form of a thixotropic gel would also reduce the hazards associated with MMH. This material is highly toxic, and when handled in liquid form, extreme precautions must be taken to avoid leakage or escape of fumes. Furthermore, MMH reacts hypergolically with many common materials so that a leak could cause a disastrous fire. The reduced mobility of a gel as compared to liquid MMH would avoid these dangers.

It is therefore an object of this invention to provide a stable suspension of metallic fuel particles in MMH.

Another object is to provide a method of converting metal-containing MMH to a thixotropic gel.

Still another object is to provide a MMH rocket fuel having increased specific impulse-density.

Other objects and advantages will be apparent from the following detailed description.

In accordance with the present invention a thixotropic MMH gel containing metallic fuel particles is prepared by dispersing the fuel particles and a cellulose or hydroxyalkyl-substituted cellulose gelling agent in the MMH. The gelled, metal-containing MMH exhibits substantially increased specific impulse-density values, and the metal particles remain in suspension indefinitely. The gel can be pumped and fed into a rocket motor combustion chamber as a liquid by application

of moderate stress. The semi-solid character of this fuel minimizes the toxicity and fire hazards associated with handling and storage of liquid MMH.

Any cellulose or hydroxyalkyl-substituted gelling agent may be employed, and the following commercially available gelling agents, listed by their chemical composition and trade mark designation, are preferred: hydroxyl methyl cellulose containing 27.5 to 3.15 weight percent methoxyl groups, Methocel; hydroxypropyl methyl cellulose containing 28 to 30 weight percent methoxyl groups and 7 to 12 weight percent propoxyl groups, Methocel HG-60; hydroxypropyl methyl cellulose containing 19 to 24 weight percent methoxyl groups and 4 to 12 weight percent propoxyl groups, Methocel HG-90; dihydroxyethyl cellulose, Cellosize; and hydroxypropyl cellulose containing about 4.6 propoxyl groups per glucose unit, Klucel.

The gelling agent is provided in an amount sufficient to impart thixotropic character to the metal-containing MMH, a room-temperature viscosity of at least about 15,000 centipoise being required, and 30,000 to 60,000 centipoise being preferred. For the preferred gelling agents given above, 1 to 3 weight percent gelling agent in the mixture is suitable for this purpose. The viscosity can be controlled by varying the amount of gelling agent, higher viscosities being obtained by larger amounts. The amount of gelling agent required to obtain a given viscosity varies somewhat with the physical properties of the metallic particles, smaller amounts being required for particles having a larger surface area.

The term "metallic fuel particles" as used herein is intended to refer to any of the finely divided metals and metal hydrides previously used as fuel in solid propellants. Aluminum, magnesium, boron, beryllium, lead and zirconium and hydrides thereof can be used. The metallic particles must be finely divided in order to remain in suspension and allow pumping of the gel as a liquid, and very fine, generally spherical particles on the order of 6 to 10 microns in diameter are preferred. Platelet-type particles, for example, rectangular shapes 40 by 25 by 0.7 to 0.8 microns in size may also be used. The composition of the metal-containing MMH gel can be varied within wide limits to obtain the performance characteristics desired for a given application. The amount of added metallic particles is selected, depending on the desired trajectory and mission for the particular missile. Up to about 70 weight percent metallic particles can be incorporated in the gel and still allow adequate mixing and pumping as a liquid over a practical range of operating temperatures. For typical applications 20 to 50 weight percent provides maximum overall advantage. The particular metal or hydride is likewise selected, depending on the properties desired. Aluminum and boron are desirable because of their favorable combustion properties and their ready availability in powder form. Beryllium and beryllium hydride provide maximum performance characteristics, but the toxicity of beryllium combustion products limit their usefulness. Lead is preferred for applications requiring maximum density.

The metal-containing MMH gel can be prepared by mixing the metallic particles and the gelling agent with the MMH in a conventional mixer. The gelling agents mentioned above are normally available as finely divided powder which disperses readily in the MMH. The mixing time required for complete dispersion varies

with the particular apparatus and the amount of metallic particles, with longer times being required for larger amounts. Under typical conditions a mixing period of one-half to 2 hours is suitable.

The invention is illustrated by the accompanying drawings wherein:

FIG. 1 is a graph showing calculated specific impulse values for MMH containing varying amounts of aluminum at varying oxidizer-to-fuel ratios, the oxidizer being inhibited red fuming nitric acid.

FIG. 2 is a graph showing calculated specific impulse-density values for the same compositions; any

FIG. 3 is a graph showing the effect of added gelling agent or the viscosity of aluminum-containing MMH.

Referring to FIG. 1, it is seen that specific impulse values are decreased with increasing amounts of aluminum, except at the lowest oxidizer-to-fuel ratios.

FIG. 2 shows that specific impulse-density values are substantially increased with increasing amounts of aluminum. For example, at an oxidizer-to-fuel ratio of 2, the specific impulse-density value increases from less than 370 at 20 weight percent aluminum content to over 400 at 50 weight percent.

FIG. 3 depicts the results obtained by adding varying amounts of hydroxypropyl-substituted cellulose containing 4.6 propoxyl groups per glucose unit (Klucel) to MMH containing 35 weight percent aluminum in the form of spherical particles averaging 6 microns in diameter. Curves A and B show the viscosities in centipoises at varying spindle speeds in standard Brookfield viscosity tests for a 125 milliliter portion of the metal-containing MMH with 1.6 and 2.2 weight percent respectively, of gelling agent. In each case the MMH, aluminum and gelling agent were placed in a mixing chamber, and the resulting mixture was agitated for a period of about 1 hour. It is apparent from the curves that a viscosity over 15,000 centipoise, as is required to maintain the particles in suspension, can be obtained by addition of a small amount of gelling agent. The resulting gels were left standing for a period of over 8 months and no settling of particles or other deterioration was observed.

The compositions given in the drawings are merely illustrative and are not to be understood as limiting the scope of the invention, which is limited only as indicated by the appended claims. It is also to be understood that various changes and modifications in appa-

ratus and procedure may be employed by one skilled in the art without departing from the scope of the invention.

What is claimed is:

1. A composition consisting of gelled monomethylhydrazine containing dispersed therein up to 70 weight percent finely divided metallic fuel particles and a cellulose or hydroxyalkyl-substituted cellulose gelling agent.
2. The composition of claim 1 wherein said gelling agent is methyl cellulose containing 27.5 to 31.5 weight percent methoxyl groups, hydroxypropyl methyl cellulose containing 28 to 30 weight percent methoxyl groups and 7 to 12 weight percent propoxyl groups, hydroxypropyl methyl cellulose containing 19 to 24 weight percent methoxyl groups and 4 to 12 weight percent propoxyl groups, dihydroxyethyl cellulose or hydroxypropyl cellulose containing about 4.6 propoxyl groups per glucose unit.
3. The composition of claim 2 wherein the amount of said gelling agent is 1 to 3 weight percent.
4. The composition of claim 3 wherein said metallic fuel particles consist of aluminum, magnesium, boron, beryllium, lead, zirconium, aluminum hydride, magnesium hydride, boron hydride, beryllium hydride, lead hydride, or zirconium hydride.
5. The composition of claim 4 wherein the amount of said particles is 20 to 50 weight percent.
6. The method of preparing a thixotropic monomethylhydrazine gel containing finely divided metallic fuel particles selected from the group consisting of aluminum, magnesium, boron, beryllium, lead, zirconium, aluminum hydride, magnesium hydride, boron hydride, beryllium hydride, lead hydride and zirconium hydride which comprises mixing said particles and said monomethylhydrazine with 1 to 3 weight percent of methyl cellulose containing 27.5 to 31.5 weight percent methoxyl groups, hydroxypropyl methyl cellulose containing 28 to 30 weight percent methoxyl groups and 7 to 12 weight percent propoxyl groups, hydroxypropyl methyl cellulose containing 19 to 24 weight percent methoxyl groups and 4 to 12 weight percent propoxyl groups, dihydroxyethyl cellulose or hydroxypropyl cellulose containing about 4.6 propoxyl groups per glucose unit.

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[54] GELLED MONOMETHYLHYDRAZINE
THIXOTROPIC FUEL

[75] Inventor: Barry D. Allan, Huntsville, Ala.

[73] Assignee: The United States of America as
represented by the Secretary of the
Army, Washington, D.C.

[21] Appl. No.: 179,217

[22] Filed: Sept. 9, 1971

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 518,489, Jan. 3, 1966,
Pat. No. 3,857,743.[51] Int. Cl.² C06B 47/08

[52] U.S. Cl. 149/36

[58] Field of Search 149/36

[56] References Cited

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Audrieth, et al., The Chemistry of Hydrazine, pp. 6-9,
197, 200, 204-207, 209 and 210, John Wiley & Sons,
Inc., (1951), New York.

Primary Examiner—Edward A. Miller

Attorney, Agent, or Firm—Nathan Edelberg; Robert P.
Gibson; James T. Deaton

[57] ABSTRACT

A thixotropic rocket fuel composed of monomethylhydrazine, metallic fuel particles, dimethylurea, and a gellant. The particular thixotropic fuel is particularly characterized by the fact that a low gellant concentration can be used and by the fact that the metallic fuel particles can be suspended with no separation or settling out of the metallic fuel particles in the fuel even when subjected to 500 g's. The particular thixotropic rocket fuel has high density quality and high specific impulse values.

3 Claims, No Drawings

GELLED MONOMETHYLHYDRAZINE THIXOTROPIC FUEL

CROSS-REFERENCE TO RELATED APPLICATION

This invention is a continuation-in-part and an improvement over the invention disclosed in the copending application of Barry D. Allan, Ser. No. 518,489, filed Jan. 3, 1966, and now U.S. Pat. No. 3,857,743.

BACKGROUND OF THE INVENTION

For applications where fuel tank volume is limited, it is desirable to increase the density of the fuel while maintaining a high specific impulse. One means of increasing the density of the fuel is to suspend finely divided particles of a metal in the fuel. An approach to suspend the metal fuel particles in the fuel has been difficult because of the necessity of maintaining the particles in suspension at high g-loadings. While applicant's previous invention has suspension capabilities, the suspensions have required high concentrations of gellant. Also, the high concentrations of gellant takes up space and therefore, a composition is needed in which a lower percentage of gellant can be used and still maintain the metal particles suspended in the fuel even at very high g-loadings.

Therefore, it is an object of this invention to provide a thixotropic fuel which has a relatively low gellant concentration.

Another object of this invention is to provide a thixotropic fuel which has the ability even with low gellant concentration to maintain metallic fuel particles dispersed therein even under several hundred g's loading.

A further object of this invention is to provide a thixotropic fuel in which the density is relatively high and the specific impulse is also high.

SUMMARY OF THE INVENTION

In accordance with this invention, a novel thixotropic fuel is disclosed that includes the fuel monomethylhydrazine in an amount of about 36 to about 40 weight percent, a gellant such as any cellulose of hydroxyalkyl-substituted gelling agent in an amount of about 1 to about 3 weight percent, an additive of dimethylurea in an amount of about 0.05 to about 0.3 weight percent, and metallic fuel particles in an amount up to about 60 weight percent. This particular composition produces a thixotropic fuel that is capable of maintaining the metallic fuel particles in suspension even under very high g-loadings which is required for rocket fuel. Also, the metallic fuel particles are maintained in suspension even though the percentage of gellant and the additive are very small in quantity. The percentage of metallic fuel particles may be even greater than 60 weight percent if the g-loading requirement is lowered.

DETAILED DESCRIPTION OF THE INVENTION

This invention is a thixotropic rocket fuel and more particularly a gelled monomethylhydrazine (MMH) containing metallic fuel particles. For applications where fuel-tank volume is limited, it is desirable to increase the density of the fuel while maintaining a high specific impulse. One means of increasing the density of the fuel is to suspend finely divided particles of a metal in the MMH.

Such an approach has been difficult because of the necessity of maintaining the particles in suspension at high g-loadings. As disclosed in applicant's copending application Ser. No. 518,489, filed Jan. 3, 1966, stabilized suspensions have used higher concentrations of gellant. Also, the particular composition under discussion here uses an additional component to that of applicant's prior invention. The additional component allows lower gellant concentration while maintaining the ability of the gel to show no separation or settling of the fuel after 30 minutes exposure to 500 g's of force. The lower gellant concentration and additional component imparts a lower yield value to this fuel composition as measured by the rising sphere rheometer.

The preferred gellant is hydroxypropyl cellulose containing about 4.6 propoxyl groups per glucose unit (Klucel). However, other cellulose or hydroxyalkyl-substituted gelling agents may be employed such as: hydroxy methyl cellulose containing 27.5 to 31.5 weight per cent methoxyl groups (Methocel); hydroxypropyl methyl cellulose containing 28 to 30 weight per cent methoxyl groups and 7 to 12 weight per cent propoxyl groups (Methocel HG-60); hydroxypropyl methyl cellulose containing 19 to 24 weight per cent methoxyl groups and 4 to 12 weight per cent propoxyl groups (Methocel HG-90); and dihydroxyethyl cellulose (Cellose).

The term "metallic fuel particles" as used herein is intended to refer to any of the finely divided metals and metal hydrides previously used as fuel in solid propellants. Aluminum, boron, beryllium, lead and zirconium and hydrides of each of these metals can be used. The metallic particles must be finely divided in order to remain in suspension and allow pumping of the gel as a liquid, and very fine, generally spherical particles on the order of 6 to 10 microns in diameter are preferred. Platelet-type particles, for example, rectangular shapes 40 by 25 by .7 to .8 microns in size may also be used.

It has been discovered that MMH of about 36 to about 40 weight percent and about 60 weight percent metallic fuel particles such as preferably aluminum, can be successfully gelled to such an extent as to hold the metallic fuel particles in suspension under high g-loading by using about 1 to about 3 weight percent gellant of Klucel and about 0.05 to 0.3 weight percent dimethylurea. This particular composition is especially adapted for rocket fuel since it contains such a high concentration of the monopropellant fuel and the metal suspended therein, and since the metallic particles can be maintained suspended even under very high g-loadings such as the 500 g's as stated supra. A particularly preferred thixotropic fuel composition is set forth in the example below:

EXAMPLE

| | | |
|-------------------------|------|-------------|
| gellant - Klucel | 1.4 | % by weight |
| additive - Dimethylurea | .1 | % by weight |
| metal - Aluminum | 60.0 | % by weight |
| Monomethylhydrazine | 38.5 | % by weight |

Metal-containing MMH gel can be prepared by mixing the metallic particles, the gelling agent, and the additive dimethylurea with the MMH in a conventional mixer. The gelling agent Klucel and the dimethylurea are finely divided powders which disperse readily in the MMH.

I claim:

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1. A composition consisting of monomethylhydrazine present in an amount of about 36 to about 40 weight percent, hydroxyalkyl cellulose present in an amount of about 1 to about 3 weight percent, metallic fuel particles, and dimethylurea present in an amount of about 0.05 to about 0.03 weight percent to form a gelled fuel.

2. The composition of claim 1, wherein said hydroxyalkyl cellulose is hydroxypropyl cellulose, and wherein the remainder is composed of said metallic fuel particles, said metallic fuel particles being selected from the group consisting of aluminum, magnesium, boron, beryllium, lead zirconium, aluminum hydride, magnesium

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hydride, boron hydride, beryllium hydride, lead hydride and zirconium hydride.

3. The composition of claim 1, wherein said monomethylhydrazine is present in an amount of about 38.5 weight percent, wherein said metallic fuel particles are aluminum and are present in an amount of about 60 weight percent, wherein said hydroxyalkyl cellulose is hydroxypropyl cellulose and is present in an amount of about 1.4 weight percent, and wherein said dimethylurea is present in an amount of about 0.1 weight percent.

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[54] **EXPLOSIVES CONTAINING AMMONIUM NITRATE AND NITRATED AMINES**

[75] Inventors: Joseph Hershkowitz, West Caldwell, N.J.; Irving B. Akst, Pampa, Tex.

[73] Assignee: The United States of America as represented by the Secretary of the Army, Washington, D.C.

[21] Appl. No.: 769,607

[22] Filed: Feb. 17, 1977

[51] Int. Cl.² C06B 31/32

[52] U.S. Cl. 149/47; 149/92

[58] Field of Search 149/47, 88, 92

[56] **References Cited**

U.S. PATENT DOCUMENTS

3,378,576 4/1968 Dinwoodie et al. 149/88 X

Primary Examiner—Stephen J. Lechert, Jr.

Attorney, Agent, or Firm—Nathan Edelberg; Robert P. Gibson; A. Victor Erkkila

[57] **ABSTRACT**

An explosive composition containing essentially of an intimate mixture of

15 to 45% by weight of a particulate high explosive from the group consisting of RDX (1,3,5-trinitro-1,3,5-triazacyclohexane) and HMX (1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane and mixtures thereof,

15 to 50% by weight of ammonium nitrate, and 20 to 60% by weight of ethylenediamine dinitrate;

wherein the weight ratio of ammonium nitrate to ethylenediamine dinitrate is from 1:2.5 to 1.5:1, respectively, and particularly about 1:1. These explosive compositions provide an unexpectedly high explosive output with a relatively low content of RDX and/or HMX, and an equivalent output with much less RDX than conventional explosive compositions consisting of mixtures of RDX with AN and/or TNT.

8 Claims, 2 Drawing Figures

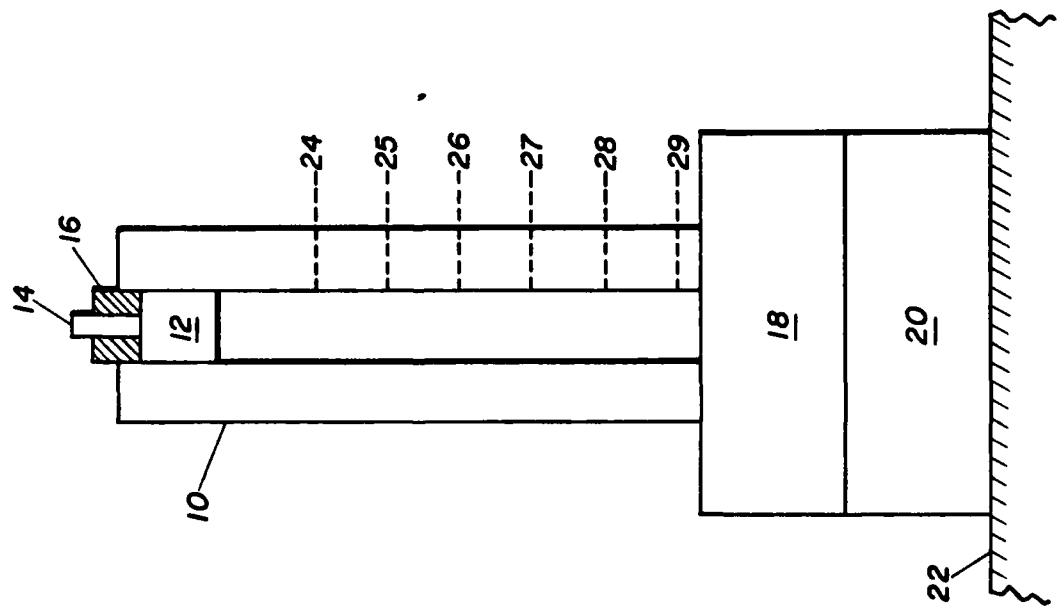


FIG. 1

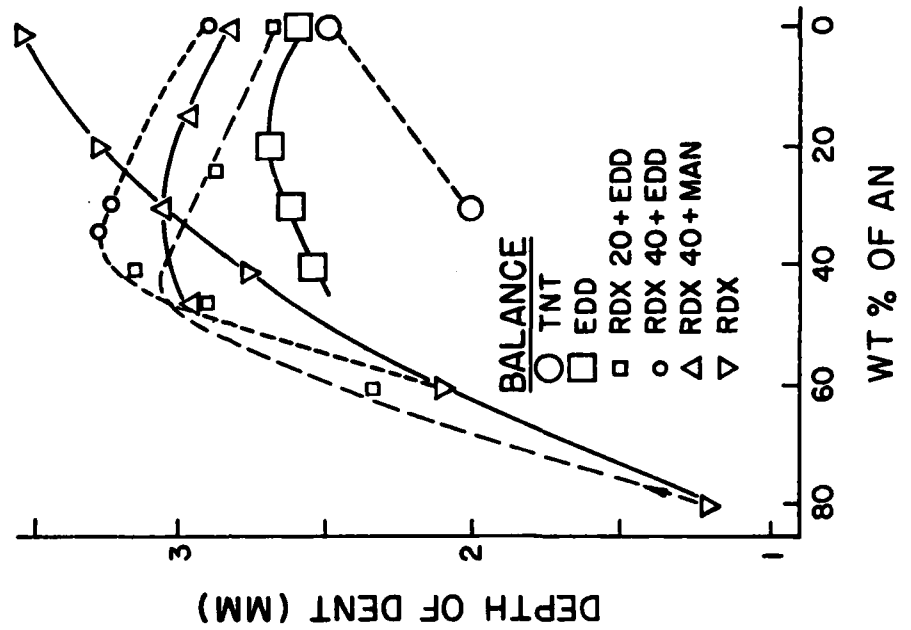


FIG. 2

EXPLOSIVES CONTAINING AMMONIUM NITRATE AND NITRATED AMINES

GOVERNMENTAL INTEREST

The invention described herein was made in the course of a contract with the Government and may be manufactured, used and licensed by or for the Government for governmental purposes without the payment to us of any royalty thereon.

BACKGROUND OF THE INVENTION

It is known to produce explosive mixtures of good homogeneity suitable for the production of cast explosive charges by melting together ammonium nitrate (AN) and an aliphatic mono- or polyamine nitrate, e.g. methylammonium nitrate (MAN) and ethylenediamine dinitrate (EDD) (U.S. Pat. No. 1,968,158). Such low-melting mixtures including eutectic mixtures, with and without other explosive and inert additives e.g. PETN, RDX or TNT were utilized as cast explosive charges by Germany in World War II and more recently have been the object of further studies. (T. Urbanski, "Chemistry and Technology of Explosives", Pergamon Press, Vol III, pp 253-4 and 271; B. T. Federoff and O. E. Sheffield, "Encyclopedia of Explosives and Related Items," Technical Report 2700, Volume 6 (1974), pp E234-7; M. H. Ficherouille, "Ethylenedinitramine, Ammonium Ethylenedinitramate, Binaries with Ammonium Nitrate," *Memorial des Poudres*, 30, 89-100 (1948) (In French); A. LeRoux, "Explosive Properties of Ethylenediamine Dinitrate," *Memorial des Poudres*, 32, 121-131 (1950); A. LeRoux, "Explosive Properties of Nitrate of Monomethylamine," *Memorial des Poudres*, 34, 129-145 (see pp. 141-2 for EDD) (1952); B. T. Federoff et al, "Dictionary of Explosives, Ammunition and Weapons (German Section)," Technical Report 2510, Picatinny Arsenal Dover, N.J. pp. Ger 35-36, 47, 48 (1959) (AD 16036); "Allied and Enemy Explosives," Aberdeen Proving Ground Report APG ST-9-2900-1 (1946), pp 145-147; and A. N. Campbell and A. J. R. Campbell, "Binary and Ternary Eutectics Involving Ammonium Nitrate," *Canadian Journal Research*, Vol. 25B pp. 90-100 (1947)).

It has also been recognized that established explosive compositions such as Amatols (AN/TNT 60/40), and Amatex 20 and 40 (RDX/TNT/AN, 20/40/40 and 40/40/20) perform as though only 19%, 50% and 50%, respectively, of the AN in the compositions participates and contributes to the explosive output (C. F. Mader, "An Equation of State for Nonideal Explosives," Los Alamos Scientific Laboratory, LA5864, April 1975).

SUMMARY OF THE INVENTION

A principal object of the present invention is to increase the participation of AN in composite explosives so as to provide a superior explosive output. Another object is to provide composite explosive compositions containing AN, which provide unexpectedly high explosive performance with a relatively small content of RDX, can be readily made from industrially available materials by existing technology with reduced hazard, possess good storage stability and can be cast, molded or pressed into suitable shapes, such as pellets.

It has been found that the foregoing and other objects can be achieved according to the present invention by means of an explosive composition consisting essentially of

15 to 45% by weight of a particulate high explosive selected from the group consisting of 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX) and 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX), and mixtures thereof,

15-50% by weight of ammonium nitrate (AN), and 20-60% by weight of ethylenediamine dinitrate (EDD),

wherein the AN and EDD components are present in the weight ratio of from 1:2.5 to 1.5:1, respectively, particularly about 1:1, and at least in part as an intimate mixture obtained by cosolidification.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a diagrammatic view of apparatus for measuring the denting power of an explosive composition.

FIG. 2 sets forth a series of graphs showing the depth of dent produced versus the AN content of various explosive compositions, including compositions of the present invention. de

DETAILED DESCRIPTION OF THE INVENTION

The novel explosive compositions of the present invention contain all or part of the EDD and AN components as an intimate mixture obtained by cosolidification as more fully described hereinafter. Due to their content of such intimate mixtures and critical proportions of EDD and AN in combination with at least 15% of RDX and/or HMX, the novel explosive compositions generally provide a greater output, as measured by depth of dent, for the same detonation velocity than (1) similar explosive compositions, wherein the EDD/AN mixture is present in other proportions and/or obtained by other methods, e.g. mechanical mixing of the finely powdered dry ingredients and (2) mixture of RDX with AN or TNT containing much higher contents of RDX. The role of the RDX and/or HMX is to provide a highly energetic component, which will provide a high pressure and high temperature, wherein the intimate mixture of AN and EDD will be caused to act synergistically.

The intimate mixture of the EDD and AN can be obtained by cosolidification as follows. A mixture, of AN and EDD in the weight ratio of from 1:2.5 to 1.5:1 respectively, is heated to a temperature somewhat above the melting point of the EDD/AN mixture until melting occurs and a smooth blend is produced. The molten mixture, which may then be admixed with finely divided RDX and/or HMX, is cooled to solidify the melt. This can be accomplished by pouring the melt into a cold mold, or onto a cold stainless steel sheet or by mixing the melt with a cold inert liquid, e.g. Freon, to form finely divided particles. According to a preferred process, a eutectic mixture of EDD and AN, preferably together with finely divided particles of RDX and/or HMX, is suspended in a carrier liquid in which the EDD and AN ingredients are insoluble, e.g. perchloroethylene. The agitated suspension is then heated to a temperature above the eutectic temperature (e.g. about 10°-15° C above the melting point of the eutectic, which is approximately 103° C) and held thereat for several minutes until the EDD and AN ingredients are completely melted and coalesced. Cold carrier liquid, which may be the same or different from that employed as the suspension liquid, is then rapidly added sufficient to drop the temperature, say about 10° C, below the eutectic temperature as suddenly as possible, thereby

causing the eutectic to solidify largely as a coating on the finely divided particles of RDX and/or HMX. The product thus obtained generally consists of small particles requiring no further grinding.

The term consolidation, as used in the present invention, is understood to include (1) a process, wherein the EDD/AN mixture in the presence or absence of a non-solvent type carrier liquid is heated above the melting point of the mixture and cooled to solidify i.e. cocrystallize the mixture, as well as (2) a process wherein the EDD/AN mixture is cocrystallized from solution in a solvent. For example, the EDD and AN, preferably in about the proportions of the eutectic mixture, are dissolved in a suitable solvent, e.g. water, after which RDX and/or HMX and other ingredients insoluble in the solvent can be added. Thereafter the solution is evaporated to dryness under heat and vacuum to remove the solvent and cocrystallize the EDD/AN mixture, and the product is pulverized for further use.

Also, the EDD/AN eutectic mixture can be first prepared by cosolidification as previously described and additional AN or EDD then added to obtain the desired proportions. The resulting mixtures can be crushed or pulverized to the desired fineness, dry-mixed with RDX and/or HMX and finally pressed into pellets.

The compositions thus obtained can be mixed with small amounts of waxes, surfactants, anti-hydroscopic agents, casting or bonding agents, etc. as needed or desired, to provide desensitization, dimensional stability, reduced caking, and improved casting and bonding properties, as known in the art.

The preferred EDD/AN/RDX (HMX) compositions of the present invention are those wherein substan-

tially all of the AN and EDD components are present as a eutectic obtained by cosolidification, wherein the EDD/AN eutectic mixture is heated above its melting point and the melted mixture is cooled to below its solidification point. Such explosive compositions, wherein substantially all of the AN and EDD are present as a cosolidified eutectic obtained by cooling the melted eutectic mixture below its solidification point, contain the most intimate mixture, namely a mutual solution of these components, and exhibit the maximum explosive output, as measured by the depth of dent, for a given RDX (HMX) content. AN/EDD mixtures produced by solidification of the melted mixture, wherein these components are present in other than the eutectic ratio (1:1 weight ratio), contain these components in part as the eutectic (wherein the AN and EDD are contained as a mutual solution) and in part as "excess" or undissolved AN or EDD.

The following examples specifically illustrate explosive compositions of this invention as well as comparative explosive compositions of the prior art. In the examples, parts and percentages reported are by weight.

EXAMPLE 1-33

Table 1 sets forth explosive compositions of the present invention as well as prior art explosive compositions together with the test results which are also plotted in FIG. 2. FIG. 2 also contains test data for explosive compositions not shown in Table 1 but obtained in the same manner.

Section C following the table describes the methods employed for preparing and testing the explosive compositions.

TABLE 1

| Results of Confined Small Scale Dent and Detonation Velocity Tests (Explosive Diameter = 9.65 mm) | | | | | | | | | | | | |
|--|-----|-----|----|-----|-----|-------|--------------------|------|------|------|--------------------|----------------------|
| Example | TNT | RDX | AN | MAN | EDD | Dens. | Depth of Dent (mm) | | | Avg. | Det. Vel. (mm/sec) | Avg. |
| 1 | | 100 | | | | 1.72 | 3.58 | 3.61 | 3.47 | 3.47 | 8.66 8.55 | 8.59 8.46 8.57 |
| 2 | 20 | 80 | | | | 1.66 | 3.43 | 3.28 | | 3.36 | | |
| 3 | 40 | 60 | | | | 1.67 | 3.33 | 3.20 | 3.10 | 3.23 | 7.73 | 7.73 |
| 4 | 60 | 40 | | | | 1.64 | 2.95 | 2.90 | | 2.93 | | |
| 5 | 80 | 20 | | | | 1.63 | 2.79 | 2.84 | | 2.82 | | |
| 6 | 100 | | | | | 1.59 | 2.53 | 2.57 | 2.41 | 2.46 | 6.92 | 6.92 6.69 6.84 |
| 7 | | | | | | | 2.49 | 2.44 | 2.46 | 2.48 | | |
| 8 | | 60 | | 100 | | 1.40 | 0.05 | 0.10 | | f | | |
| 9 | | 40 | | | 40 | 1.67 | 3.25 | 3.18 | | 3.22 | | |
| 10 | | 20 | | | 60 | 1.64 | 2.90 | 2.82 | | 2.86 | 7.96 | 7.66 7.81 |
| 11 | | | | | 80 | 1.59 | 2.69 | 2.72 | | 2.71 | 7.56 | 7.52 7.54 |
| 12 | | 80 | 20 | | 100 | 1.55 | 2.72 | 2.46 | 2.59 | 2.64 | 6.77 | 6.77 |
| 13 | | 60 | 40 | | | 1.70 | 3.30 | 3.20 | | 3.25 | | |
| 14 | | 40 | 60 | | | 1.73 | 2.69 | 2.77 | | 2.73 | | |
| 15 | | 20 | 80 | | | 1.71 | 1.89 | 1.93 | 2.21 | 2.26 | 7.17 | 7.17 7.12 7.15 |
| 16 | | | | | | | 2.26 | | | 2.11 | | |
| 17 | | | | | | 1.66 | 1.19 | 1.22 | | 1.21 | | |
| 18 | | | | | | 1.48 | 2.67 | 2.69 | | 2.68 | 6.18 | 6.58 6.38 |
| 19 | | | | | | 1.51 | 2.64 | 2.49 | 2.49 | 2.72 | 5.85 | 5.60 5.90 5.78 |
| 20 | | | | | | | 2.74 | | | 2.61 | | |
| 21 | | | | | | 1.47 | 2.52 | 2.57 | | 2.54 | 5.90 | 5.69 5.30 |
| 22 | | | | | | 1.55 | 1.52 | 1.70 | 2.18 | 1.52 | 5.19 | 5.18 5.20 5.19 |
| 23 | | | | | | | 0.76 | 0.86 | 1.96 | 1.50 | | |
| 24 | | | | | | 1.58 | 0.91 | 2.13 | 2.72 | 0.40 | 5.81 | 5.23 5.52 |
| 25 | | | | | | | 1.98 | 2.52 | 0.15 | f | | |
| 26 | | | | | | 1.55 | 1.70 | 1.32 | 1.52 | 1.83 | 1.20 | |
| 27 | | | | | | 1.63 | 2.01 | 2.03 | | 2.02 | 6.48 | 6.25 6.37 |
| 28 | | | | | | 1.66 | 2.97 | 2.97 | 2.96 | 2.97 | 7.34 | 7.31 7.07 7.24 |
| 29 | | | | | | 1.62 | 3.05 | 3.07 | 2.99 | 3.04 | 7.49 | 7.51 7.16 7.39 |
| 30 | | | | | | 1.57 | 2.97 | | | 2.97 | 7.57 | 7.57 |
| 31 | | | | | | 1.67 | 3.22 | 3.25 | 3.28 | 3.23 | 3.25 | |
| 32 | | | | | | 1.66 | 3.28 | 3.15 | 3.30 | 3.20 | 3.23 | 7.38 7.38 |
| 33 | | | | | | 1.67 | 2.29 | 2.36 | | 2.33 | | |
| 34 | | | | | | 1.62 | 2.95 | 2.92 | | 2.94 | 6.16 | 6.16 |
| 35 | | | | | | 1.61 | 3.05 | 3.02 | 3.30 | 3.23 | 3.15 | 6.39 6.39 |
| 36 | | | | | | 1.51 | 2.90 | 2.84 | | 2.87 | 6.93 | 6.93 |
| 37 | | | | | | 1.65 | 2.54 | 2.46 | 2.71 | 2.67 | 2.60 | 7.10 7.10 |

TABLE 1-continued

| Results of Confined Small Scale Dent and Detonation Velocity Tests (Explosive Diameter = 9.65 mm) | | | | | | | | | |
|--|-----|-----|----|-----|-----|-------|--------------------|-------------------------|------|
| Example | TNT | RDX | AN | MAN | EDD | Dens. | Depth of Dent (mm) | Avg. Det. Vel. (mm/sec) | Avg. |
| 33 | 40 | | 34 | | 26 | 1.61 | 2.79 2.82 | 2.81 | |

Compositions given in weight percents.

AN = ammonium nitrate;

MAN = methylammonium nitrate;

EDD = ethylenediamine dinitrate;

Dens. = average density in g/cm³;

f = fails to propagate;

AN = 100 and

AN/EDD = 75/25 did not propagate.

Referring to Table 1 and the graphs shown in FIG. 2, it is noted that the depth of dent decreases steadily as the AN content of the RDX/AN composition is in-

foam on 19 mm thick plywood resting on a steel base.

The test results are set forth in Table 2.

TABLE 2

| Explosive Diameter 19.2 mm | | | | | | | | | | | | | | | |
|----------------------------|-----|-----|------|------|-------------------------------|-------|-------|-------|-------------------|-------|--------------------|-------|-------|-------|-------|
| Example | TNT | RDX | AN | EDD | Detonation Velocity (mm/μsec) | | | Avg. | Density | | Depth of Dent (mm) | Avg. | | | |
| | | | | | Individual Values | | | | Individual Values | | | | | | |
| 34 | 40 | 60 | | | 7.688 | 7.885 | 7.673 | 7.749 | 1.645 | 1.636 | 7.462 | 7.430 | 7.446 | | |
| 35 | | 40 | 30 | 30 | 7.390 | 7.412 | 7.372 | 7.566 | 7.769 | 1.634 | 1.637 | 7.551 | 7.945 | 7.748 | |
| 36 | | 25 | 37.5 | 37.5 | 7.131 | 7.075 | 6.430 | 6.520 | 6.789 | 1.645 | 1.642 | 7.767 | 7.874 | 7.821 | |
| 37 | | 20 | 40 | 40 | 6.529 | 6.336 | 6.836 | 6.759 | 6.615 | 1.627 | 1.629 | 8.230 | 7.912 | 8.071 | |
| 38 | | 15 | 42.5 | 42.5 | 7.042 | 6.899 | 6.786 | 6.766 | 6.665 | 1.632 | 1.633 | 1.629 | 7.836 | 7.811 | 7.824 |
| 39 | 100 | | | | 6.795 | 6.524 | 6.669 | | 6.663 | 1.553 | 1.561 | 6.299 | 6.375 | 6.337 | |

creased. By contrast, with RDX 20/EDD/AN and RDX 40/EDD/AN compositions, wherein the RDX content is held constant at 20% and 40% respectively, it is surprising that the depth of dent curve in each case rises to a peak as the AN content is increased with corresponding decrease of the EDD content. The intersections of these curves with the RDX/AN curve indicate an equivalent depth of dent for the RDX 75/AN25 and RDX40/EDD35/AN25 compositions as well as for the RDX65/AN35 and RDX20/EDD45/AN35 compositions. The curves demonstrate that RDX/EDD/AN compositions of the present invention containing cosolidified EDD/AN mixtures provide an increased participation of the AN in the explosive output and produce equivalent output with a much lower content of RDX than mixtures of RDX with AN or TNT. Further, a comparison of the curves for RDX40/EDD/AN and RDX40/MAN/AN shows that EDD gives superior results in combination with AN/RDX than does MAN.

Similar results are obtained when part or all of the RDX is replaced by HMX.

B. EXAMPLES 34-39

Dent and detonation velocity tests with Composition B (RDX/TNT/60/40) and EDD/AN/RDX compositions, prepared in similar manner to that described in section C, were carried out at a larger explosive diameter in apparatus which possessed a similar configuration to that described above and shown in FIG. 1 except as follows:

- The explosive pellets had a diameter of 19.2 mm;
- The tube (10) had an ID of 19.2 mm, an OD of 50.8 mm and a length of 152 mm;
- The distance between the pins (24-29) was twice that in the apparatus of Section C;
- The witness plates (18 and 20) were SAE1117 cold drawn steel cylinders (see Metals Handbook 8th Ed. Vol. 1, American Society for Metals, pages 62 and 188) of 101.6 mm diameter and 50.8 mm thickness supported on a pad of 76 mm thick urethane

The results show that the EDD/AN/RDX compositions of the present invention, using much less RDX, are equal or superior to Composition B (example 34) in explosive output, as measured by the aforesaid dent test, notwithstanding their lower detonation velocities.

When the tests were repeated except that the aforesaid witness plates were replaced by two witness plates of CRS 1018 steel, 76.2 mm diameter and 38.1 mm thickness supported on a steel base plate, the EDD/AN/RDX compositions produced more damage and had a greater shearing effect at the periphery of the explosive column (as shown by the greater depth of dent and extent of cracking of the top witness plate) than the reference explosive RDX/TNT 60/40.

Also, the explosive composition EDD/AN/RDX 37.5/37.5/25, prepared as described in Section C, was tested with a 4 inch 42° copper shaped charge at stand-off distances of two and twenty cone diameters, and produced jet parameters and penetration indicating performance equal or superior to that similarly produced with Composition B containing 60% RDX although with a content of only 25% RDX.

From the foregoing it is evident that the compositions of the present invention, containing the aforesaid critical proportions of the low cost, cosolidified complementary explosives EDD and AN in combination with the powerful ideal explosives RDX and/or HMX, provide a synergistic result whereby they produce an unexpectedly high explosive output with a relatively low RDX content and an equal or superior explosive performance with a much lower RDX content as compared with conventional relatively costly explosives containing RDX, such as Composition B.

C. Preparation and Testing of the Explosive Compositions

Preparation of Cosolidified EDD/AN Compositions

The AN (mp 169° C) and EDD (mp 185° C) were weighed and dry-mixed and charged to a flask partially submerged in silicone oil in a larger beaker on a thermostatically controlled hot-plate. A mercury glass thermometer was kept in the silicone oil. For 50/50 (eutec-

tic) mixtures the temperature was kept at 120° C; for the other mixtures the temperature was held at about 140° C for just long enough to melt the materials as visually observed. The melt was then poured into a relatively large quantity of room temperature trichlorotrifluoroethane (Freon TF or Genetron 113) with rapid stirring. The spherical beads thus formed, ranging in diameter from less than 1 mm to about 2 mm, were separated from the trichlorotrifluoroethane by filtration and crushed in an electric mortar and pestle to a moderately fine granular size suitable for pressing, namely about 350 microns median particle diameter.

Preparation of EDD/AN/RDX Compositions

The RDX was military grade, Type II, Class A, median particle diameter 250 microns.

The components, RDX and the cosolidified EDD/AN mixtures obtained as described above, were weighed and then thoroughly mixed in beakers.

Preparation of MAN*/AN/RDX Compositions

These mixtures were made in similar manner to the EDD/AN/RDX mixtures.

* MAN is methyl ammonium nitrate, mp 109°-110° C.

Other Compositions

The RDX/AN and RDX/EDD mixtures were prepared by dry-mixing the RDX with AN or EDD ground to the usual size in the mortar and pestle.

The TNT/AN formulations were made by mixing the finely ground AN with a solution of the TNT in toluene, and evaporating the solvent with a dry nitrogen sweep over the surface. The product was lightly crushed to break up small, soft lumps.

Fabrication and Assembly for Confined Small Scale Detonation Velocity and Depth of Dent Tests

All compositions were pressed in a die of 9.525 mm inner diameter, unheated, unevacuated, at about 3800 kg/cm² with a dwell of about two minutes. Length of pellet varied from 6 to 12 mm. Density was measured soon after pressing, by weighing to 0.1 milligram and measuring diameter and length by micrometer to the nearest 0.0025 mm. Density was also measured again prior to assembly into shot tubes because it had been found that some pellets would not fit into the 9.652 mm ID of the tubes due to spring-back. This was quite significant, especially in the EDD/AN formulations and in pure EDD. Because of this factor and occasional slight irregularity of pellets (corner chipped, etc.) density results were rounded from the nearest milligram/cc to the nearest 0.01 gm/cc.

The tube (10) for the confined small-scale detonation velocity and dent tests (FIG. 1) was a steel cylinder 76.2 mm long with 25.4 mm OD and 9.65 mm ID. Pellets were assembled into this tube with a pellet near the average density of the stack placed next to the witness plate. Those pellets whose density differed most from the average were placed nearest the detonator. Additive height was checked against height in tube to avoid gaps. Pellets that could not be inserted as they were because of spring-back were first lightly abraded dry. All pellets fitted quite tightly. In no case would there have been radial gaps greater than 0.025 mm.

A booster pellet (12), normally Composition B (RDX/TNT 60/40) was placed in the tube and an exploding bridgewire (EBW) detonator (14) in a plastic

holder (16) was glued in with a drop of cyanoacrylate adhesive or fast-setting epoxy.

Two witness plates (18) and (20), each of SAE1018 cold drawn (see Metals Handbook 8th Ed. Vol. 1, American Society for Metals pp 62 and 188), 50.8 × 50.8 × 17 mm were adhered together with a drop of cyanoacrylate and the loaded tube was similarly adhered to it, taking care not to touch the explosive with the adhesive. All surfaces were flat to better than 0.025 mm and the nature of the adhesive assured flatness and contact, as it will not set except in thin layers. Two witness plates were used because with powerful explosives small tensile cracks were found in the first few shots when only one witness plate was employed.

The assembly was then placed in a special chamber able to confine the shock, blast, and debris. The assembly rested vertically with the witness plates on thick foamed polyethylene or foamed polyurethane (22). The six pin wires (24-29) for measuring detonation velocity D, when used, were connected, as was the coaxial detonator firing cable. The chamber was closed and the shot fired behind blast doors in an explosives safety hood.

Detonation Velocity (D)

The D records were obtained from the output signals from the pins (see FIG. 1) by the following combination of instruments. The pin mixer circuit output was put into a channel of a transient digitizer (Biomation Model 8100 marketed by Biomation Co., Cupertino, California) that provides 2,000 samplings at a variable pre-selected sampling rate. The smallest sampling interval, 10 nanoseconds, was used. The input voltage is measured, digitized and "memorized" at each of these intervals. Output is a voltage proportional to the digitized value (the digitalization is for storage purposes) and the time of output is 20 seconds for the 2,000 points. The output was connected to a galvanometer of a Honeywell Visicorder (paper) oscillograph, Model 906C (marketed by Honeywell, Inc., Test Instrument Div., Denver, Colorado) — set to run at 127 mm per second. Simultaneously, outputs of a time-mark generator, Tektronix Model 184 (marketed by Tektronix, Inc., Beavertown, Ore.), at 1 second, 0.1 second, and 0.01 second were paralleled at successively lower voltages and connected to another of the oscillograph's galvanometers. These gave crystal-controlled time marks along the paper at what are effectively 1 microsecond, 0.1 microsecond and 0.01 microsecond (10 nanoseconds) because the digitizer playback time of 20 seconds is 10⁶ times as long as the input sampling time (2,000 × 10 ns). The digitizer oscillator is also crystal controlled at high accuracy, similar to the time-mark generator.

The oscillograph paper, UV-light activated, develops in fluorescent room lighting in a minute or so. Reading the time interval between pin signals then is simply a matter of counting the time marks between signals. Precision and accuracy is 10 ns, with no linearity or reading error greater than that. The space interval between pins was a constant 9.525 mm ± 0.013 mm (as a tolerance; dispersion was actually lower). D thus had an intrinsic resolution in one space interval not statistically poorer than about 25 m/s. Other potential sources of error (e.g. pin not fully inserted and touching the explosive) can make individual interval error greater than that. But averaging over several intervals or considering several intervals as a larger one increases the proportional accuracy, so that the overall statistical preci-

sion and accuracy was on the order of 10-15 m/s. All the values obtained were rounded to the nearest 10 m/s.

Depth of Dent

After the shot, it was always found that the two thicknesses of the witness plate had come apart. The upper piece was measured for dent depth by dial indicator with a small-radius tip, reading to the nearest 0.025 mm. The witness plate was put on a flat surface plate and the dial indicator zeroed to the upper surface of the witness plate by trials at the midpoints of the four edges. There was usually some overall curvature (concavity of the top, convexity of the bottom) especially in those dented the deepest; and sometimes there was edge damage from collision with the chamber or other plate after separation, etc. The effects of these distortions were avoided by care in the zeroing process. Depth of dent was then measured to the deepest point, without regard to its width. The deepest point was in the center of the dent and was usually of small width. Sometimes the deepening toward the center was gradual over much of the total width. Lip height was read a number of times, but, like the few volume measurements tried, seemed to be an irregular or insensitive measurement, possibly due to inadequate precision in the measurement.

We wish it to be understood that we do not desire to be limited to the exact details of construction shown and described, because obvious modifications will occur to a person skilled in the art.

We claim:

1. An explosive composition consisting essentially of a mixture of
15 to 45% by weight of a particulate high explosive
selected from the group consisting of 1,3,5-trinitro-

1,3,5-triazacyclohexane and 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane, and mixtures thereof; 15 to 50% by weight of ammonium nitrate; and 20 to 60% by weight of ethylenediamine dinitrate; wherein the ammonium nitrate and the ethylenediamine dinitrate are present in the weight ratio of from 1:2.5 to 1.5:1, respectively, as an intimate mixture of which the major portion is obtained by cosolidification.

2. The explosive composition of claim 1, wherein substantially all of said ammonium nitrate and ethylenediamine dinitrate are present as an intimate mixture obtained by cosolidification.

3. The explosive composition of claim 2, wherein the ammonium nitrate and ethylenediamine dinitrate are present in essentially the eutectic weight ratio of about 1:1 as an intimate mixture obtained by cosolidification of a molten mixture thereof.

4. The explosive composition of claim 3, obtained by heating the mixture in an inert carrier liquid to a temperature above the melting point of the eutectic mixture of ethylenediamine dinitrate and ammonium nitrate, and cooling the mixture to solidify said eutectic mixture largely as a coating on the particles of the high explosive.

5. The explosive composition of claim 3, wherein the high explosive amounts to about 40% by weight of the mixture.

6. The explosive composition of claim 1, wherein the high explosive is 1,3,5-trinitro-1,3,5-triazacyclohexane.

7. A cast explosive of the composition of claim 1.

8. A pressed explosive of the composition of claim 1.

* * * * *

THE BDM CORPORATION

U.S. NAVY PATENTS

Patent Number: 3,969,979

Author: Abraham Schneider, Overbrook Hills, PA; Stanley E. Wood,
Inyokern, CA; T. Bryant, Inyokern, CA

Title: Liquid Propellant for a Gun

Date: July 29, 1975

Patent Number: 4,004,415

Author: Stanley E. Wood, Inyokern, CA

Title: Propellant for Liquid Propellant Gun

Date: January 25, 1977

Patent Number: 4,094,713

Author: B. Arthur Breslow, Ridgecrest, CA

Title: Sensitizing Liquid Explosives with High Gamma Gas

Date: June 13, 1978

- [54] **LIQUID PROPELLANT FOR A GUN** 3,470,040 9/1969 Tarpley..... 149/74 X
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 3,888,159 6/1975 Elmore et al. 89/7

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[22] Filed: July 29, 1975

[21] Appl. No.: 600,016

- [52] U.S. Cl. 89/7; 149/74
 [51] Int. Cl.² F41F 1/04
 [58] Field of Search 149/74, 87; 89/7

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Primary Examiner—Edward A. Miller
Attorney, Agent, or Firm—J. Edward Hess; Donald R. Johnson; Anthony Potts, Jr.

[57] **ABSTRACT**

An improvement to a liquid propellant gun system wherein a hydrocarbon used in conjunction with nitric acid is predominantly the exo form of tetrahydrodicyclopentadiene and/or its methyl or dimethyl or ethyl derivatives or a mixture thereof. Other suitable hydrocarbons are as follows: a mixture of trans-syn-2-methyldecalin and trans-anti-1-methyldecalin, trans-perhydroacenaphthene and perhydrofluorene.

3 Claims, 2 Drawing Figures

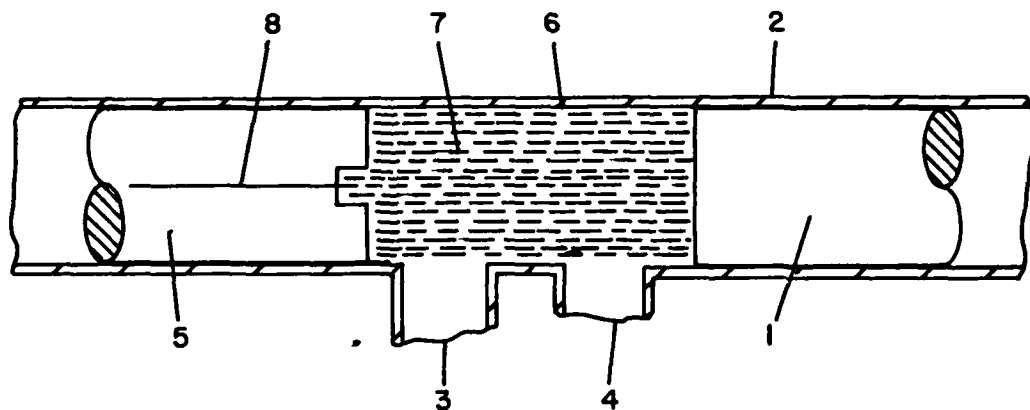


Fig. 1

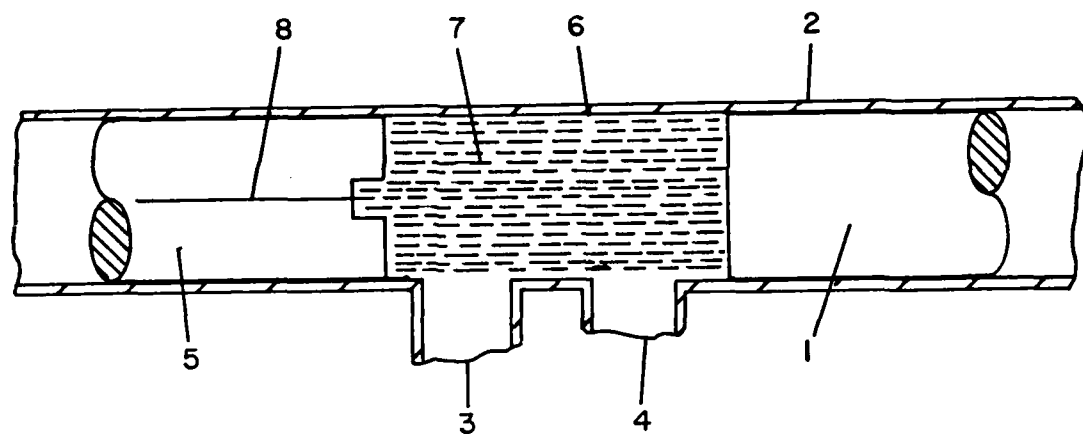
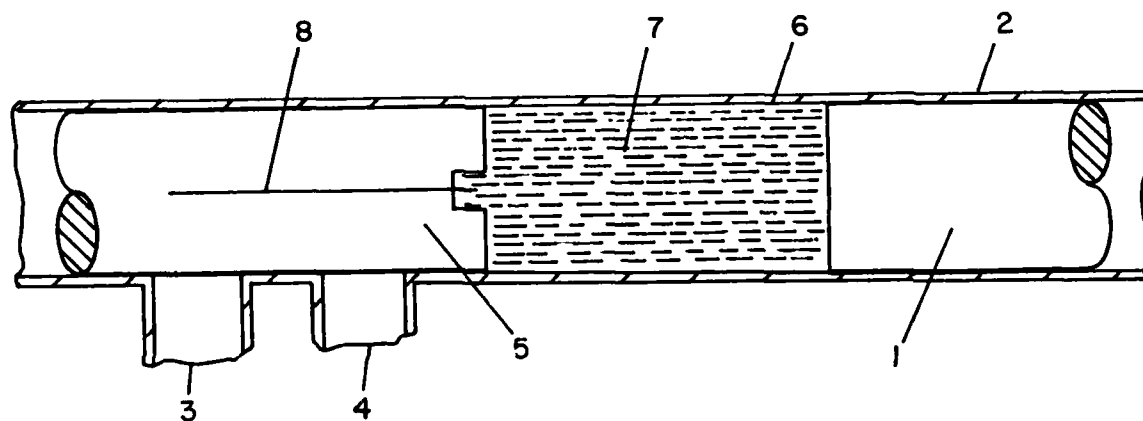


Fig. 2



LIQUID PROPELLANT FOR A GUN

BACKGROUND OF THE INVENTION

This invention is directed towards an improvement in a liquid propellant gun system. More particularly it is directed towards the liquid propellant used with such a system. It is directed toward the hydrocarbon used with other components of the liquid propellant.

In a liquid propellant gun, hereinafter referred to as LPG, system a liquid supplies energy to drive the projectile forward. This is in contrast to the solid, e.g., gunpowder, or nitrocellulose-based and other smokeless propellants used in a conventional gun. The liquid used in LPG is a combination of several components. Generally a liquid hydrocarbon and nitric acid are the components. Thus the combination can be referred to as bipropellant. Just prior to ignition, the bipropellant is an emulsion.

A LPG system generally operates as follows. The projectile is inserted in the barrel of a gun and its fit is such that it forms a liquid tight seal. A bolt and injection nozzle are located behind the projectile when it is in position. Nitric acid and hydrocarbon are simultaneously mixed and injected into the chamber, i.e., the space between projectile and the bolt. After the chamber is filled with the bipropellant, the bolt moves forward and seals the injection nozzle. A spark ignition device is used to generate a spark which ignites the bipropellant. The spark device can be located in the bolt or elsewhere.

Hydrocarbons such as n-octane have been tried and found not totally satisfactory. More recently a mixture of endo and exo tetrahydrodimethyldicyclopentadienes has been used. A mixture of the foregoing is often referred to as a TH-dimer. However, the TH-dimer has deficiencies. For example, TH-dimer upon mixing with aqueous nitric acid undergoes nitration at ambient temperature with evolution of considerable heat.

Surprisingly applicants have discovered that if, for example, the hydrocarbon used contains a majority of the exo form of several hydrocarbons the foregoing premature nitration problem does not exist. Also, other types of hydrocarbons were also found to be usable.

A method for preparing tetrahydrodicyclopentadienes is disclosed in U.S. Pat. No. 3,381,046, Apr. 30, 1968 and JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, Vol. 82, 1960, pages 4645-4651. Methods of preparation for the other hydrocarbons found suitable are known to those skilled in the art.

SUMMARY OF THE INVENTION

In a LPG system certain hydrocarbons and mixtures thereof have utility as the hydrocarbon portion of the bipropellant. These hydrocarbons are:

- a. exo-tetrahydrodicyclopentadiene,
- b. a mixture of a major amount of (a) and a minor amount of its endo form,
- c. exo-tetrahydrodimethyldicyclopentadiene,
- d. a mixture of a major amount of (c) and a minor amount of its endo form,
- e. exo-tetrahydromethyldicyclopentadiene,
- f. a mixture of a major amount of (e) and a minor amount of its endo form,
- g. exo-tetrahydroethyldicyclopentadiene,
- h. a mixture of a major amount of (g) and a minor amount of its endo form;

- i. a mixture of trans-syn-2-methyldecalin and trans-anti-1-methyldecalin;
- j. trans-perhydroacenaphthene;
- k. perhydrofluorene; and
- l. a mixture of any of the foregoing.

DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic drawing which shows the position of the various parts of a LPG system during the injection of the bipropellant.

FIG. 2 shows the LPG system after the injection of the bipropellant and just prior to the ignition of the bipropellant.

DESCRIPTION OF THE INVENTION

The way the LPG system generally operates is as follows. FIGS. 1 and 2 help describe the sequence of steps. The projectile 1 is placed in the barrel 2 and forced into its proper position. FIG. 1 shows the relative position of the projectile to the injection nozzles 3 and 4 and the bolt 5. Other relative positions are operative. Through nozzles 3 and 4 acid and hydrocarbon are separately injected into chamber 6. In this illustration only two nozzles are shown and the components are injected separately. Other alternatives are feasible; thus premixing of the acid and hydrocarbon would be operative. Also, more than two nozzles can be used, and other relative locations are permissible. In the chamber 6 the acid and hydrocarbon form an emulsion 7.

Once the chamber 6 is filled with emulsion 7 the bolt 5 moves forward and seals the nozzles 3 and 4. After the forward movement the LPG would be as shown in FIG. 2. An alternative would be that the bolt does not move forward but rather nozzles 3 and 4 are sealed by other mechanical means. The emulsion 7 is ignited by a spark ignition device 8 in the bolt. Location of the spark device elsewhere is feasible.

The bipropellant mixture used in the LPG system would contain nitric acid and hydrocarbon in a range of volume ratios of about 1.5 to about 5.0. The acid can contain at least about 70 weight percent nitric acid. The products of combustion would principally consist of nitrogen, hydrogen, oxygen, water, carbon dioxide and carbon monoxide.

At the present time a range of tentative specifications on the hydrocarbon used in a LPG system are as follows:

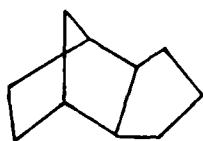
| | |
|--------------------|----------------------------|
| freezing point | -60°F to -40°F (Max) |
| viscosity at -40°F | 60 to 100 centipoise (Max) |
| flash point | 130°F to 140°F (Min) |

and stability towards aqueous nitric acid particularly in the aforementioned range.

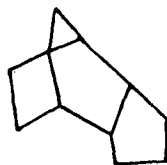
The applicants have found that the following hydrocarbons or certain hydrocarbon mixtures meet the foregoing specifications. The structures of these hydrocarbons are given hereinafter. The first structures shown are the tetrahydrodicyclopentadienes, the one to the left is the exo form. The characteristic of this form is that both the methylene bridge in the bicycloheptane system and the trimethylene ring attached thereto are oriented more or less in the same direction. Thus, as shown, both are pointed toward the top of the page. The form to the right is the endo form, here the methylene bridge and the trimethylene ring are oriented in the opposite direction. Thus, as shown the trimethylene ring is pointed toward the bottom of the

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page, the methylene bridge is pointed toward the top of the page.



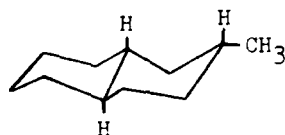
Exo



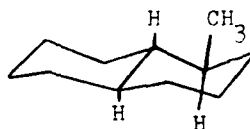
Endo

The methyl group of either exo or endo tetrahydromethylcyclopentadiene can be located generally anywhere on the ring; the same holds for the two methyls of the tetrahydrodimethylcyclopentadienes and the ethyl group of tetrahydroethylcyclopentadienes.

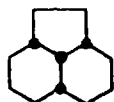
The structural formulas for the other suitable hydrocarbons are as follows:



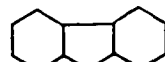
trans-syn-2-methyldecalin



trans-anti-1-methyldecalin



trans-perhydroacenaphthene



perhydrofluorene

For the perhydroacenaphthene the solid circles represent hydrogens which are facing the reader whereas the other circle represents a hydrogen facing on the other side. The perhydrofluorene formula includes several isomers.

The foregoing discussion mentions the exo and endo structure of a particular compound. The most preferable material would be the 100% exo form. However, because of economic considerations it might be advantageous to use less than 100%. Thus a mixture of exo and endo hydrocarbons wherein the exo form made up at least a majority (i.e., an excess of 50%) of the volume of the hydrocarbon would be operable. A more preferable material would contain at least 75% of the

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exo structure, a still more preferable material would contain at least 90% of the exo structure. The larger the content of exo structure the smaller is the tendency of the whole mixture to react with nitric acid prior to passage of the igniting spark.

The invention claimed is:

1. In a liquid propellant gun system wherein an emulsion of a liquid hydrocarbon and nitric acid is employed in the breech of a gun behind the projectile, the improvement comprises that the hydrocarbon is selected from the group consisting of

- a. exo-tetrahydrodicyclopentadiene;
- b. a mixture of a major amount of (a) and a minor amount of its endo form;
- c. exo-tetrahydrodimethylcyclopentadiene;
- d. a mixture of a major amount of (c) and a minor amount of its endo form;
- e. exo-tetrahydromethylcyclopentadiene;
- f. a mixture of a major amount of (e) and a minor amount of its endo form;
- g. exo-tetrahydroethylcyclopentadiene;

- h. a mixture of a major amount of (g) and a minor amount of its endo form;
- i. a mixture of trans-syn-2-methyldecalin and trans-anti-1-methyldecalin;
- j. trans-perhydroacenaphthene;
- k. perhydrofluorene; and
- l. a mixture of any of the foregoing.

2. Improvement according to claim 1 wherein the mixtures of exo and endo hydrocarbons contain at least 75% of the exo form.

3. Improvement according to claim 1 wherein the mixtures of exo and endo hydrocarbons contain at least 90% of the exo form.

* * * * *

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[54] **PROPELLANT FOR LIQUID PROPELLANT GUN**

[75] Inventor: Stanley E. Wood, Inyokern, Calif.

[73] Assignee: The United States of America as represented by the Secretary of the Navy, Washington, D.C.

[22] Filed: Dec. 11, 1974

[21] Appl. No.: 532,534

[52] U.S. Cl. 60/214; 60/211; 89/7; 149/74

[51] Int. Cl.² C06D 5/08

[58] Field of Search 89/7; 149/74; 60/211, 60/214

[56]

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| 2,563,532 | 8/1951 | Kistiakowsky | 149/74 X |
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| 3,031,839 | 5/1962 | Larson | 60/214 |
| 3,086,356 | 4/1963 | Craig et al. | 60/214 |
| 3,800,657 | 4/1974 | Broxholm et al. | 89/7 |
| 3,944,448 | 3/1976 | Marlowe | 149/74 X |

Primary Examiner—Edward A. Miller

Attorney, Agent, or Firm—R. S. Sciascia; Roy Miller; L. E. K. Pohl

[57]

ABSTRACT

Nitric acid and n-octane are injected into a gun and utilized to propel projectiles.

3 Claims, No Drawings

PROPELLANT FOR LIQUID PROPELLANT GUN BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to propellants for liquid propellant guns.

2. Description of the Prior Art

The military is, at the present time, experimenting with what are commonly called liquid propellant guns or, still more commonly, LPG's. A liquid propellant gun (LPG) is one which utilizes, instead of the usual solid powder and primer propulsion means, a liquid propulsion means. The potential advantages of such a gun over presently used guns are many. One advantage is that brass cartridges are not used. This eliminates storage and policing up problems. Another advantage resides in the probability that greater muzzle velocities can be achieved with LPG's than are presently possible with conventional guns. Still other potential advantages exist. However, this invention resides in a propellant for a liquid propellant gun and not in a liquid propellant gun per se so these further potential advantages will not be gone into here.

One method for firing a liquid propellant gun is to inject two liquid chemical components into a chamber behind the projectile and apply a spark to cause the two liquid components to combust and produce gases which, in turn, propel the projectile. (This, with the exception that both components are liquids, is very similar to the way in which an automobile is propelled by injecting gasoline and air and subjecting them to a spark behind a piston.)

When two liquids are injected to fire a LPG, they are injected from separate containers into the gun chamber. When they come together, in the gun chamber, they must not react spontaneously. That is, they must mix and wait until a spark is applied before reacting.

SUMMARY OF THE INVENTION

It has been found that red fuming nitric acid and various solutions of nitric acid and water in combination with n-octane can be utilized as propellants for liquid propellant guns. A nitric acid component and a n-octane component may be simultaneously injected into a gun chamber and ignited by means of a spark but do not react spontaneously (without sparking).

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The term nitric acid component may be taken, insofar as this invention is concerned, to mean red fuming nitric acid or nitric acid-water solution containing nitric acid in the range of from 98 to 82 weight percent and, correspondingly, water in the range of from 2 to

18 Weight percent. Red fuming nitric acid is nitric acid which contains dissolved nitrogen dioxide and a small amount of water (about 1 to 2 weight percent). According to this invention, the nitric acid components, whether it be red fuming nitric acid or a nitric acid-water solution encompassed by the above weight percentage ranges, may contain on the order of 1 weight percent of hydrofluoric acid. Hydrofluoric acid is a corrosion inhibitor. Experiments have shown that the nitric acid component works equally well with or without it.

The fuel, according to this invention is n-octane. In many test shots, both with experimental single shot liquid propellant guns and with experimental multi-shot liquid propellant guns, it has been demonstrated that a nitric acid component and n-octane may be safely simultaneously injected, from separate containers, into a gun chamber and ignited by means of a spark. By the term safely, it is meant that a nitric acid component and n-octane will not react spontaneously, i.e., without means of a spark, when they are simultaneously injected into a gun chamber.

Test shots have been conducted with as many as five parts by volume of the nitric acid component to one part by volume of n-octane to as few as two parts by volume of the nitric acid component to one part by volume of n-octane; all with good results. The preferred volume to volume ratio appears to be on the order of four parts of the nitric acid component to one part n-octane.

Going once again to the nitric acid component, the preferred component is one which has from about 90 weight percent nitric acid and about 10 weight percent water to about 82 weight percent nitric acid and about 18 weight percent water. The reason for this preference is that nitric acid-water solutions in this weight percentage range have a longer shelf life than do those with higher weight percentages of nitric acid.

What is claimed is:

1. In a method for propelling a projectile from a gun wherein two liquid chemical components are injected into a chamber behind the projectile and spark ignited to produce gases which propel the projectile, the improvement residing in utilizing, as one of the components, n-octane and, as the other component, a nitric acid component selected from the group consisting of red fuming nitric acid and nitric acid-water solutions containing from 98 to 82 weight percent nitric acid and 2 to 18 weight percent water.

2. A method according to claim 1 wherein about 2 to about 5 parts by volume of the nitric acid component are injected for every 1 part by volume of n-octane.

3. A method according to claim 2 wherein the nitric acid component contains, additionally, about 1 weight percent hydrofluoric acid.

* * * * *

United States Patent [19]

Breslow

[11]

4,094,713

[45]

June 13, 1978

[54] SENSITIZING LIQUID EXPLOSIVES WITH
HIGH GAMMA GAS

[75] Inventor: B. Arthur Breslow, Ridgecrest, Calif.

[73] Assignee: The United States of America as
represented by the Secretary of the
Navy, Washington, D.C.

[21] Appl. No.: 761,189

[22] Filed: Jan. 21, 1977

[51] Int. Cl.² C06B 47/08

[52] U.S. Cl. 149/36; 149/2;
149/46; 149/88; 149/101

[58] Field of Search 149/2, 36, 46, 88, 101

[56]

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| 3,797,392 | 3/1974 | Eckels | 149/2 |
| 4,008,108 | 2/1977 | Chrisp | 149/2 |

Primary Examiner—Edward A. Miller

Attorney, Agent, or Firm—R. S. Sciascia; Roy Miller;
Lloyd E. K. Pohl

[57]

ABSTRACT

Bubbles of high gamma gas are incorporated into the liquid component of a liquid or slurried explosive to sensitize the explosive.

16 Claims, No Drawings

SENSITIZING LIQUID EXPLOSIVES WITH HIGH GAMMA GAS

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to the sensitization of explosive compositions.

2. Description of the Prior Art

When a liquid explosive is to be transported on a truck or train or the like, it usually must be desensitized. That is, it usually must be treated in some manner whereby it is made safe for transportation. When a slurried explosive is to be transported on a truck or train or the like it must be in a desensitized condition wherein the sensitizers have not yet been added. Inadvertent explosions are highly undesirable to say the least.

On the other hand, when such an explosive, whether it be liquid or slurried, is to be detonated it is undesirable to have it desensitized. At this time, easy detonation is desirable—not undesirable.

It is common practice to obtain a desensitizing agent, mix it with or dissolve it in a liquid explosive when the explosive is to be transported and then separate it from the explosive just before the explosive is to be detonated. For example, alcohol is commonly mixed with nitroglycerine for desensitization purposes and then removed just prior to use of the nitroglycerine in propellant processing. Slurried explosives are mixed at the point of usage in order to add the sensitizers. For example a large tank truck of slurried explosive ingredients will be pumped into a blasting hole via a pump track wherein the sensitizer ingredients are metered into the flow line. These practices are cumbersome and time-consuming. It would be desirable to avoid the necessity for the practices altogether but, unfortunately, no one has yet devised a way whereby the use of desensitizing agents in conjunction with highly sensitive liquids can be avoided if the liquids are to be transported and, additionally, the on sight sensitization of slurried explosives goes on. Accordingly, the next best thing would be to avoid the necessity for removing desensitizing agents from liquid explosives and, additionally, it would be advantageous to provide a simple means for sensitizing liquids which are explosive but are naturally hard to detonate, i.e., liquids which need no desensitizing agents and to provide a similar means for sensitizing slurried explosives. (Note that, according to this invention, liquids which require no desensitizing agents are equated with slurried explosives which also need no desensitizing agents.)

SUMMARY OF THE INVENTION

According to this invention, the necessity for removing a desensitizing agent from a liquid explosive prior to detonation of the explosive is removed by dispersing bubbles of a high gamma gas in the explosive just prior to detonation. The high gamma gas sensitizes the explosive and overcomes the effect of any desensitizing agent present. Such a gas may also be used to sensitize liquid explosives which contain no desensitizing agent, i.e., liquids which lack sensitivity and further, may be used to sensitize slurried explosives.

DESCRIPTION OF THE PREFERRED EMBODIMENT

The mechanical aspect of this invention may be practiced by utilizing any known technique for dispersing a

gaseous material into a liquid at a desirable time. That is, those skilled in the mechanical arts will be quite capable of providing a gas containing a high gamma gas, providing the container with proper tubing leading from it into a manifolded container containing a liquid or slurried explosive to be sensitized and providing for the metering of gas into the explosive in a desirable amount at a desirable time. Therefore, no great detail is needed to enable one skilled in the art to practice the mechanical aspect of the invention.

As indicated above, a high gamma gas is used as the sensitizing material. The term gamma as used herein means the ratio of specific heat at constant pressure (Cp) to specific heat at constant volume (Cv). The term high means 1.6 or greater. Among gases which have gammas of 1.6 or greater are such well known gases as argon, krypton and helium.

To practice this invention, bubbles of high gamma gas are dispersed in the explosive, preferably just prior to use. This is true whether the explosive is a desensitized liquid, a non-desensitized liquid or a slurry.

High gamma gas bubbles will further sensitize an already highly sensitive liquid such as n-propyl nitrate. Additionally, high gamma gas will sensitize a mixture or solution of n-propyl nitrate and a desensitizing agent by overcoming the effect of the desensitizing agent.

High gamma gas will overcome the desensitizing effect of alcohol in nitroglycerine. It will also sensitize nitroglycerine. It will also sensitize nitroglycerine which contains no desensitizing agent.

High gamma gas will sensitize a slurry such as a slurry of ammonium nitrate, water and aluminum powder and other similar slurried explosives.

High gamma will sensitize a relatively insensitive composition such as a hydrazine-hydrazine nitrate composition. And, of course, it will sensitize hydrazine which is highly sensitive.

To be most effective, it is preferred that at least 1 volume percent of the composition be high gamma gas bubbles when the composition is ready for detonation. Up to 5 volume percent or more may be high gamma gas bubbles.

It is theorized that, when the gas in the bubbles is acted on by pressure produced by an initiator, the gas temperature is greatly increased and the hot gas decomposes surrounding liquid assisting the explosion to occur. The gas in any given gas bubble will not, of course, be entirely high gamma gas. It is practically impossible to keep gases such as oxygen and nitrogen from being present in liquids and such gases will naturally make up a portion of any bubble formed in the liquid. However, it is not necessary that the bubbles contain only high gamma gas. Bubbles need only contain a substantially large amount of suitable gas.

What is claimed is:

1. A method for sensitizing a liquid explosive that has a desensitizing agent added, said method comprising the steps of:

A. providing a high gamma gas, bubbles of which are capable of overcoming the effect of said desensitizing agent and

B. bubbling said high gamma gas into said explosive.

2. A method according to claim 1 wherein said liquid explosive that has a desensitizing agent added is a solution of n-propyl nitrate and a desensitizing agent.

3. A method according to claim 1 wherein said liquid explosive is nitroglycerine and wherein said desensitizing agent is alcohol.

4. A method according to claim 1 wherein said liquid explosive that has a desensitizing agent added is a hydrazine-hydrazine nitrate composition.

5. A method according to claim 2 wherein said high gamma gas is selected from the group consisting of argon, krypton and helium.

6. A method according to claim 3 wherein said high gamma gas is selected from the group consisting of argon, krypton and helium.

7. A method according to claim 4 wherein said high gamma gas is selected from the group consisting of argon, krypton and helium.

8. A method according to claim 5 wherein enough of said high gamma gas is bubbled into said explosive to make up from about 1 to about 5 volume percent of the total composition.

9. A method according to claim 6 wherein enough of said high gamma gas is bubbled into said explosive to make up from about 1 to about 5 volume percent of the total composition.

10. A method according to claim 7 wherein enough of said high gamma gas is bubbled into said explosive to

make up from about 1 to about 5 volume percent of the total composition.

11. A sensitized explosive composition consisting essentially of n-propyl nitrate, a desensitizing agent and bubbles of a high gamma gas.

12. A sensitized explosive composition consisting essentially of nitroglycerine, alcohol and bubbles of a high gamma gas.

13. A sensitized explosive composition consisting essentially of hydrazine, hydrazine nitrate and bubbles of high gamma gas.

14. A composition according to claim 11 wherein said high gamma gas is selected from the group consisting of argon, krypton and helium.

15. A composition according to claim 12 wherein said high gamma gas is selected from the group consisting of argon, krypton and helium.

16. A composition according to claim 13 wherein said high gamma gas is selected from the group consisting of argon, krypton and helium.

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THE BDM CORPORATION

THIOKOL CORPORATION PATENTS

Patent Number: 2,970,899
Author: D. W. Ryker
Title: Ammunition Propellant
Date: February 7, 1961

Patent Number: 3,749,615
Author: E. G. Dorsey, Jr., et al
Title: Gun Ammunition Composed of Encapsulated Monopropellants
Date: July 31, 1973

Patent Number: 3,921,394
Author: Stanley Tannenbaum, Morristown, NJ
Title: Heterogeneous Monopropellant Compositions and Thrust Producing Method
Date: November 25, 1975

Patent Number: 4,090,895
Author: Edward Outten, Rockaway, NJ
Title: High Energy Fuel Slurry
Date: May 23, 1978

Feb. 7, 1961

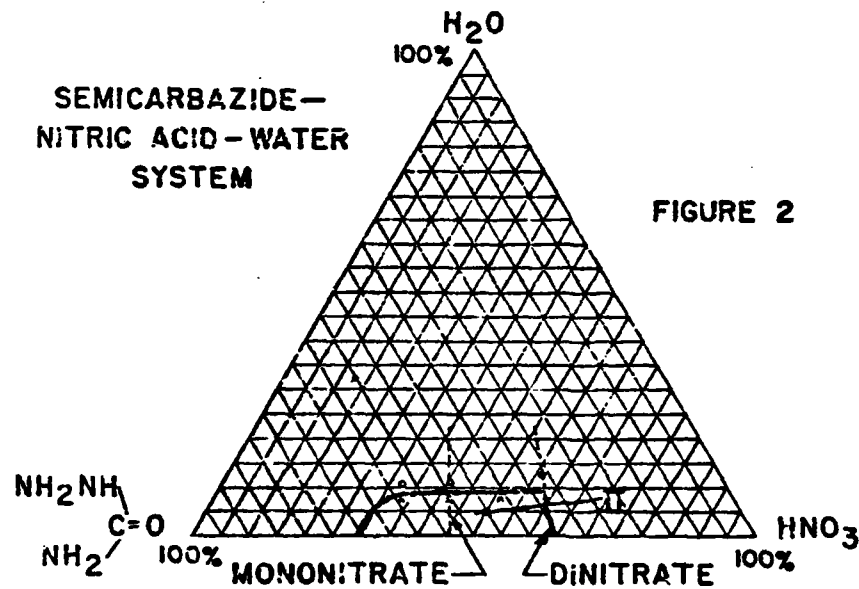
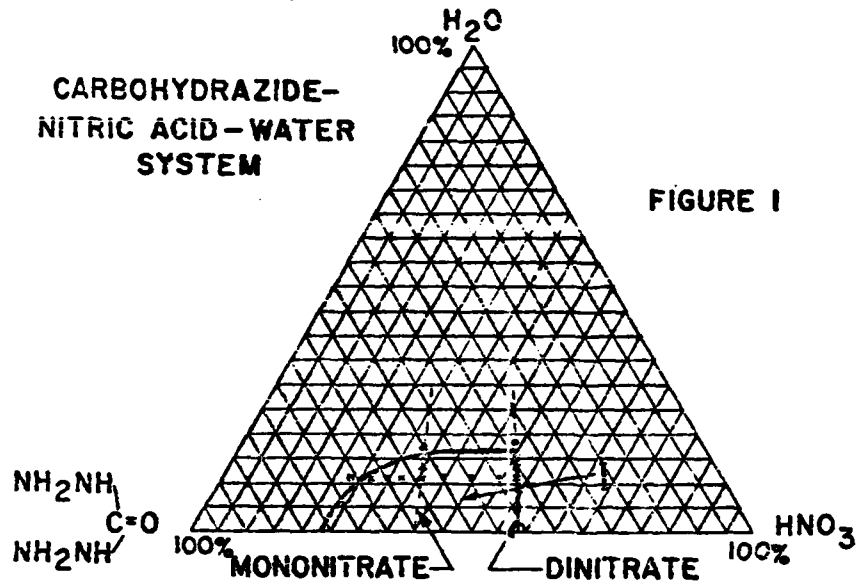
D. W. RYKER

2,970,890

AMMUNITION PROPELLANT

Filed Sept. 29, 1955

3 Sheets-Sheet 1



FIRING RESULTS

- 1 CC CHARGES
- NO FIRE
- x FIRE
- SOLID

INVENTOR
DON W. RYKER
BY *Stephen M. Stein*
ATTORNEY

Feb. 7, 1961

D. W. RYKER

2,970,899

AMMUNITION PROPELLANT

Filed Sept. 28, 1958

3 Sheets-Sheet 2

EFFECT OF CHARGE VOLUME ON CHAMBER PRESSURE

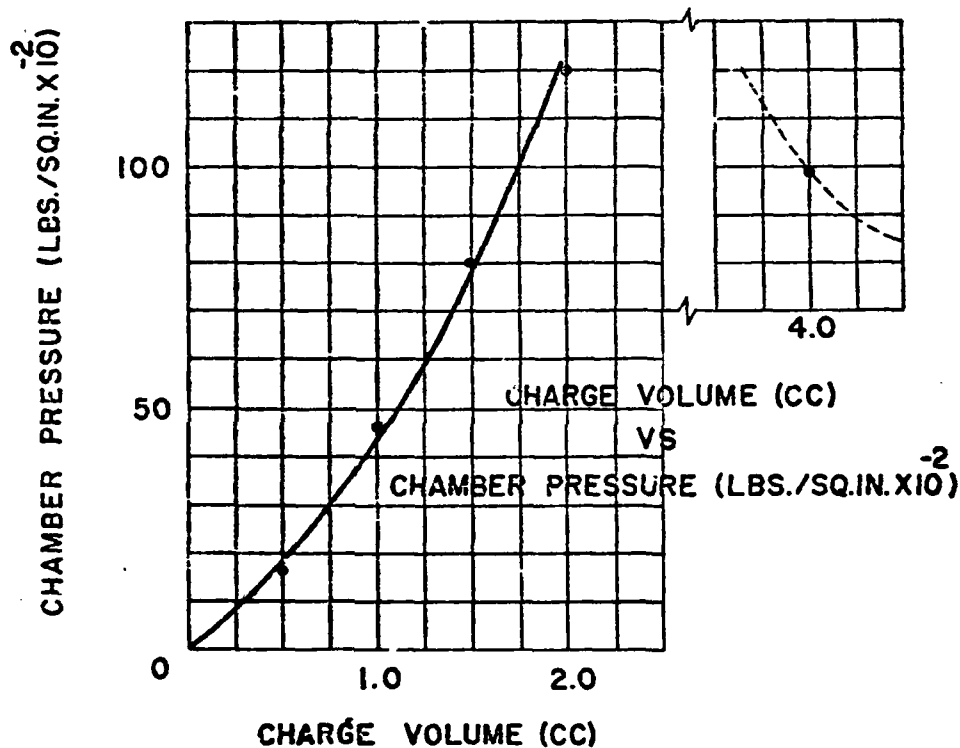


FIGURE 3

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2,970,899

AMMUNITION PROPELLANT

Filed Sept. 28, 1965

3 Sheets-Sheet 3

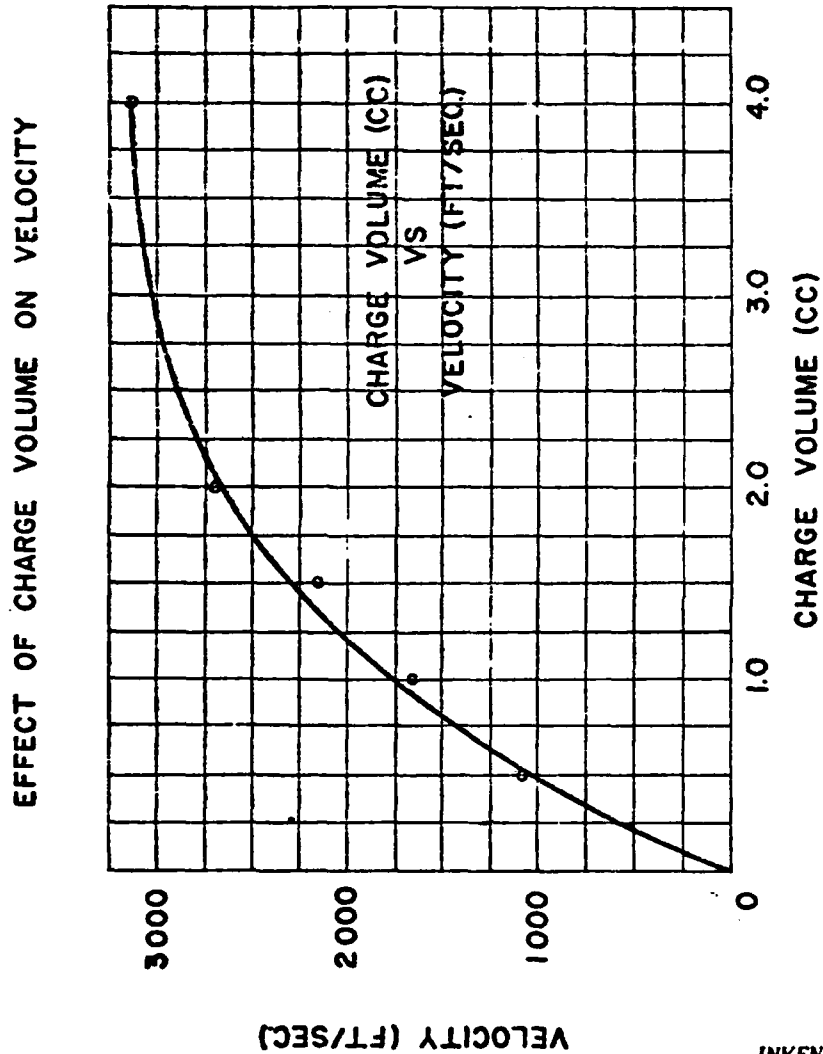


FIGURE 4

VELOCITY (FT/SEC)

INVENTOR

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BY

Stephen M. Stein
ATTORNEY

1

2,970,899

AMMUNITION PROPELLANT

Don W. Ryker, Woodbridge, Conn., assignor to Olin Mathieson Chemical Corporation, New Haven, Conn., a corporation of Virginia

Filed Sept. 28, 1955, Ser. No. 537,151

6 Claims. (Cl. 52-1)

This invention relates to a propellant and more particularly to a liquid propellant.

The recent trend in propellants for use in the ammunition field has been directed toward those of the liquid type. Liquid propellants are favored because they are easy to store, do not require grain formation, are easily loaded and dispensed and can be used in such manner to utilize substantially all of their potential. There are many known liquid propellants. However all of these are not useful for use in ammunition because they are either unstable, sensitive, brisant, too slow or too fast burning or of an undesirable low or high potential.

An object of this invention is to provide a novel class of liquid propellants. Another object of this invention is to provide a method for making this novel class of liquid propellants. A further object of this invention is to provide compositions utilizing this novel class of liquid propellants useful for ammunition. And a further object of this invention is to provide liquid propellant compositions that are stable, insensitive and slow burning. Other objects will become apparent to those skilled in the art upon reading the following detailed disclosure and description, with accompanying drawings in which

Figure 1 is a graph illustrating the desirable range of mixtures of carbonylhydrazide-nitric acid-water particularly useful as propellants.

Figure 2 is a graph showing the desirable range of mixtures of semicarbazide-nitric acid-water particularly useful as propellants.

Figure 3 is a graph showing the effect of charge volume of the carbonylhydrazide nitrate of Figure 1 on chamber pressure, and

Figure 4 is a graph showing the effect of charge volume of the carbonylhydrazide nitrate of Figure 1 on velocity.

Broadly, the objects of this invention are accomplished by the use of carbonylhydrazide and/or semicarbazide-nitric acid-water mixtures with or without additives, such as urea, urea mono-nitrate, guanidine nitrate, methanol and benzene.

In one of its aspects the invention may be accomplished by providing a liquid propellant composition consisting essentially of a 100 part composition of about 34 to 64 parts by weight of a substance selected from the group consisting of semicarbazide and carbonylhydrazide, about 25 to 55 parts by weight nitric acid and about 7.5 to 16 parts by weight water.

A more thorough discussion of the method of making and using the propellants of this invention can be shown by reference to specific examples, illustrating preferred techniques.

EXAMPLE I.—SYNTHESIS OF CARBOHYDRAZIDE

Carbonylhydrazide is synthesized by the action of hydrazine on organic carbonates (see C. C. Clark, "Hydrazine," first edition, 1953, page 75, published by Mathieson Chemical Corporation, Baltimore, Maryland) according to the following equation:



For every mole of diethyl carbonate used, two moles plus some excess of hydrazine in the form of an 85% hydrazine hydrate solution is used. The mixture is heated and distilled until the temperature reaches about 120° C. The reaction is then allowed to cool to enable the carbo-

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hydrazide to crystallize. The crystals are filtered and dried. A yield of about 65-85% is obtained.

EXAMPLE II.—CARBOHYDRAZIDE-NITRIC ACID-WATER SYSTEM

The required quantities of carbonylhydrazide and concentrated nitric acid (70%) were mixed to form the desired ratio by slowly adding the nitric acid to the carbonylhydrazide. Heat and some slight vaporization of the water of the nitric acid occurred. The nitrate salts formed were clear, faintly yellow, viscous liquids.

A liquid reaction product made by use of equimolar quantities of the carbonylhydrazide and nitric acid was dehydrated by an extraction with ethyl alcohol and then dried over anhydrous magnesium perchlorate in a vacuum dessicator at 10 mm. pressure.

An analysis of the resultant "dried" solution of the mononitrate was performed using the Karl Fisher method and the xylene distillation method for water determination. The ethyl alcohol content was determined by distillation of the liquid salt product with water, oxidizing with dichromate and back titrating the dichromate with ferric sulfate. The purity of the salt was checked with a nitrate determination. The percentages of each ingredient were determined to be (by weight):

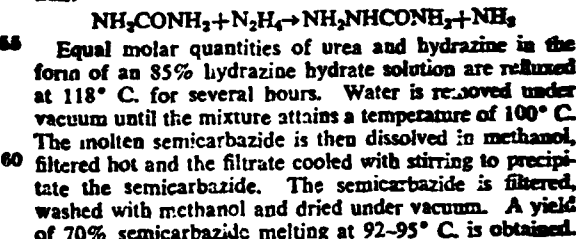
| | Percent |
|-------------------------------|---------|
| Carbonylhydrazide mononitrate | 87.1 |
| Water | 10.8 |
| Ethyl alcohol | 0.9 |

The properties of the mono and dinitrate of carbonylhydrazide in the liquid salt form are tabulated as follows:

| | Carbonylhydrazide Mononitrate | Carbonylhydrazide Dinitrate |
|--------------------|---|---|
| Impact Sensitivity | Insensitive to hammer blow. | Insensitive to hammer blow. |
| Detonability | Not detonated by small lead azide charge. | Partially detonated by small lead azide charge. |
| Flame Sensitivity | Ignited by high temperature flame. | Ignited by high temperature flame. |
| Solubility in: | | |
| Water | Miscible | Miscible |
| Ethyl alcohol | Immiscible | Immiscible |
| Methyl alcohol | Immiscible | Immiscible |
| Acetone | Reacts | Reacts |
| Benzene | Immiscible | Immiscible |
| 90% Hydrazine | Heat evolution | Heat evolution, bubbling. |

EXAMPLE III.—SYNTHESIS OF SEMICARBAZIDE

Semicarbazide may be synthesized by various techniques as disclosed in C. C. Clark, "Hydrazine," first edition, 1953, pages 59-61, published by the Mathieson Chemical Corporation, Baltimore, Maryland. The method here used involves the refluxing of urea and hydrazine hydrate in amyl alcohol according to the following equation:



EXAMPLE IV.—SEMICARBAZIDE-NITRIC ACID-WATER SYSTEM

The required quantities of semicarbazide and concentrated nitric acid (70%) were mixed to form the desired ratio by slowly adding the nitric acid to the semicarbazide. Heat and slight vaporization of the water of the nitric acid occurred. The nitrate salts formed were clear, faintly green, viscous liquids.

An aqueous salt mixture made by use of equimolar quantities of the semicarbazide and nitric acid was concentrated by an extraction with ethyl alcohol. A similar analysis as performed on the carbonylhydrazide nitrate mixture of Example II was performed on the semicarbazide nitrate mixture and gave the following result: (by weight):

| | Percent |
|---------------------------|---------|
| Semicarbazide mononitrate | 92.0 |
| Water | 7.5 |
| Ethyl alcohol | 0.7 |

These systems were subjected to ballistic tests in their aqueous solution form with or without additives.

Table II.—Ballistic tests
SEMICARBAZIDE-NITRIC ACID-WATER SYSTEM

| System (by weight) | | | Charge (cc.) | Velocity, ft./sec. | Pressure, lbs./sq. in. |
|----------------------------|-------------|-------|--------------|--------------------|------------------------|
| Semicarbazide | Nitric Acid | Water | | | |
| IMR ¹ (control) | | | 50 gr. | 2,600 | 49,000 |
| 57.9 | 34.0 | 7.5 | 2 | 1,827 | 38,000 |
| 49.3 | 41.2 | 9.0 | 2 | 1,823 | 34,300 |
| 40.9 | 48.8 | 10.6 | 2 | 2,014 | 44,800 |
| 32.6 | 54.8 | 12.0 | 2 | 1,883 | 42,800 |

¹ Nitrocellulose 88.3%, dinitrotoluene 8.8%, K₂SO₄ 0.6%, diphenylamine 0.6%.

Table III.—Ballistic tests
CARBOHYDRAZIDE AND SEMICARBAZIDE-NITRIC ACID-WATER SYSTEM

| System (by weight) | | | | Charge (cc.) | Velocity, ft./sec. | Pressure, lbs./sq. in. |
|----------------------------|---------------|-------------|-------|--------------|--------------------|------------------------|
| Carbohydrazide | Semicarbazide | Nitric Acid | Water | | | |
| IMR ¹ (control) | | | | 50 gr. | 2,600 | 49,000 |
| 51.6 | 1.3 | 35.5 | 10.6 | 2 | 1,751 | 43,900 |
| 50.5 | 4.6 | 33.7 | 10.3 | 2 | 1,770 | 30,700 |
| 50.2 | 2.7 | 35.6 | 13.5 | 2 | 1,802 | 33,250 |
| 49.4 | 3.4 | 36.7 | 10.6 | 2 | 1,843 | 34,500 |
| 49.4 | 6.7 | 33.0 | 10.1 | 2 | 1,792 | 32,900 |
| 48.2 | 8.1 | 32.1 | 9.8 | 2 | 1,794 | 22,400 |
| 48.0 | 4.6 | 35.9 | 10.5 | 2 | 1,919 | 29,900 |
| 1.4 | 48.7 | 41.7 | 7.5 | 2 | 1,870 | 55,100 |
| 2.4 | 47.8 | 41.5 | 7.7 | 2 | 1,871 | 52,300 |
| 3.9 | 46.3 | 41.3 | 7.7 | 2 | 1,826 | 58,100 |
| 8.8 | 44.9 | 41.1 | 7.9 | 2 | 1,852 | 51,000 |

¹ Nitrocellulose 88.3%, dinitrotoluene 8.8%, K₂SO₄ 0.6%, diphenylamine 0.6%.

Ballistic tests

Test firings using a carbonylhydrazide or semicarbazide-nitric acid-water system made by the technique of Examples II and IV were made using a commercially available brass cartridge case (Super X 30-06 caliber) with a centerfire primer (Type 257W) (both manufactured by the Western Cartridge or Winchester Repeating Arms Plants of the Olin Mathieson Chemical Corporation of New Haven, Connecticut). Before loading, the flash hole leading from the primer into the main cavity of the cartridge was covered with a polyethylene disc prior to seating the primer.

Tabulations of the ballistic tests performed for each system are given in Tables I, II and III.

Table I.—Ballistic tests

CARBOHYDRAZIDE-NITRIC ACID-WATER SYSTEM

| System (by weight) | | | Charge (cc.) | Velocity, ft./sec. | Pressure, lbs./sq. in. |
|----------------------------|-------------|-------|--------------|--------------------|------------------------|
| Carbohydrazide | Nitric Acid | Water | | | |
| IMR ¹ (control) | | | 50 gr. | 2,600 | 49,000 |
| 51.5 | 36.5 | 10.8 | 2 | 1,714 | 48,200 |
| 50.1 | 35.9 | 13.0 | 2 | 1,782 | 35,200 |
| 49.6 | 35.5 | 14.0 | 2 | 1,791 | 41,500 |
| 56.0 | 23.6 | 9.5 | 2 | 1,754 | 46,700 |
| 50.0 | 31.8 | 8.4 | 2 | 1,655 | 45,000 |
| 61.7 | 29.6 | 7.9 | 2 | 1,620 | 44,600 |
| 48.2 | 39.5 | 10.5 | 2 | 1,871 | 18,200 |
| 43.8 | 43.8 | 11.6 | 2 | 1,855 | 38,800 |
| 36.9 | 47.6 | 12.6 | 2 | 1,906 | 60,600 |
| 35.6 | 50.3 | 13.4 | 2 | 1,929 | 58,300 |
| 34.7 | 49.0 | 15.6 | 2 | 1,941 | 66,700 |
| 34.0 | 48.1 | 17.2 | 2 | 1,735 | 45,000 |

¹ Nitrocellulose 88.3%, dinitrotoluene 8.8%, K₂SO₄ 0.6%, diphenylamine 0.6%.

The systems carbonylhydrazide-nitric acid-water and semicarbazide-nitric acid-water were further studied to determine the range of concentrations which gave no misfires under the conditions used. The liquids to be fired were prepared by adjusting ethyl alcohol-washed CMN or SMN with the desired amount of water. The amount of alcohol retained by the washed nitrate was less than 1%. Pressures and velocities were not measured during these firings. Results for 1 cc. charges are plotted on Figures 1 and 2. The area bounded by the black lines on each figure indicates the operable compositions.

In another series of tests under the same conditions the charge volume was varied from 0.5 cc. to 4 cc. of CMN and the pressure and velocity measured. Results are shown on Figures 3 and 4.

In attempting to dehydrate the carbonylhydrazide mononitrate by heating (165° C.), it was found that water was driven off. At the cessation of this water evolution, heating was discontinued. The distillate was opaque milky white and very viscous. Upon standing, it separated into two phases into a clear, colorless, viscous liquid and the white solid. It was found that the solid constituted about 18% of the total weight of the distillate. Repeated attempts at analyzing and classifying this substance were unsuccessful. It was assumed that the solid material was either a decomposition product or a product of molecular rearrangement or both.

The white solid behaved as a propellant. This was demonstrated by firing caliber .30 rounds with a charge containing the solid. Table IV shows the results.

Table IV.—Test of CMN dehydration product

| Propellant Composition | | Charge (cc.) | Velocity, ft./sec. | Pressure, lbs./sq. in. |
|--|----------------|--------------|--------------------|------------------------|
| Propellant | Water, percent | | | |
| Carbohydrazide mononitrate (CMN) | | | | |
| Carbohydrazide mononitrate—CMN Dehydration Product 1-1 | 10.8 | 1 | 1,404 | 43,100 |
| | | 1 | 1,532 | 47,000 |

The CMN dehydration product was found to be insensitive to the impact of a 2 kilogram weight dropped 80 centimeters. It could not be detonated with a #6 electric blasting cap.

The ballistic results shown above were varied to a more desirable range by adding certain additives to the carbonylhydrazide and/or semicarbazide-nitric acid-water system. The addition was carried out by adding the additive to the propellant system, mixing it and then loading cartridge cases with the proper amount of the mixture. A tabulation of the firing tests is seen in Table V.

Table V.—Ballistic tests

ADDITIVES TO CARBOHYDRAZIDE AND/OR SEMICARBAZIDE-NITRIC ACID-WATER SYSTEM

| System (by weight) | | | | Additives | Charge (cc.) | Velocity, ft./sec. | Pressure, lbs./sq. in. |
|--------------------|---------------|-------------|-------|-------------------|--------------|--------------------|------------------------|
| Carbonylhydrazide | Semicarbazide | Nitric Acid | Water | | | | |
| 100% (control) | | | | | 60 gr. | 2,000 | 49,000 |
| 51.5 | | 24.5 | 10.5 | Urea | 2.6 | 1,729 | 54,000 |
| 51.6 | | 24.5 | 10.5 | Urea mononitrate | 2.5 | 1,821 | 56,700 |
| 50.4 | | 24.6 | 10.3 | do | 4.8 | 1,755 | 52,700 |
| 49.2 | | 32.8 | 10.0 | do | 7.2 | 1,792 | 47,400 |
| 45.0 | | 32.0 | 9.9 | do | 9.3 | 1,850 | 58,100 |
| 51.5 | | 24.5 | 10.5 | Guanidine Nitrate | 2.7 | 1,805 | 56,300 |
| | 43.7 | 40.4 | 7.2 | do | 2.7 | 1,649 | 53,600 |
| 51.5 | | 35.7 | 10.8 | Benzene washed | 2 | 1,767 | 51,600 |
| | 50.5 | 42.5 | 7.5 | do | 2 | 1,756 | 49,400 |

: Nitrocellulose 88.3%, dinitrotoluene 8.8%, K_2SO_4 0.6%, diphenylamine 0.6%.

As seen in the data above the propellant compositions of this invention are aqueous solutions of carbonylhydrazide or semicarbazide mono or dinitrate or dehydration products or their mixtures with or without additives in trace to substantial quantities of the mixture. The additives may be semicarbazide, carbonylhydrazide, urea, urea mononitrate, guanidine nitrate, methanol and benzene. By "trace to substantial" quantities is meant anything within the range of 0.1% to 10% by weight. A "trace" quantity generally results from washing of the aqueous mixture with an additive.

While a detailed description of this invention has been provided, it is realized that those skilled in the art may make modifications in and adaptations of the propellant composition and its method of manufacture described herein without departing from the spirit and scope of this invention. It is, therefore, to be specifically understood that such obvious modifications are to be considered within the scope of the herein described propellant and method of manufacture.

The invention having thus been described what is to be secured by Letters Patent is as follows:

1. A liquid propellant composition consisting essentially of a 100 part composition of about 34 to 64 parts by weight of a substance selected from the group consisting of semicarbazide and carbonylhydrazide, about 25 to 55 parts by weight nitric acid and about 7.5 to 16 parts by weight water.

2. A liquid propellant composition consisting essentially of a carbonylhydrazide-nitric acid-water mixture as indicated by I of Figure 1 of the drawing.

3. A liquid propellant composition consisting essentially of a semicarbazide-nitric acid-water mixture as indicated by II of Figure 2 of the drawing.

4. The method of developing a projectile propelling pressure within an enclosed chamber which comprises inserting within said chamber a quantity of a composition made up of 100 parts, said composition consisting essentially of about 34 to 64 parts by weight of carbonylhydrazide about 25 to 55 parts by weight of nitric acid and 7.5 to 16 parts by weight of water, and locally igniting said mixture.

5. A method of developing a projectile propelling pressure within an enclosed chamber which comprises inserting within said chamber a composition made up of 100 parts, said composition containing as its essential ingredients about 34 to 64 parts by weight of a compound selected from the group consisting of semicarbazide and carbonylhydrazide, about 25 to 55 parts by weight of nitric acid and about 7.5 to 16 parts by weight of water and locally igniting said mixture.

6. A method of developing a projectile propelling pressure within an enclosed chamber which comprises inserting within said chamber a composition made up of 100 parts, said composition consisting essentially of 34 to 64 parts by weight of semicarbazide, about 25 to 55 parts by weight of nitric acid and about 7.5 to 16 parts by weight of water and locally igniting said mixture to cause a burning of the liquid composition therein.

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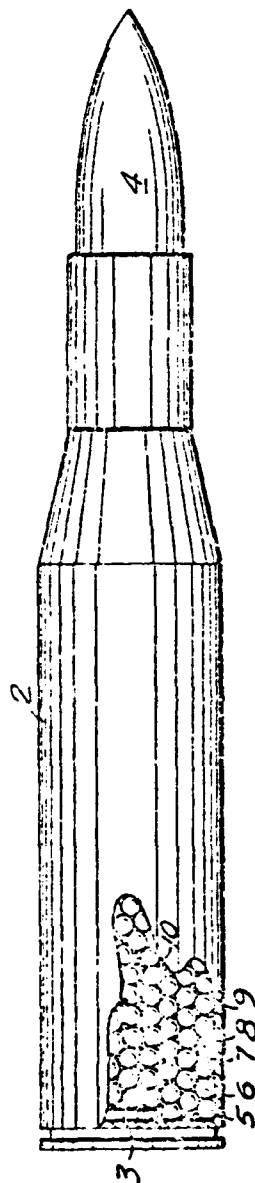
July 31, 1973

E. G. DORSEY, JR., ET AL

3,749,615

GUN AMMUNITION COMPOSED OF ENCAPSULATED MONOPROPELLANT

Filed June 11, 1971



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AGENT

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3,749,615

GUN AMMUNITION COMPOSED OF ENCAPSULATED MONOPROPELLANTS

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Int. Cl. C06d 5/08, 5/10

U.S. Cl. 149—6

11 Claims

ABSTRACT OF THE DISCLOSURE

Microcapsules of liquid monopropellants provide propellant charges for gun ammunition. A capsule wall material may be chosen that will contribute to the energy of the charge; and high loading density of propellant may be achieved by the use of capsules having carefully selected bimodal sizes.

BACKGROUND OF THE INVENTION

This invention relates to gun propellants, and particularly to those having encapsulated, liquid fuels. The invention herein described was made in the course of or under a contract with the U.S. Air Force.

Liquid propellants have characteristics that yield several advantages over conventional solid propellants in guns, such as low flame temperature, reduced smoke and flash, reduced fouling of gun parts, and longer tube life for the gun barrel. Rapid fire weapons, especially, have notoriously short barrel lives. These anticipated advantages prompted extensive experimentation wherein liquid monopropellants were loaded directly into cartridge cases, and variables such as ignition parameters, propellant compositions and geometric factors were systematically investigated. These experiments proved that the above advantages are indeed available in liquid propellants. Fouling of gun parts, production of smoke, and muzzle flash were reduced significantly. Also, bore erosion was greatly reduced because of the lower flame temperature and absence of erosive particles in liquid propellants.

However, instantaneous burning surface areas in bulk loaded liquid propellants are unpredictable. Modes such as Taylor instabilities, wherein surface irregularities may grow exponentially in the liquid, the Rayleigh instabilities, that result from the passage of gas bubbles through the liquid, have been predicted theoretically and verified experimentally. Such turbulences may cause high, erratic pressures accompanied by high frequency, high amplitude pressure excursions. This action damages guns, causes erratic behavior of gas operated automatic weapons, and produces variations in muzzle velocities. Although the fluid dynamics of the system wherein a liquid monopropellant is accelerated and consumed by its own combustion gases have been treated theoretically, the instabilities that characterize the process and the many variables that are not analytically tractable indicate that bulk liquid propellants cannot be easily controlled. Extensive experimentation has failed to solve this problem in use of bulk loaded, liquid propellants.

SUMMARY OF THE INVENTION

The present invention, which solves this difficulty in the use of liquid propellants in gun ammunition, is essentially the microencapsulation of liquid monopropellants, which may comprise propellant charges for gun ammunition.

Encapsulated liquid propellants containing two hypergolic components, such as a fuel and an oxidizer encapsu-

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lated in separate capsules, are taught in U.S. Pat. 2,960,935 to D. A. Colpitts. In this patent they are intended for use in rocket igniters. Large, elongated capsules are arranged geometrically in a tubular housing so that each capsule of fuel is adjacent a capsule of oxidizer. When an appropriately severe shock is applied, the capsules are ruptured and the hypergolic liquids are mixed. Although this invention is suitable for its intended use in rocket igniters, it would have a number of disadvantages as propellant for gun ammunition. Large capsules would individually produce the same erratic liquid burning surfaces that create unpredictable pressures in bulk loaded liquid propellants as described above. Although varying pressures are tolerable within limits in rocket igniters, they are very objectionable in gun ammunition, wherein the range and velocity of a projectile must be predictable with considerable precision. Also, the configuration and arrangement of the capsules of the Colpitts patent do not afford a sufficiently high loading density of propellant in the tubular housing to be useful in gun ammunition.

For these reasons, the present invention uses microcapsules, which may be used in sufficiently large numbers that their burning surfaces average out to produce predictable pressures and impart replicable velocities to the projectiles. Monopropellants are used in the present invention to insure uniform burning; since it would be virtually impossible to be certain that microcapsules containing two different propellant components are uniformly mixed in a cartridge case.

Greater propellant loading density is achieved in the present invention by the use of capsules of two different sizes, so that the smaller capsules tend to fill the interstices between the larger capsules. Other interstitial fills may be used for special applications.

U.S. Pat. 3,441,455 teaches encapsulation of solid propellant components and cites materials useful in the present invention. However, it is primarily concerned with preventing particles of solid, chemically active ingredients from reacting with the solid propellant matrix in which they are embedded. Hence, it does not suggest the primary features of the present invention, such as liquids, monopropellants, encapsulation for gun ammunition, or bimodal size distribution of the capsules.

Objects of the present invention are to provide a controlled means for using liquid propellants in gun ammunition, thereby realizing the benefits of low flame temperatures, smooth pressures, and absence of erosive particles; and to achieve maximum loading density of encapsulated liquid monopropellants in cartridge or shell cases. Important features of the invention are the general simplicity of the manufacturing process, and the use of monopropellants to eliminate the problem of uniform mixing that would be difficult if two or more components of propellant were encapsulated. Another important feature of the invention is that it can produce standard projectile velocities using conventional shell and gun equipment designs.

These and other objects and advantages of the invention, will become more apparent as the following detailed description of the invention is read with reference to the accompanying drawing.

BRIEF DESCRIPTION OF THE DRAWINGS

The accompanying figure is an enlarged side elevation of a typical rifle shell, with parts broken away to show the propellant of the invention installed therein. The propellant capsules are enlarged relative to the shell size to clarify the bimodal capsule size distribution.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The typical rifle shell shown in the figure comprises a tubular shell case 2, an explosive primer cap 3 in one end thereof, a projectile 4 held in the opposite end of the tubular case 2, and a propellant 5 in the shell case 2 between the primer cap 3 and the projectile 4. The propellant 5 comprises microcapsules 6, each having a capsule wall 7 filled with a monopropellant 8. Interstices 9 between the capsules 6 are filled with interstitial fill material, which in a preferred embodiment of the invention comprises smaller capsules 10 of the same type as the capsules 6.

In the present invention, a preferred monopropellant is in general selected from the alkyl nitrates. Specifically useful is a mixture by weight of 60% ethyl nitrate and 40% normal propyl nitrate. For specific purposes, however, virtually any liquid monopropellant could be used. Other monopropellants that are especially useful are hydrazines and nitromethanes.

It has been found that some advantages in handling and storage life of the resulting propellants may be realized by gelling the monopropellants. Inclusion of approximately 3 to 10% of high molecular weight polyethylene glycol, together with a small amount of curing and cross-linking agents (e.g., toluene diisocyanate and a small amount of benzyl dimethylamine), produces very satisfactory gels when mixed with the alkyl nitrates. Low molecular weight polyethylene glycols have been found not only to produce gels, but also, within limits, they can be used to adjust the burning rates of the monopropellants.

The capsule walls are made of a mixture of a polyvinyl alcohol dissolved in water, carrageenin, and optionally a curing agent such as tris (hydroxymethyl) nitromethane.

The encapsulation process is well known and is not considered to be a part of the present invention. However, two types of equipment were used to prepare the capsules of the present invention.

A centrifugal extrusion device used in the present invention consisted of a rotating head with concentric orifice nozzles directed radially outward from the axis of rotation. Monopropellant pumped into the inner chamber flowed through tubes in the orifices in the periphery of the head, the tubes being smaller than the orifices so that a small annulus of space surrounded each tube. The shell material, in fluid form, was gear pumped into the head and flowed through the annuli. In effect, this extruded rods of fluid monopropellant encased in sheaths of fluid shell material. These rods broke into individual capsules when being projected to a collection area surrounding the base of the encapsulation apparatus. The extrusion head was about seven feet above the collection area, and the capsules were sufficiently firm that they did not rupture on reaching the collection sheet.

The encapsulation head, shell material lines, and pump were all heated to about 50° to 60° C. to insure fluidity of the carrageenin, which, though quite fluid when warm, forms a firm gel when cool. Without the carrageenin, higher temperatures and increased amounts of polyvinyl alcohol would be necessary and poor ratios of monopropellant to shell material would result.

This apparatus was used to prepare the larger capsules of the bimodal capsule-size system. The larger capsules ranged in diameter size from about 840 to about 1500 microns, although capsules as large as 2000 microns in diameter were successfully made. The larger capsules were deliberately kept in the microcapsule ranges to promote predictable and controllable burning surfaces of the monopropellants.

The smaller capsules of the bimodal system generally ranged in size from about 50 to about 400 microns in diameter, although some capsules as small as 10 microns in diameter were produced. These smaller capsules were

made by a second apparatus, also well known as an encapsulation device. These capsules were prepared by gravity feeding an emulsion of alkyl nitrate in an aqueous polymer solution onto the center of a three inch diameter, high speed, air driven, rotating disk. Very small emulsion droplets were projected from the periphery of the disk and fell two feet to a collection area. The resulting small capsules were gelled and almost dry when collected. As in the case of the centrifugal extrusion apparatus, the capsules were collected on a polyethylene film. After collection the capsules were transferred to a fluidized bed for final drying and removal of the starch (which was used to coat the collection film).

The resulting propellant was found to comprise approximately 86.8% monopropellant and about 13.2% capsule wall material. Volumetric loading of the monopropellant was enhanced further by removing the empty and partially filled capsules. This was done by pouring the capsules into a bath of ethyl-propyl nitrate (in which they are insoluble) and skimming off the empty and partially filled capsules that floated to the surface. The remaining capsules were then removed from the bath and dried. An average increase in projectile velocity of 146 feet per second was realized by this procedure.

Other interstitial fill materials may be used instead of the smaller capsules to fill the interstices between the larger capsules. By this means, the total energy of the propellant may also be adjusted as desired. Examples of such interstitial fill material that were used successfully for this purpose are baled smokeless powder of the type used in conventional ammunition, granular nitrocellulose, and granular ammonium nitrate.

The energy of the capsule wall material was optionally enhanced by inclusion therein of up to 14% by weight of nitrocellulose. Alternatively, good results were obtained by spraying the completed capsules with a nitrocellulose solution. This solution was prepared by mixing, in percentages by weight: butyl acetate 50%, isopropyl alcohol 40%, ethyl cellulose 8%, and dioctyl phthalate 2%.

Optimum relative proportions of large to small capsules to achieve maximal loading of propellant per volume is, of course, dependent on the sizes of the capsules. However, this desirable condition is approximated with the capsule size range cited above if the mixture of capsules contains from about 60% to about 70% of the larger capsules. Using specific capsule diameter sizes of 1000 microns and 50 microns, optimal loading can be achieved by a 67.5% and 32.5% loading, respectively.

The following specific examples illustrate preparation of monopropellants and capsule wall compositions.

Example I

A gelled monopropellant was prepared by mixing, in parts by weight, 40 parts of ethyl nitrate, 40 parts of normal propyl nitrate, 18.6 parts of polyethylene glycol (Carbowax 6000), 3 parts of ethyl cellulose (N-300) dissolved in normal propyl nitrate, 0.7 part of toluene diisocyanate (Hylene TM), and one drop of benzyl dimethylamine per 25 ml. of the mixture. This mixture was thoroughly stirred and was allowed to stand at room temperature for 24 hours. A firm gel was formed in that length of time, and almost no free liquid was observed after two weeks.

Example II

Capsule shell material was prepared by mixing a solution in parts by weight, 91.6 parts of water, 7.5 parts of polyvinyl alcohol (Elvanol 46-22), and 0.9 part of carrageenin (Carrageenin HWG). After thorough mixing, this solution was used for the capsule wall material and capsules of monopropellant were formed as described above with very good results.

Example III

Another shell material was prepared by mixing a solution, in parts by weight, of 90.6 parts of water, 7.5 parts of polyvinyl alcohol (Elvanol 46-22), 0.9 part of carrageenin (Carrageenin HWG), and one part of tris (hydroxymethyl) nitromethane. After thorough mixing, this solution was used for capsule wall material as described above. Although satisfactory, somewhat more breakage of the resulting capsules was observed than in the preceding example.

Other materials, such as gelatin, were used with moderate success for the basic encapsulation material.

An invention has been described that constitutes an advance in the art of gun ammunition; and, although the preferred embodiments have been described with considerable specificity with regard to detail, it should be noted that such details may be altered somewhat without departing from the scope of the invention as defined in the following claims.

The invention claimed is:

1. Propellant for gun ammunition comprising capsules of liquid monopropellant smaller than 2,000 microns in diameter, wherein the monopropellant is selected from the group consisting of alkyl nitrates, hydrazines, and nitromethanes and wherein the capsule wall is a cured mixture of water, polyvinyl alcohol and carrageenin.

2. The propellant of claim 1 wherein the capsules are of two diameter sizes uniformly mixed, the larger ranging from about 840 to about 1500 microns and the smaller ranging from about 50 to about 400 microns, and the larger capsules comprising from about 60% to about 70% by weight of the mixture, whereby the smaller capsules may fill interstices between the larger capsules to achieve maximal density of propellant per volume.

3. The propellant of claim 1 wherein the liquid monopropellant is selected from the alkyl nitrates.

4. The propellant of claim 1 wherein the liquid monopropellant comprises a mixture of about 60% by weight of ethyl nitrate and about 60% by weight of ethyl nitrate and about 40% of normal propyl nitrate.

5. The propellant of claim 3 wherein the liquid monopropellant is gelled.

6. The propellant of claim 5 wherein the gelled liquid monopropellant comprises, in approximate percentages by weight:

| | |
|--------------------------------|------|
| Ethyl nitrate | 40.0 |
| n-Propyl nitrate | 40.0 |
| Polyethylene glycol | 12.6 |
| Curing and crosslinking agents | 1.4 |

7. The propellant of claim 1 wherein the capsule walls comprise a mixture of a polyvinyl alcohol, carrageenin, and a polymerizing agent.

8. The propellant of claim 1 wherein the capsule wall comprises, in percentages by weight:

| | |
|-------------------|------|
| Water | 91.6 |
| Polyvinyl alcohol | 7.5 |
| Carrageenin | 0.9 |

9. The propellant of claim 6 wherein the capsule walls include up to 14% by weight of the composition of nitrocellulose, whereby the total energy of the propellant may be enhanced on combustion.

10. The propellant of claim 1 wherein the capsules are spray coated with nitrocellulose, whereby the energy thereof may be enhanced on combustion.

11. The propellant of claim 1 further including an interstitial fill material to fill the interstices between the capsules thereof, said material being selected such that its energy output on combustion may be used to adjust the total energy output of the propellant as desired.

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BENJAMIN R. PADGETT, Primary Examiner

U.S. Cl. X.R.

149-11, 12, 21, 36, 88, 89, 90; 102-38, 101, 104

United States Patent [19]

Tannenbaum

[11] 3,921,394

[45] Nov. 25, 1975

[54] HETEROGENEOUS MONOPROPELLANT COMPOSITIONS AND THRUST PRODUCING METHOD

[75] Inventor: Stanley Tannenbaum, Morristown, N.J.

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EXEMPLARY CLAIM

1. Novel thixotropic, monopropellant compositions comprising a mixture of a fuel selected from the group consisting of inorganic carbides, inorganic borides and inorganic boride-carbide mixtures, a liquid oxidizer selected from the group consisting of nitric acid, nitric acid enriched with NO₂, nitric acid enriched with NO₂ and HF, nitrogen tetroxide, hydrogen peroxide, and perchloric acid dihydrate and a thixotroping agent selected from the group consisting of carbon, silica, clay, and mixtures thereof.

23. A method of developing thrust in a reaction motor, having a combustion chamber and a discharge opening, comprising the steps of igniting in said combustion chamber, a heterogeneous propellant composition of from about 15-40 parts by weight of a solid fuel selected from the group consisting of inorganic carbides, inorganic borides and inorganic boride-carbide mixtures, from about 60-95 parts by weight of a liquid oxidizer selected from the group consisting of perchloric acid dihydrate, concentrated H₂O₂ and N₂O₄, and up to about 10 parts by weight of optional propellant adjuvants and a thixotroping agent selected from the group consisting of carbon, silica, clay, and mixture thereof; and venting the combustion gases derived therefrom through said discharge opening.

36 Claims, No Drawings

HETEROGENEOUS MONOPROPELLANT COMPOSITIONS AND THRUST PRODUCING METHOD

This invention relates to novel heterogeneous monopropellant compositions.

More particularly, this invention concerns the preparation of highly energetic, thixotropic propellant compositions which are superior in certain respects to presently utilized solid or liquid propellant compositions.

The novel, thixotropic propellant compositions of this invention are composed essentially of:

- A. Carbide and/or Boride fuels
- B. Liquid Oxidizer
- C. Thixotroping or Gelling Agents and optional propellant adjuvants

The use of liquid propellant compositions offers several significant advantages over comparable solid propellant compositions. For example, liquid propellant formulations are much more energetic than currently used solid compositions and have greater specific impulse. Increased specific impulse gives the missile a longer range and a higher velocity for the same weight of propellant charge.

A further superiority of liquid propellants over solid propellants is that the combustion of liquid propellants can be mechanically controlled during flight. Combustion can be stopped and started at will, by controlling the flow of the propellant into the combustion chamber. Reducing the flow of the propellant into the combustion chamber decreases the thrust of the propellant, while increasing the flow rate has the opposite effect. Since the heterogeneous propellants of this invention are in the liquid state when utilized, their flow rate can be controlled mechanically. This control is accomplished by adjusting the pumps and valves in the missiles fuel transport system.

The significance of mechanical control is that all liquid propellant systems have a "built-in" throttleability feature that is absent in solid propellants. Throttleability allows the missiles velocity to be varied, controls the attitude of the missile, makes evasive action possible, permits the rendezvous of two or more space ships during flight and reduces the hazards of landing.

In contrast, since solid propellants cannot flow, no comparable fuel transport takes place and no comparable control of combustion through varying the flow rate is possible. In fact, after ignition, using the present technology, no method is presently available to control the combustion of the solid propellant charge after ignition. Thus, the difference of physical state alone makes all solid propellants inherently disadvantageous to liquid propellants for many applications.

Further significant disadvantages of solid propellants compared to liquid propellants arise in a number of ways because of the extreme sensitivity of solid propellants toward temperature and pressure fluctuations. This occurs both during storage and use. For example, the temperature of a solid propellant grain substantially influences performance. A given grain of solid propellant will produce more thrust on a hot day than on a cold day. Further, the physical state of the solid propellant is effected by temperature extremes. For instance, at very low temperatures many solid propellants become brittle and subject to cracking. Cracks in the propellant grain increase the propellants burning rate significantly and can cause a fracture or explosion. On the other hand a solid propellant exposed to high tempera-

tures prior to firing can lose its shape and have its performance adversely affected. This sensitivity of solid propellants toward temperature fluctuation necessitates expensive storage under constant temperature prior to use.

For all of the foregoing reasons solid propellants are presently inferior to comparable liquid propellant compositions for many applications.

Even more advantageous than liquid propellants per se are liquid monopropellant compositions. These monopropellant formulations unlike bipropellant formulations contain oxidizer, fuel and any other required adjuvant materials, combined and stored as a single formulation. Since these formulations already have sufficient oxygen no additional source of oxidizer is required and they can be handled after formulation as a single complete composition. Thus, only one storage tank and but one pumping system is needed both on the ground and in the missile. In contrast, bipropellant formulations consist of at least two separate compositions since the fuel and oxidizer components are kept physically separate until they are injected into the missiles combustion chamber. Both at the storage facility and in the missile, duplicate storage and pumping systems are essential. Furthermore, in many instances where the oxidizer is a gas such as oxygen, the oxidizer must be refrigerated under high pressure. Halving the pumping and storage requirements, particularly the pumping system, reduces the mechanical complexity of the fuel transport system and decreases the likelihood of mechanical malfunction of the missile. In addition, the need for only one set of storage and pumping facilities greatly simplifies design and construction of the missile, decreases the weight of the hardware and increases the fuel load of the missile. An ancillary but not unimportant result of simplifying the transport and storage systems is the reduction of maintenance time and maintenance and storage costs.

Unfortunately, while monopropellant formulations offer all of the above enumerated advantages over bipropellant formulations, these advantages heretofore have been largely unrealized. The reasons for this have been several. Among other things, monopropellant compositions have been too easily ignited, become unstable upon prolonged storage, too readily detonate upon being disturbed and give erratic and relatively poor performance.

For example, the prior art monopropellant compositions are typified by the following: heptane-nitrogen tetroxide, n-propyl nitrate, nitromethane, propargyl nitrate-nitramine and the like. All of these materials suffer from the failing of poor thermal stability, high sensitivity toward detonation and/or the tendency to deteriorate under prolonged storage. Poor thermal stability requires refrigerated storage, while a high sensitivity toward detonation by shock makes the propellants hazardous to store, transport and use. The deterioration of propellants after prolonged storage causes erratic performance and makes it continually necessary to substitute fresh propellant for aged propellant in order to maintain the initial high specific impulse. These stability factors among others greatly negate the value of the liquid monopropellants particularly in military retaliatory weapons.

An additional disadvantage of bipropellant liquids compared to monopropellants is in the criticality of the oxidizer to fuel ratio and the narrow margin of mal-

function allowed in the performance of the fuel metering and injection system.

While the oxidizer to fuel ratio is extremely critical to performance in all liquid propellants, in monopropellants the demands are much less stringent. This is because the oxidizer is added to the fuel during formulation and prior to use. Therefore the critical oxidizer to fuel ratio in monopropellants can be accurately determined and corrected if necessary to assure optimum performance prior to firing. In bipropellants this adjustment of oxidizer to fuel ratio cannot be made prior to firing. The reason for this is that the oxidizer and fuel are separately stored until they are injected into the missile combustion chamber for use. Thus the ratio of oxidizer to fuel in the final propellant mixture is determined only at the instant of firing and cannot be corrected. Since the metering device like any complex mechanism is subject to failure, a deviation or even abortion of the missile flight can result.

Since this malfunction cannot be foreseen until it occurs no preventive measures are possible. In a similar vein, because of the losses of fuel and oxidizer which are known to occur because of the injection and combining of the separate streams of fuel and oxidizer in the missile combustion chamber, it is necessary to store an additional supply of both propellant components in the rocket.

These losses of fuel and oxidizer are an inherent part of bipropellant systems and are referred to as outage losses. The extra weight of the outage reservoir reduces the payload the missile could carry and hence is disadvantageous. All of these shortcomings of bipropellant liquids are absent in monopropellants since the propellant is premixed and requires no metering.

For the above reasons among many others, the preparation of liquid monopropellant formulations which retain their initial high specific impulse and/or density impulse after prolonged storage is to be desired. Especially valuable would be liquid propellant formulations which retained their high specific impulse and/or density impulse yet do not become hypersensitive to detonation by shock. This combination of a highly energetic liquid propellant charge relatively insensitive to accidental detonation would be a major advance in the propellant art. Ideally these formulations would combine a low freezing point with the aforementioned properties and could be prepared from commercially available innocuous components and would have thixotropic properties. The low freezing point would prevent "freeze-up" during flight or storage while the thixotropic state would allow the formulations to be stored as a solid and pumped as a liquid.

Thus it is an object of this invention among others to prepare highly energetic, monopropellant formulations.

It is an additional object of this invention to prepare monopropellant compositions which retain their original high specific impulse and/or density impulse after long periods of storage at ambient or even higher temperatures.

It is yet another object of this invention to prepare liquid monopropellant compositions which are not readily subject to accidental ignition.

Yet another object of this invention is to prepare liquid monopropellant compositions which are insensitive to detonation by vibrational or thermal shock.

A further object of this invention is to prepare liquid propellant compositions having a low freezing point and thixotropic properties.

It is still another object of this invention to prepare highly energetic liquid propellant compositions from readily available and individually safe components.

Other objects of this invention will become apparent to those skilled in the propellant art by a further reading of this patent application.

These objects among others are achieved by the heterogeneous monopropellant compositions and processes described herein.

In practice, novel and superior thixotropic propellant compositions are derived by preparing uniform mixtures of (a) a finely divided solid inorganic fuel selected from the group of inorganic carbides, borides and carbide-boride mixtures (b) liquid oxidizer and (c) thixotroping agents with or without propellant adjuvants.

The propellant compositions of this invention consist essentially of:

A. from about 15 to 40 parts by weight of a finely divided solid fuel selected from the group consisting of inorganic borides, carbides and boride-carbide mixtures.

B. from about 60 to 95 parts by weight of liquid oxidizer.

C. up to about 10 parts by weight of thixotroping agents with or without optional propellant adjuvants. These latter propellant adjuvants include surface active agents, conditioning agents, modifiers and the like which while not necessary for operable propellant compositions, are desirable for optimum performance. The propellant adjuvants change, modify or impart to the propellant certain desirable physical and combustion characteristics so that they can be most effectively used. Typical adjuvants include surface active agents, viscosity modifiers, combustion catalysts, stabilizing agents and the like. Where such adjuvants are used they will more customarily comprise between about 1/2 to 6 parts by weight of the final propellant compositions.

The above components of the propellant composition are thoroughly mixed or blended to form a uniform thixotropic mixture then pumped into the rocket motor as a viscous liquid which soon sets to a gel. When the propellant is to be ignited it is exposed to a shearing force converting it to a pumpable liquid. The liquid is then pumped into the combustion chamber for use. The pumping procedures are well known in the propellant art. Since the propellant compositions contain at least three classes of ingredients, it is essential for satisfactory performance that the composition be uniform in content. Thus throughout this disclosure and claims the propellant compositions referred to are understood to be those uniform in content.

A. Fuel

The fuels referred to throughout this application are selected from the group of inorganic carbides and borides and mixtures of these inorganic carbides and borides. These inorganic carbides and borides can be further broken down into metallic and non-metallic carbides and borides. Illustrative non-metallic carbides include among others, boron, silicon, zirconium, tungsten, and the like. Typical metallic carbides among others include beryllium, calcium, aluminum, and the like. Illustrative non-metallic borides include silicon, zirconium and tungsten. Suitable metallic borides include aluminum, beryllium, calcium, etc. While all of the

above carbides and borides are better than average fuels in the inventive propellant compositions, as in any large group, certain members of the group are advantageous to the group as a whole and are preferred. Thus by far the most preferred fuels in the inventive propellant compositions are boron carbide, silicon carbide and silicon boride as well as mixture of these fuels. Less preferred fuels are the calcium, aluminum and beryllium carbides and borides. Fuels of more marginal interest are the other borides and carbides enumerated above.

B. Liquid Oxidizers

The liquid oxidizers of this invention are of diverse structure and origin. Among the various oxidizers which can be used are the following: nitric acid, nitric acid enriched with NO_2 (RFNA), and nitric acid enriched with NO_2 and HF (IRFNA and HIRFNA) nitrogen tetroxide (N_2O_4), concentrated hydrogen peroxide (H_2O_2), perchloric acid (concentrated) and the like. The preferred oxidizers of this invention are HIRFNA whose composition is disclosed infra, concentrated H_2O_2 , N_2O_4 , and perchloric acid dihydrate. These oxidizers are preferred because of their low cost; commercial availability and most important, because of the highly energetic propellant compositions that are produced when they are used in conjunction with the aforementioned fuel components.

C. Thixotropic Agents or Gelling Agents

These agents which are alternatively referred to as thickening agents are used to thicken the propellant compositions so that they can be stored as thixotropic solids, yet under a shearing force will revert to the liquid state. These gelling or thickening agents can be present in amounts ranging from 0 to 6 parts by weight or higher. More generally the thickener will be used in amounts ranging from 1 to 4 parts by weight. The exact amounts used will depend upon the type and amount of the particular fuel and oxidizer used as well as the thickener employed. An abbreviated but illustrative list of thickeners includes among others: the preferred thickener powdered carbon, the various anhydrous and particulate colloidal silicas, and colloidal clays such as bentonite.

D. Optional "propellant adjuvant"

This is the generic designation used to describe the various conditioning, modifying agents, solvents and the like used to produce optimum performance from the propellant compositions of this invention. These adjuvants ordinarily make up a minor proportion of the final propellant composition, seldom exceeding 10 parts by weight of the propellant composition and more typically comprising 0 - 6 parts by weight of the compounded propellant exclusive of thixotropic agents. The adjuvants listed previously are the most important utilized although many other adjuvants can be employed if desired.

E. Compounding the Propellant Formulations

In preparing the novel liquid propellant formulations of this invention, several compounding procedures among many can be followed. The following represents the preferred formulative procedure:

The weighted, dry solid fuel ingredient(s), of the formulation are mixed until a homogeneous and uniform solid mixture is obtained. The mixing or blending operation can be accomplished using any number of commercial tumblers, blenders, agitators or mixers. Since the components are not detonable both individually

and as a mixture, no special precautions in mixing need be taken. When the solid ingredients have been satisfactorily blended, they are blended into the required amount of oxidizer until a highly viscous liquid thixotropic mixture is obtained. This gelled propellant mixture is pumped into a rocket engine as a viscous liquid and rapidly sets to a heavy gel. When the gel is exposed to a shear force, it liquifies and its viscosity and flow properties will then depend on the rate of shear. At this stage its flow rate into the missile combustion chamber can be controlled mechanically as is the case in a typical liquid propellant composition.

Because of their exceptional stability, the novel heterogeneous propellants of this invention are preferably ignited using anyone of several possible techniques. One method is referred to as the hypergolic technique. In this method a small amount of chemical agent reactive with one or more of the propellant components is injected into the missile's combustion chamber with the flow of propellant mixture. The ignition is initiated by the reaction of chemical agent with the propellant components and the propellant once ignited burns smoothly. A satisfactory chemical agent for this purpose among others is unsymmetrical dimethyl hydrazine.

In a second method, the combustion is initiated using a squib of solid propellant. The ignition of the solid propellant can be electrically actuated.

F. Preferred Heterogeneous Monopropellant Compositions

As indicated supra many different factors are involved in determining whether a given propellant composition is to be favored over another. Among these factors are high specific impulse, high density impulse, insensitivity toward detonation, cost, availability of the components as well as the type of use contemplated. For use as rocket propellants the most preferred heterogeneous monopropellants consist essentially of the following:

15 to 40 parts by weight of a fuel selected from the group consisting of silicon carbide, boron carbide and silicon boride.

60 to 95 parts by weight of an oxidizer selected from the group consisting of perchloric acid dihydrate, HIRFNA, nitrogen tetroxide and concentrated hydrogen peroxide (above 90%) and from about 1 to 6 parts by weight of thixotroping or gelling agent.

HIRFNA's composition is given below:

72.0 parts by weight fuming HNO_3

26.8 parts by weight N_2O_4

0.7 parts by weight HF

0.8 parts by weight H_2O

The workings of this invention can be shown more clearly by the typical embodiments which follow below:

EXAMPLE I

A 21.4 parts by weight portion of SiB_4 , 2.5 parts by weight of carbon black (having a particle size below 1 micron) and a surface area of 64-70 sq. meter/gram and a bulk density of 6.25 lbs/cu.ft.) and 1 part by weight of pyrogenic silica (Cab-O-sil-HS-5 having a particle size of 7-10 millimicrons and a surface area of 300-350 sq. meters/gram and a bulk density of 2.3 lbs/cu.ft.) are blended in a PREMIER Dispersator fitted with a 1 inch Triplex Head. The mixing time is 15 minutes. The blended SiB_4 carbon-silica mixture is added to a 75.1 parts by weight of a perchloric acid di-

hydrate (72% perchloric acid) in the same type of dispersator. Again the blending is continued for 15 minutes. A highly viscous gel is obtained which has a Specific Impulse above 239. After 3 months storage at room temperature the mixture is found to be virtually unchanged.

EXAMPLE 2

In another embodiment using the same equipment and blending time and techniques as before, silicon boride (SiB_4) based propellant is prepared by blending a previously blended mixture of 3.5 parts by weight of the above described finely divided carbon thickener, and 25.1 parts by weight of silicon boride with 71.4 parts by weight HIRFNA (nitric acid as defined above). Again a viscous gel is obtained. The propellant has a Specific Impulse of 246 after blending. These properties are retained even after 3 months storage at room temperature.

EXAMPLE 3

In still another embodiment of this invention a propellant formulation is prepared having a boron carbide-silicon boride fuel. The preparation is as follows. Using the same equipment and techniques described earlier, a 12.5 parts by weight portion of boron carbide, 12.5 parts by weight of silicon boride, 3.5 parts by weight of the previously described carbon black are blended together for 20 minutes. At the end of this time 71.5 parts by weight portion of HIRFNA oxidizer is added and the blending is continued for an additional 30 minutes. The viscous propellant formulation had an initial Specific Impulse of about 252 which remained unchanged after 6 months storage at room temperature.

EXAMPLE 4

A 24.8 parts by weight portion of calcium carbide 3.5 parts by weight of the afore-described fine particle size silica are blended for 30 minutes. After the blending is completed 71.7 parts by weight of N_2O_4 is added to the blend and the blending is resumed for an additional 15 minutes. A gel-like propellant having a Specific Impulse substantially above average is produced.

EXAMPLE 5

A 19.3 parts by weight portion of Boron Carbide, 3.5 parts by weight of finely divided silica are blended for 20 minutes. At the end of this time a 77.2 parts by weight portion of 98% hydrogen peroxide (H_2O_2) is blended in for an additional 20 minutes. The resultant propellant is a thick gel having a Specific Impulse of 277. This impulse remains substantially unchanged even after 90 days storage.

EXAMPLES 6, 7 and 8

Comparable propellant compositions can be obtained by combining stoichiometric proportions of concentrated (98 parts by weight) H_2O_2 with various other fuels. In each instance 3.5 parts by weight of finely divided carbon black is used as the thixotropic agents. Typical formulations include lithium boride — H_2O_2 — carbon black, tungsten carbide — H_2O_2 — carbon black, boron carbide — H_2O_2 — carbon black among others.

EXAMPLE 9

Preparation of B_4C /HIRFNA/Carbon Gel

Materials:

Boron Carbide - 1000 mesh

Carbon (Shawenigan Black) — Particle size in the submicron area

HIRFNA — Normal Composition:

72.0% HNO_3

26.5% NO_2

0.7% HF

0.8% H_2O

Experimental:

The following materials are weighed out in the following proportions:

75.6% HIRFNA

20.9% B_4C

3.5% Carbon

The HIRFNA mixture is then added to the mixing container, followed by the previously blended mixture of Boron Carbide and Carbon. The mixing is carried out by a Premier Dispersator fitted with a 1 inch Duplex Head. Mixing time varies from 3 minutes to $\frac{1}{2}$ hour for batch sizes ranging from 100 grams to 20 lbs. Transformer setting for the Dispersator is at 120. A gelled dispersion is obtained which has a Specific Impulse above 255. The mixture was tested and found to be stable after more than 6 months at room temperature.

EXAMPLE 10

Preparation of $\text{B}_4\text{C}/\text{N}_2\text{O}_4/\text{CAB-O-SIL GEL}$

Materials:

Boron Carbide — 1000 mesh

Nitrogen tetroxide (N_2O_4)

Cab-O-Sil-(Pyrogenic colloidal silica). Particle size 0.007 to 0.010 microns

Experimental:

The following materials are weighed out in the following proportions:

73.9% N_2O_4

24.6% B_4C

1.5% Cab-O-Sil

Then all the propellant ingredients and mixing container are cooled down to 0°C . Then N_2O_4 is added to the chilled container for mixing, followed by the previously prepared mixture of B_4C and Cab-O-Sil. The mixing is carried out by a Premier Dispersator fitted with a 1 inch Duplex Head. Mixing time for a 100 gm to 2 lb. batch is 3 minutes with the transformer setting on the Dispersator at 120. The mixing container is closed to the atmosphere during mixing and kept at 0°C . during the entire mixing process. The resultant thixotropic gel has a Specific Impulse above 255 and is stable for more than 6 months.

EXAMPLE 11

Preparation of $\text{B}_4\text{C}/\text{HClO}_4\cdot 2\text{H}_2\text{O}/\text{CAB-O-SIL GEL}$

Materials:

Boron Carbide -- 1000 mesh

Perchloric Acid Dihydrate ($\text{HClO}_4\cdot 2\text{H}_2\text{O}$)

Cab-O-Sil-(Pyrogenic colloidal silica). Particle size 0.007 to 0.010 microns

Experimental:

The following materials are weighed out in the following proportions:

79.6% $\text{HClO}_4\cdot 2\text{H}_2\text{O}$

16.9% B_4C

3.5% Cab-O-Sil

Then $\text{HCO}_2\cdot 2\text{H}_2\text{O}$ is added to a previously prepared glass or polyethylene mixing container, followed by the previously weighed out and mixed B_4C and Cab-O-Sil. The mixing is carried out by a Premier Dispersator fitted with a 1 inch Duplex Head. Mixing time for a 100 gram to 2 lb. batch is 3 minutes with the transformer setting on the dispersator at 120. The resultant thixotropic gel has a Specific Impulse above 240 and was found to be stable after more than 6 months.

The above B₄C based propellant formulation is especially advantageous as a propellant for torpedos and small submarines. For example, the Isp is in the order of 240 seconds, the Ispd about 440 seconds and the Tc about 3400°K. In addition the major combustion products (HBO_2 , HCl and H_2O) are non-toxic substances. Additional advantages of this propellant formulation, particularly where use in submarines are contemplated, are the water solubility of the major combustion gases, low shock sensitivity and wakeless exhaust. Comparable advantages are obtained in the above formulation when stoichiometric quantities AlB_{12} and SiB_4 fuels are substituted for the B_4C fuel.

As indicated by the previously disclosed illustrative embodiments, numerous modifications and variations can be made in the invention without departing from the inventive concept. Thus the metes and bounds of this invention can best be determined by an examination of the claims which follow.

We claim:

1. Novel thixotropic, monopropellant compositions comprising a mixture of a fuel selected from the group consisting of inorganic carbides, inorganic borides and inorganic boride-carbide mixtures, a liquid oxidizer selected from the group consisting of nitric acid, nitric acid enriched with NO_2 , nitric acid enriched with NO_2 and HF , nitrogen tetroxide, hydrogen peroxide, and perchloric acid dihydrate and thixotroping agent selected from the group consisting of carbon, silica, clay, and mixtures thereof.

2. The thixotropic monopropellant compositions of claim 1 wherein the components are present in about the following proportions:

15-40 parts by weight of fuel
60-95 parts by weight of liquid oxidizer
up to 10 parts by weight of thixotroping agents.

3. The thixotropic monopropellant compositions of claim 2 wherein up to 6 parts by weight or propellant adjuvants are present.

4. The thixotropic monopropellant compositions of claim 2 wherein the fuel is an inorganic carbide.

5. The thixotropic monopropellant compositions of claim 2 wherein the fuel is an inorganic boride.

6. The thixotropic monopropellant compositions of claim 2 wherein the fuel is an inorganic boride-carbide mixture.

7. A thixotropic monopropellant composition comprising a mixture of from about 15-40 parts by weight of a non-metallic boride, from about 60-95 parts by weight of a liquid oxidizer selected from the group consisting of nitric acid, nitric acid enriched with NO_2 , nitric acid enriched with NO_2 and HF , N_2O_4 , and concentrated H_2O_2 , and up to about 10 parts by weight of a thixotroping agent selected from the group consisting of carbon, silica, clay and mixtures thereof.

8. The thixotropic monopropellant composition of claim 7 wherein the non-metallic boride fuel is silicon boride.

9. The thixotropic monopropellant composition of claim 7 wherein the non-metallic boride fuel is zirconium boride.

10. A thixotropic monopropellant composition comprising from about 15-40 parts by weight of metallic boride fuel, from about 60-95 parts by weight of liquid oxidizer selected from group consisting of nitric acid, nitric acid enriched with NO_2 , nitric acid enriched with NO_2 and HF , HCIO_4 , N_2O_4 , and H_2O_2 , ClO_3F , N_2F_4 , $\text{C}(\text{NO}_2)_4$ and $\text{O}_2\text{N.O.CH}_2\text{CH}_2\text{O.NO}_2$ and up to about 10 parts by weight of a thixotroping agent selected from the group consisting of carbon, silica, clay, and mixtures thereof.

11. A thixotropic monopropellant composition comprising 15-40 parts by weight of aluminum boride (AlB_{12}) fuel, from about 60-95 parts by weight of nitric acid enriched with NO_2 , and up to about 10 parts by weight of a thixotroping agent selected from the group consisting of carbon, silica, clay, and mixtures thereof.

12. A thixotropic monopropellant composition comprising 15-40 parts by weight of beryllium boride fuel, from about 60-95 parts by weight of nitric acid enriched with NO_2 , and up to about 10 parts by weight of a thixotroping agent selected from the group consisting of carbon, silica, clay, and mixtures thereof.

13. A thixotropic monopropellant composition comprising 15-40 parts by weight of calcium boride fuel, from about 60-95 parts by weight of N_2O_4 oxidizer and up to about 10 parts by weight of a thixotroping agent selected from the group consisting of carbon, silica, clay, and mixtures thereof.

14. A thixotropic monopropellant composition comprising a mixture of from about 15-40 parts by weight of a non-metallic carbide fuel, from about 60-95 parts by weight of a liquid oxidizer selected from the group consisting of nitric acid enriched with NO_2 , N_2O_4 , and H_2O_2 , and up to about 10 parts by weight of a thixotroping agent selected from the group consisting of carbon, silica, clay, and mixtures thereof.

15. The thixotropic monopropellant composition of claim 14 wherein the non-metallic carbide fuel is boron carbide.

16. The thixotropic monopropellant composition of claim 14 wherein the non-metallic carbide fuel is silicon carbide.

17. The thixotropic monopropellant composition of claim 14 wherein the non-metallic carbide fuel is zirconium carbide.

18. The thixotropic monopropellant composition of claim 14 wherein the non-metallic carbide fuel is a mixture of boron carbide and silicon carbide.

19. A thixotropic monopropellant composition comprising a mixture of from about 15-40 parts by weight of metallic carbide fuel, from about 60-95 parts by weight of liquid oxidizer selected from the group consisting of N_2O_4 and concentrated H_2O_2 , and up to about 10 parts by weight of a thixotropic agent selected from the group consisting of carbon, silica, clay, and mixtures thereof.

20. The thixotropic monopropellant composition of claim 19 wherein the metallic carbide fuel is aluminum carbide.

21. The thixotropic monopropellant composition of claim 19 wherein the metallic carbide fuel is beryllium carbide.

22. The thixotropic monopropellant composition of claim 19 wherein the metallic carbide fuel is calcium carbide.

23. A method of developing thrust in a reaction motor, having a combustion chamber and a discharge opening, comprising the steps of igniting in said combustion chamber, a heterogeneous propellant composition of from about 15-40 parts by weight of a solid fuel selected from the group consisting of inorganic carbides, inorganic borides and inorganic boride-carbide mixtures, from about 60-95 parts by weight of a liquid oxidizer selected from the group consisting of perchloric acid dihydrate, concentrated H_2O_2 and N_2O_4 , and up to about 10 parts by weight of optional propellant adjuvants and a thixotroping agent selected from the group consisting of carbon, silica, clay, and mixtures thereof; and venting the combustion gases derived therefrom through said discharge opening.

24. The method of claim 23 wherein the liquid oxidizer is H_2O_2 and the solid fuel is boron carbide.

25. The method of claim 23 wherein the liquid oxidizer is perchloric acid dihydrate and the solid fuel is boron carbide.

26. The method of claim 23 wherein the solid fuel is silicon carbide and the liquid oxidizer is perchloric acid dihydrate.

27. The method of claim 23 wherein the solid fuel is silicon carbide and the liquid oxidizer is concentrated H_2O_2 .

28. The method of claim 23 wherein the solid fuel is silicon boride and the liquid oxidizer is perchloric acid dihydrate.

29. The method of claim 23 wherein the solid fuel is silicon boride and the liquid oxidizer is concentrated H_2O_2 .

30. A method of developing thrust in an aquatic vessel having a reaction motor, combustion chamber and discharge opening, comprising the steps of igniting in said combustion chamber a heterogeneous propellant composition of from about 15-40 parts by weight of a solid fuel selected from the group consisting of inorganic carbides, inorganic borides and inorganic carbide-boride mixtures, from about 60-95 parts by weight of a liquid oxidizer selected from the group consisting of concentrated H_2O_2 and perchloric acid dihydrate, and up to 10 parts by weight of optional propellant adjuvants and a thixotroping agent selected from the group consisting of carbon, silica, clay and mixtures thereof, and venting the combustion gases derived therefrom through said discharge opening.

31. The method of claim 30 wherein the liquid oxidizer is concentrated H_2O_2 and the elemental solid fuel is boron carbide.

32. The method of claim 30 wherein the liquid oxidizer is concentrated H_2O_2 and the elemental solid fuel is silicon carbide.

33. The method of claim 30 wherein the liquid oxidizer is concentrated H_2O_2 and the elemental solid fuel is silicon boride.

34. The method of claim 30 wherein the liquid oxidizer is perchloric acid dihydrate and the elemental solid fuel is boron carbide.

35. The method of claim 30 wherein the liquid oxidizer is perchloric acid dihydrate and the elemental solid fuel is silicon carbide.

36. The method of claim 30 wherein the liquid oxidizer is perchloric acid dihydrate and the elemental solid fuel is silicon boride.

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[54] HIGH ENERGY FUEL SLURRY

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[73] Assignee: Thiokol Corporation, Newtown, Pa.

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[51] Int. Cl.² C06B 43/00

[52] U.S. Cl. 149/22; 60/216;
149/1; 149/108.2; 149/114; 149/118

[58] Field of Search 60/216; 149/87, 22,
149/108.2, 118

[56] References Cited

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Primary Examiner—Leland A. Sebastian

Attorney, Agent, or Firm—Stanley A. Marcus; William R. Wright, Jr.

[57]

ABSTRACT

A fuel for rocket motors is provided in the form of a slurry of particulate metal or metalloid particles having a particle size of about 0.1 to 10 microns suspended in an alcohol having from 1 to 3 carbon atoms in the presence of a non-thixotropic amount of high viscosity grade hydroxypropyl cellulose.

8 Claims, No Drawings

HIGH ENERGY FUEL SLURRY

This invention relates to rocket propellants. More particularly, this invention relates to high energy fuels for packaged liquid propellant systems and to a method of utilizing these fuels.

Air launched missiles have proved to be effective weapon systems for destroying both air and ground targets. The requirements of such missiles can best be realized by the use of packaged liquid propellants, i.e., propellants which can be hermetically sealed within the storage tanks of a missile and which, after being held in such tanks for extended periods of time under extreme environmental conditions, can be successfully and reliably ignited and burned to propel the missile to its target. However, fuels and oxidizers for packaged liquid propellant systems must satisfy many stringent requirements, some of which have not been completely met by the fuels and oxidizers employed heretofore. For example, the fuel and oxidizer for a packaged liquid propellant system of an air-to-air or air-to-ground missile should provide, in order to fulfill the need for higher missile velocities under conditions of modern aerial warfare, a delivered specific impulse and density impulse of at least 240 seconds and 415 gm-sec/cc respectively under conditions of 1000 psi chamber pressure exhausted to 14.7 psi, which values are difficult to attain by means of liquid fuels containing no high energy additives. Also both the fuel and oxidizer of a packaged liquid propellant system should be storable for periods of up to 10 years, under temperatures as low as -65°F . and as high as 160°F ., without undergoing extensive deterioration or corroding the containers in which they are held. However, it has been found that when high energy additives such as powdered boron are added to certain liquid fuels (e.g., mixtures of hydrazine, monomethylhydrazine and hydrazine nitrate), the fuels evolve gas at a rate that is unacceptable from the standpoint of their long term storage in propellant tanks of missiles. Among the many additional properties which are desirable for packaged liquid fuels and oxidizers are low shock sensitivity, low viscosity, low freezing point, high boiling point, high autoignition point, and nontoxicity. Where a powdered material such as boron is added to a liquid fuel to increase its energy, it is also necessary that the additive does not settle from suspension to any great extent when the mixture is subjected to long storage, either under conditions of quiescence or vibration, or is subjected to high gravitational forces such as those encountered in the operation of high-speed aircraft. In addition, any gelling agent added to such as fuel-additive mixture to maintain the solid component in suspension must not produce undesirable side effects, such as for example, formation of a fuel-additive mixture that has poor flow characteristics because of the inclusion of cohesive clumps of material therein. Furthermore, to eliminate the need for a complicated ignition system in an air launched missile, it is advantageous to utilize hypergolic fuels and oxidizers in packaged liquid propellant systems. Thus the problem of providing a suitable fuel-oxidizer combination for a liquid propellant missile of the type described is not easy to solve, particularly where the fuel contains a powdered metal or metalliod to increase its energy.

It is accordingly a broad object of this invention to provide an improved packaged liquid propellant system.

Another object of this invention is to provide a high energy fuel for use with a hypergolic oxidizer in a packaged liquid propellant system.

An additional object of this invention is to provide a stable fuel slurry comprising a finely divided solid interspersed in a liquid fuel.

Still another object of this invention is to provide a method of propelling a rocket by means of a high energy fuel slurry and an oxidizer that reacts spontaneously therewith.

In accordance with this invention the above and other objects are accomplished by a propellant system which utilizes as a fuel a mixture of a finely divided metal or metalliod and an alcohol selected from the group consisting of methanol, ethanol, 1-propanol and 2-propanol, and which utilizes as an oxidizer a halogen or an interhalogen that reacts hypergolically with said fuel mixture. The named alcohols are advantageous as liquid carriers for high energy solid additives primarily because of their low freezing points and because the oxygen they contain helps to oxidize some or all of their carbon to carbon monoxide during burning with a halogen containing oxidizer. Furthermore, they are readily available and have low cost, low toxicity and high stability to thermal degradation. Particularly preferred as a fuel for a packaged liquid propellant is a mixture of methanol and powdered boron which is hypergolically reactive with a halogen such as fluorine, and with interhalogens such as chlorine trifluoride and chlorine pentafluoride, to thereby provide a high density impulse propellant system. Moreover, this fuel mixture has been found to possess good storage characteristics and to be insensitive to shock.

The addition of a high energy solid additive to the fuel component of a packaged liquid propellant system raises the density impulse of the system significantly while the specific impulse is only slightly lowered. This trend continues until the fuel component comprises nothing but solid additive. At this point the highest theoretical energy can be achieved from the propellant system. Obviously, however, a fuel consisting only of solid additive cannot be flowed or considered for use in a liquid propellant rocket engine. However, it is desirable to use as much solid additive as possible and the maximum is limited by the flow properties of the resulting fuel slurry.

Also, because of practical considerations in the design of valves, injectors, etc. of the fluid flow system of a liquid propellant rocket motor and because of the problem of maintaining a high energy solid additive in suspension in a liquid fuel, the ratio of solid to liquid fuel that produces a useful fuel slurry for a packaged liquid propellant system is critical. The particle size of the solid is also of importance. The viscosity of a slurry is higher when it contains higher amounts of solid additive or solid additives of a smaller particle size. Higher viscosity is reflected in higher pressure drops in fuel lines and injectors for which maximums have been set. Therefore when solid additives with particle sizes of 5-10 microns are used, concentrations of up to about 80 weight percent may possibly be used before the slurry becomes too thick whereas when particle sizes are in the submicron range, solids may be added only to about 40 weight percent before the slurry becomes too thick.

Since higher solid additive concentrations are desirable from an energy viewpoint, a large (5-10 micron) particle size additive should be used to achieve higher solids. This cannot always be done because it is more

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difficult to efficiently burn larger particles in the rocket engine. Thus a balance must be found in each instance between the particle size which will produce lower viscosities and the particle size which will burn efficiently.

It has been found that boron, aluminum, titanium, zirconium, aluminum boride, titanium boride and zirconium boride form free-flowing fuel slurries when divided to a particle size in the range of from about 0.1 micron to about 10 microns and intimately mixed (as will be described hereinafter) with one of the above-named alcohols to form liquid fuel-solid additive mixtures containing from 40 to 80 percent by weight of solid and 0 to 2 percent by weight of gellant. These slurries also exhibit a low tendency to settle from suspension even after long storage. A preferred fuel slurry that has been found to have excellent flow and suspension properties is a mixture comprising 50 parts by weight of particulate boron having a particle size of from 1 to 2 microns, 49 parts by weight of methanol, and 1 part by weight of hydroxypropyl cellulose as a gellant.

This invention is illustrated by the following examples.

EXAMPLE 1

A mixture of 49 parts by weight of methanol of a purity of 99.85 percent, 50 parts by weight of amorphous boron with a 1-2 micron particle size and 1 part by weight of high viscosity grade hydroxypropyl cellulose gellant is prepared in the following manner. The gellant is intimately mixed with the boron and this mixture is added to methanol using a low shear mixer such as a dough mixer to blend in the solids. Low shear mixing is continued until the slurry is homogeneous (~30 minutes) and only slightly granular. The slurry is then subjected to a short period (1-2 minutes) of high shear mixing such as can be accomplished with a saw-toothed disc with a tip speed of approximately 3,000-6,000 ft/sec. This breaks up the small aggregates of boron and produces a smooth slurry in which no particles can be seen. All mixing is conducted at ambient temperature and pressure and in closed vessels due to the high evaporation rate of methanol.

The fuel slurry thus formed has a viscosity of 15 poise at a shear rate of 100 sec^{-1} , 4 poise at a shear rate of 1000 sec^{-1} and 1 poise at a shear rate of $10,000 \text{ sec}^{-1}$, as determined at 25°C using a Ferranti Shirley cone and plate viscometer. Thus it is readily injected by conventional means into the combustion chamber of a rocket motor. Chlorine trifluoride simultaneously injected into the combustion chamber of a rocket motor with the described fuel slurry reacts with it upon contact, producing a specific impulse of 252 sec and a density impulse of 420 g sec/cc when the oxidizer and fuel in the slurry are in the ratio of 6 to 1. All impulse figures given herein are for 1000 psi chamber pressure exhausted to 14.7 psi. Other halogens and interhalogens, such as F_2 , ClF , ClF_3 , BrF_3 and BrF_5 , also react hypergolically with the fuel slurry.

The safety of the aforementioned fuel slurry was tested using the JANAF card gap test. At a gap of zero cards, no evidence of detonation was observed in duplicate tests.

The fuel slurry produces a pressure rise of less than 0.006 psi/day when stored at 160°F in tanks with 5 percent vapor space. This is equivalent to a decomposition rate of less than 10^{-8} moles of gas per gram of

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slurry per day and is well within the limit specified for a packaged propellant. The fuel slurry when subjected to vibration of 10 to 36 cycles per second for 32 hours under a 9 g maximum acceleration undergoes a very minimum amount of settling of the solid additive (less than 5 percent) which is within the acceptable limits for a packaged slurry propellant.

EXAMPLE 2

A fuel slurry containing 49 parts by weight of ethanol with a minimum purity of 99 percent, 50 parts by weight of amorphous boron with a particle size of 1-2 microns and 1 part by weight of high viscosity grade hydroxypropyl cellulose gellant is formed by the same steps described in Example 1.

The fuel slurry thus formed has a viscosity of 20 poise at a shear rate of 100 sec^{-1} , 4 poise at a shear rate of 1000 sec^{-1} and 1 poise at a shear rate of $10,000 \text{ sec}^{-1}$, as determined at 25°C using a Ferranti Shirley cone and plate viscometer. Thus it is readily injected by conventional means into the combustion chamber of a rocket motor. Chlorine pentafluoride simultaneously injected into the combustion chamber of a rocket motor with the described fuel slurry reacts with it upon contact, producing a specific impulse of 260 sec and a density impulse of 430 g sec/cc when the oxidizer and fuel in the slurry are in the ratio of 5.5 to 1.

The safety, thermal stability and resistance to settling of this slurry are the same as that of Example 1.

EXAMPLE 3

A fuel slurry containing 49 parts by weight of 1-propanol with a minimum purity of 99 percent, 50 parts by weight of amorphous boron with a particle size of 1-2 microns and 1 part by weight of high viscosity grade hydroxypropyl cellulose gellant is formed by the same steps described in Example 1.

The properties of this fuel slurry are essentially the same as that of Example 2 with the exception that its performance in a rocket engine is slightly lower than in Example 2 due to the lower percentage of oxygen in the propanol molecule. Chlorine pentafluoride simultaneously injected into the combustion chamber of a rocket motor with the described fuel slurry reacts with it upon contact, producing a specific impulse of 258 sec and a density impulse of 426 g sec/cc when the oxidizer and fuel slurry are in the ratio of 5.5 to 1.

EXAMPLE 4

A fuel slurry formed of 2-propanol and boron is prepared by the same process steps described in the preceding example, the parts by weight and purity of the constituents being as stated therein.

The fuel slurry thus formed has substantially the same properties as the 1-propanol and boron fuel slurry described in Example 3 and, when contacted with chlorine trifluoride in the combustion chamber of a rocket motor, reacts hypergolically with this oxidizer to produce a specific impulse of 249 sec and a density impulse of 415 g sec/cc when the oxidizer and fuel in the slurry are in the ratio of 6.2 to 1.

EXAMPLE 5

A fuel slurry containing 24 parts by weight of methanol with a purity of 99.85 percent 75 parts by weight of spherical aluminum powder with a particle size of 5 microns and 1 part by weight of high viscosity grade

hydroxypropyl cellulose is formed by the same steps described in Example 1.

The fuel slurry thus formed has a viscosity of 100 poise at a shear rate of 100 sec^{-1} , 16 poise at a shear rate of 1000 sec^{-1} and 1 poise at a shear rate of $10,000 \text{ sec}^{-1}$ as determined at 25°C using a Ferranti Shirley cone and plate viscometer. Thus it is readily injected by conventional means into the combustion chamber of a rocket motor. Chlorine trifluoride simultaneously injected into the combustion chamber of a rocket motor with the described fuel slurry reacts with it upon contact, producing a specific impulse of 240 sec and a density impulse of 426 g sec/cc when the oxidizer and fuel in the slurry are in the ratio of 3.0 to 1.

The safety, thermal stability and resistance to settling of this slurry are the same as that of Example 1.

EXAMPLE 6

A fuel slurry consisting of 39 parts by weight of ethanol with a minimum purity of 99 percent, 60 parts by weight of zirconium with a particle size of 2-10 microns and 1 part by weight of high viscosity grade hydroxypropyl cellulose gellant is formed by the same steps described in Example 1.

The fuel slurry thus formed has a viscosity of 70 poise at a shear rate of 100 sec^{-1} , 12 poise at a shear rate of 1000 sec^{-1} and 1 poise at a shear rate of $10,000 \text{ sec}^{-1}$ as determined at 25°C using a Ferranti Shirley cone and plate viscometer. Thus it is readily injected by conventional means into the combustion chamber of a rocket motor. Chlorine pentafluoride simultaneously injected into the combustion chamber with the described fuel slurry reacts with it hypergolically, producing a specific impulse of 245 sec and a density impulse of 428 g sec/cc, when the oxidizer and fuel in the slurry are in the ratio of 1.8 to 1. The safety, thermal stability and resistance to settling of this slurry are the same as that of Example 1.

EXAMPLE 7

A fuel slurry consisting of 39 parts by weight of 1-propanol with a minimum purity of 99 percent, 60 parts by weight of ZrB_2 with a particle size of 3-5 microns and 1 part by weight of high viscosity grade hydroxypropyl cellulose is formed by the same steps described in Example 1.

The fuel slurry thus formed has a viscosity of 100 poise at a shear rate of 100 sec^{-1} , 15 poise at a shear rate of 1000 sec^{-1} and 1.5 poise at a shear rate $10,000 \text{ sec}^{-1}$ as determined at 25°C using a Ferranti Shirley cone and plate viscometer. Thus it is readily injected by conventional means into the combustion chamber of a rocket motor. Chlorine pentafluoride simultaneously injected into the combustion chamber with the described fuel slurry reacts with it upon contact, producing a specific impulse of 243 sec and a density impulse of 423 g sec/cc

when the oxidizer and fuel in the slurry are in the ratio of 2.4 to 1.

The safety, thermal stability and resistance to settling are the same as that of Example 1.

In any of the fuel slurries disclosed in Examples 1 through 7, the solid additive employed therein can be replaced with one of the metals or metalloids of the following group: boron, aluminum, titanium, zirconium, aluminum boride, titanium boride and zirconium boride.

Two or more of these metals and metalloids can also be mixed with methanol, ethanol, 1-propanol and 2-propanol to form fuel slurries with superior properties for packaged liquid propellant systems. Preferably the ratio of solid to alcohol in each of these fuel slurries is stoichiometric.

The oxidizers that are hypergolically reactive with the above-described fuel slurries are not limited to those specified in Example 1 through 7. Each of the fuel slurries formed of a solid selected from the named metals and metalloids of a methyl, ethyl or propyl alcohol reacts hypergolically with, among other oxidizers, F_2 , ClF , ClF_3 , ClF_5 , BrF_3 and BrF_5 . Preferably the fuel slurry and oxidizer selected for a particular packaged liquid propellant system are injected into the combustion chamber of a rocket motor in stoichiometric ratio.

What is claimed is:

1. A fuel for rocket motors consisting essentially of a slurry of a high energy solid additive in non-settling suspension in a liquid fuel, said slurry comprising finely divided solids having a particle size of less than about 10 microns selected from the group consisting of boron, aluminum, aluminum boride, titanium boride, zirconium boride and mixtures thereof, and a liquid fuel selected from the group consisting of methanol, 1-ethanol, 1-propanol and 2-propanol, and mixtures thereof, said solids being suspended in said liquid in an amount less than about 80 percent by weight of the slurry in the presence of less than a thixotropic amount of a high viscosity grade of hydroxypropyl cellulose, and said fuel having a gas evolution rate within standard test limits for a packaged propellant when the fuel slurry is stored in a tank at 160°F . with 5% vapor space.

2. A fuel as defined in claim 1 wherein said solid is boron.

3. A fuel as defined in Claim 1 wherein said solid is boron and said liquid fuel is methanol.

4. A fuel as defined in claim 1 wherein said solid is boron and said liquid fuel is ethanol.

5. A fuel as defined in claim 1 wherein said solid is boron and said liquid fuel is 1-propanol.

6. A fuel as defined in claim 1 wherein said solid is boron and said liquid fuel is 2-propanol.

7. A fuel as defined in claim 1 containing from 40 to 80 percent by weight of solid.

8. A fuel as defined in claim 1 wherein said solid has a particle size in the range of from about 0.1 micron to about 10 microns.

* * * * *

THE BDM CORPORATION

U.S. FIRM PATENTS

Patent Number: 3,444,014
Author: Joseph D. Chrisp, Claymont, Delaware
Title: Gelled Aqueous Acid Composition and Method of Making Same
Date: May 13, 1969

Patent Number: 3,811,970
Author: C. B. Henderson
Title: Gelled Hydrazine Propellant Compositions Containing Hydrazine Nitrate and a Finely Divided Metal
Date: May 21, 1974

Patent Number: 3,861,138
Author: Robert M. Birdeforth, Jr., Mercer Island, WA; George S. Sutherland, Seattle, WA
Title: Method of Propulsion Using Stable, High Energy Compositions With Hydrazine Containing Working Fluid
Date: January 21, 1975

Patent Number: 3,912,560
Author: Charles D. Forrest, Hollister, CA
Title: Thin Layer Propagating Slurry Explosive
Date: October 14, 1975

Patent Number: 4,097,316
Author: John J. Mullay, Hazelton, PA
Title: Method for Gelling Nitroparaffins in Explosive Compositions
Date: June 27, 1978

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3,444,014

GELLED AQUEOUS NITRIC ACID COMPOSITION AND METHOD OF MAKING SAME

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No Drawing. Filed Aug. 8, 1967, Ser. No. 659,034

Int. Cl. C36b 1/00

U.S. Cl. 149—45

14 Claims

ABSTRACT OF THE DISCLOSURE

Nitric acid compositions gelled by reacting in situ an acrylic polymer, and preferably polyacrylamide, with a metal ion having a positive valence of from 2 to 6 and selected from chromium, vanadium, manganese, titanium, antimony, zirconium and scandium. Explosive compositions are provided by the presence of fuels and/or sensitizers in the gelled nitric acid to form compositions having an oxygen balance of about from -25 to +10%.

BACKGROUND OF THE INVENTION

Liquid nitric acid finds use in the metallurgical, fertilizer, explosive, and general chemical process industries, where it serves principally in the preparation of inorganic nitrate salts or as a nitrating or oxidizing agent. However, use of the liquid acid as a chemical reactant or as an acidulating agent has always required special protection of both personnel and material, inasmuch as the inherent corrosiveness normally characteristic of a strong acid is accompanied by particularly strong oxidizing capacity. These protective considerations also apply in the case of chemical propellants and explosives in which the oxidizing power of nitric acid is harnessed by reacting it under controlled conditions with one or more fuels.

The potential of liquid nitric acid as sole or principal oxidizing component in such high-energy compositions apparently was first clearly recognized by Dr. Hermann Sprengel in the early 1870's. Since the time of Sprengel's initial work on this type of charge, safer fuels and improvements in packaging and dispensing of the charges have been introduced, especially under the impetus of World Wars I and II, during which charges of the Sprengel type were of increased interest for military use.

However, in spite of these modifications, explosive containing liquid nitric acid have never received widespread acceptance, either for military purposes or in the civil explosives market. Principal reasons for this lack of acceptance are the corrosive nature of liquid nitric acid as well as the "fumes" (nitrogen oxides) that can evolve from the liquid acid under some conditions.

Another disadvantage of some of the explosives containing liquid nitric acid is their sensitivity to detonation by impact, or high "shock sensitivity." Even when carefully prepared to avoid highly incompatible components and excessive heats of mixing, certain explosives of this type also have been known to "fume off" during formulation. Following Sprengel's procedure of mixing the liquid acid and fuel at the time and site of use, including mixing in the blast hole in the case of use of the charges as blasting explosives, can minimize the more serious consequences of these problems but simultaneously may generate new ones. For example, in loading of the charges into blast holes containing appreciable amounts of water, sealing or packaging material that is watertight after several days' or weeks' exposure is generally necessary. Otherwise, ingress of water can lead not only to desensitization so that the charges cannot be detonated, but also to decomposition reactions associated with the high heat of dilution of nitric acid in water. Even in so-called

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"dry holes," losses of liquid components through subterranean fissures or similar faults and reaction of the nitric acid with some minerals, e.g., carbonate-containing formations, decreases their effectiveness as explosives.

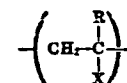
To permit storage of nitric acid explosives in the mixed state, several methods for immobilizing by thickening have been tried. For example, mineral substances of high absorptive capacity, such as kieselguhr and other diatomaceous earths, clays of various types, colloidal silicas, and, more recently, a number of high-molecular-weight organic compounds, particularly certain linear polymers of the vinyl type, have been added to the nitric acid compositions. However, none of these types of additives is inherently capable of giving products of high viscosity, cohesiveness or flexibility. Water resistance, a desirable characteristic especially in explosives to be used in wet, or potentially wet, locations, also is not markedly improved by their use. Furthermore, what thickening and stabilizing action is initially imparted by the linear polymer additives often is lost, in whole or in part, inasmuch as certain of these additives tend to undergo degradation in the presence of nitric acid.

SUMMARY OF THE INVENTION

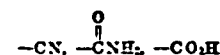
This invention provides a simple and effective means for obtaining modified aqueous nitric acid which is easier and safer to handle than that known heretofore and which has controlled free acidity and excellent stability.

Improved gelled nitric acid compositions are provided of the type comprising nitric acid having a strength of about from 70 to 99%, water, and a gelling system, the improvement comprising providing a gelling system comprising the in situ reaction products of:

(1) About from 0.5 to 10% by weight based on the weight of aqueous nitric acid of a polymer having recurring units of the general formula



wherein R is selected from hydrogen, lower alkyl, and hydroxyalkyl having up to 4 carbon atoms and X is selected from



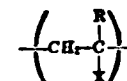
and CO_2M , wherein M is selected from ammonium and alkali metal, and

(2) About 1 to 20% by weight based on (1) of at least one metal ion having a positive valence of from 2 to 6 and selected from chromium, vanadium, manganese, titanium, antimony, zirconium and scandium.

The invention also provides a process for the production of these compositions which comprises bringing into contact:

(1) A nitric acid composition having a strength of about from 70 to 99%,

(2) A polymer having recurring units of the general formula



wherein R is defined as above, and

(3) A salt of at least one of the metal ions specified above.

The invention further provides explosive compositions comprising the nitric acid compositions indicated above in addition to about from 5 to 30% of a fuel, up to 40%

of a self-explosive sensitizer and up to 50% of an inorganic oxidizing salt.

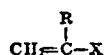
DESCRIPTION OF THE PREFERRED EMBODIMENTS

The expression "soluble in nitric acid" and similar terms as used herein refer to components having appreciable solubility at ambient temperatures of (typically) 20 to 25° C. in the particular strength of aqueous nitric acid being employed. This solubility of the polymer should be at least about 10% by weight and preferably appreciably greater, e.g., at least about 50%. Furthermore the polymer should not precipitate from the aqueous nitric acid or agglomerate into flocculates or "lumps." Crosslinking of the polymer by the polyvalent metal ions forms a structure which is a gel rather than a solid precipitate. This gelled structure swells in the aqueous nitric acid, holding the aqueous nitric acid, and is of substantially constant composition throughout. The gelled, crosslinked structure contains a fairly low ratio of polymer solids to liquid phase, e.g., less than about 1:10, this ratio being roughly equal to the weight ratio of the polymer to liquid phase, in contrast to precipitates or agglomerates in which there is a high ratio of polymer solids to liquid phase.

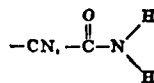
Reference to stability in nitric acid unless indicated otherwise indicates the absence of significant degradation of or attack on the polymer, or of the metallic ions, in the particular strength of aqueous nitric acid involved. Since prolonged stability often is of special significance in gelled compositions, stability refers particularly to absence of significant degradation of the gelled structure for a period of 4 to 12 hours.

Strength, as used with regard to nitric acid, expresses in percent the relationship between 100% (dry) nitric acid and the weight of nitric acid plus water in a particular acid. The aqueous nitric acid used in forming compositions of this invention generally will have a strength of about from 70 to 99%. Most effective use of the gel products, especially for explosive and propellant compositions is usually made when the strength of the acid is 75% or greater, particularly 75 to 97%, and this latter range of strengths is, accordingly, particularly preferred. In general, for a given amount of polymer employed, firmer gels are obtained in nitric acid of higher strengths.

The polymers which can be used in this invention comprise units derived from acrylic monomers of the formula



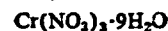
where R is hydrogen, lower alkyl or hydroxy alkyl having up to 4 carbon atoms; X is



COOH, or COOM; and M is ammonium or an alkali metal. Examples of such monomers are amides such as acrylamide, methacrylamide, α -2-hydroxymethyl acrylamide, or α -ethyl acrylamide; nitriles such as acrylonitrile, methacrylonitrile, and α -butylacrylonitrile; acids such as acrylic acid per se, methacrylic acid, α -ethylacrylic acid and α -propyl acrylic acid; and salts such as sodium or ammonium acrylate and alkyl ammonium acrylates. Particularly preferred polymers from the viewpoint of solubility and commercial availability are homopolymers formed of acrylamide, acrylonitrile, or acrylic acid and copolymers of these monomers, particularly copolymers containing at least 5% of acrylonitrile or acrylamide. The polymers are preferably preformed, i.e., formed before their addition to the nitric acid, and have a molecular weight within the range of about from 1 to 6 million. Acrylamide polymers having a molecular weight of about from 5 to 6 million, such as commercially available from American Cyanamid

as "Cyanomer" P-250, are particularly preferred. The higher molecular weight polymers, providing that they are soluble in the nitric acid of a particular strength, tend to provide firmer gels in shorter periods of time for a given weight of polymer added to the system than do polymers of lower molecular weight. When acrylonitrile polymers are used, they preferably have a molecular weight of about from 500,000 to 5 million. The polymers of acrylic acids and salts thereof employed usually will have a molecular weight of at least about 500,000.

The polyvalent metal ions are most conveniently added to aqueous nitric acid in the form of salts of which the particular anion is not critical. These metal ions can be provided, for example, by the nitrates, e.g.,



sulfates, chlorides, carbonates, acetates, chlorates, or perchlorates of the individual metals. Of these, the nitrates are usually preferred since they are readily soluble and since they contribute no foreign ions; however, vanadyl ions are most conveniently supplied by vanadyl sulfate, $\text{VOSO}_4 \cdot 2\text{H}_2\text{O}$.

Preparation of the gelled nitric acid compositions of this invention can be accomplished by simply mixing of the nitric acid, optionally containing fuel or sensitizer components and dissolved salts such as ammonium nitrate, with the polymer followed by the addition of the source of crosslinking metal ions. Fuels or sensitizer components can alternatively be mixed with the polymer and this mixture then dispersed in aqueous nitric acid. When such additives are soluble in the system or easily dispersible and are of sufficient stability and inertness they normally are dissolved or dispersed in the aqueous nitric acid prior to the addition of polymer and source of the aforesaid polyvalent metal ions. When the additives are of marginal stability or have an inhibiting effect on ionization of the source of polyvalent metal ions or the crosslinking reaction, they usually are incorporated in the compositions after the composition has been gelled.

Solution of the polymer in nitric acid can be facilitated by first dissolving it in a small amount of water; such water is of course taken into consideration in determining the desired final acid strength. The mixing usually is conducted at ambient temperatures (20 to 25° C.), but temperatures down to the freezing point of the mixture can also be used without deleterious effects. Temperatures above about 40° C. should ordinarily be avoided in that at such temperatures hazardous, premature degradative oxidation of some fuels and sensitizers, including the acrylic polymers, can be initiated.

The viscosity of the gelled compositions can be varied according to the needs of a particular application. In general, the viscosity of the gel can be increased by increasing the strength of the acid, by increasing the percentage of polymer in the system, and by increasing the relative proportion of polyvalent metal ion used for a given quantity of polymer.

The compositions of this invention have greater homogeneity, resistance to disintegration or leaching by water, and stability, i.e., resistance to degradation and settling out of components, than compositions which are merely thickened. This greater homogeneity, stability and water-resistance is particularly advantageous when the gelled nitric acid compositions, which can contain added fuels and sensitizers, are to be used as explosives particularly in wet locations, since disintegration and leaching of a composition of water, if such occurs, can lead to failures to detonate or to propagate a detonation throughout the length of an explosive column. If the explosive structure degrades, i.e., by virtue of disintegration of the gel structure, subsequent segregation of components, particularly undissolved (solid) fuels and sensitizers, as discussed hereinafter, can occur under the force of gravity, and the components in a borehole, whether in a container or cartridge, shucked therefrom, or simply pumped into a borehole will become so heterogeneous that complete

failure of detonation or propagation of detonation through the entire length of the column of explosive charge will occur.

The gelled nitric acid compositions of this invention can be employed for a variety of applications in which liquid aqueous nitric acid is ordinarily employed, e.g., as an oxidizing or nitrating agent in chemical synthesis, as an acidifying agent in mineralogical and other processes, in preparing nitrate salts, and in like operations. The gelled nitric acid compositions find particular merit in such applications when delayed action is desirable or required, inasmuch as the gels tend to release the acid slowly. However, the gelled nitric acid compositions of this invention have been found to have particular utility as explosives, and they are readily formulated to meet the specific requirements of such use.

Several of the gelled nitric acid compositions described above are inherently satisfactory as detonating explosives with further additives, i.e., they can be detonated with moderate-strength primers in diameters of 6 inches or less under moderate conditions of confinement, such as provided by a borehole or a container of moderate wall thickness. Preferably for explosive applications, the compositions of this invention also contain one or more fuels and/or nonexplosive sensitizers which are stable in the nitric acid of the strength used in preparing the gels. Examples of nonexplosive fuels are the mono- and dinitroaromatic hydrocarbons, such as nitrobenzene, o-monomonitrotoluene and dinitrotoluene; liquid and solid hydrocarbons and hydrocarbon fractions, particularly refined petroleum and mineral oils and the aromatic hydrocarbons, such as benzene, toluene, and the xylenes, carbohydrates, including various cellulose and starch products, e.g., cornstarch, potato starch, wood and paper pulps and sugar; siliceous fuels, including silicon itself and mixtures and alloys of silicon with heavy metals, e.g., ferrosilicon; and sulfur. Light metal fuels such as aluminum also are potentially useful in some of the gelled compositions, provided that they are, or can be made, sufficiently resistant to attack by the nitric acid. The gel copolymer per se acts as a fuel and except as otherwise indicated is included in calculating the amount of nonexplosive fuel and oxygen balance. Ordinarily, the gels for use as explosive compositions will be formulated to have an oxygen balance of about from -25 to +10%. Surfactants can be employed to insure complete dispersion of some fuels, e.g., the petroleum and mineral oils, in the explosive composition.

In addition to the nonexplosive fuels and/or sensitizers named above the explosive compositions of this invention can, if desired, contain an additive of the art-recognized self-explosive type, provided that such additive is stable in the strengths of nitric acid used in preparing the gels. TNT, for example, exhibits a high degree of stability in all strengths of aqueous nitric acid and hence is a particularly useful additive of the "self-explosive" type. Examples of other "self-explosive" components which can be used in the gelled nitric acid based compositions of this invention are RDX, nitrocellulose, smokeless powder, and other organic nitramines, nitrates and nitrocompounds. For reasons of economy and compatibility, TNT is preferred for use in the composition of this invention. The TNT or its mixtures (e.g., with ammonium or sodium nitrate) can be introduced into the compositions in the form of crystals, grains, pellets, flakes, or other particulate form which allows ready dispersion thereof. In general, up to 85%; and preferably up to 40%, by weight of self-explosive additive based on weight of the composition is used.

As an additional component, the explosive compositions of this invention can contain up to about 85%, and preferably 5 to 50%, based on the total weight of composition, of an inorganic oxidizing salt, particularly an inorganic nitrate salt such as ammonium or sodium nitrate. The presence of the salt is beneficial in that it con-

tributes to the total energy of the composition. At least part of the salt, when used, will be dissolved in the system; however, some of the salt can be undissolved providing that it is uniformly distributed throughout the gelled nitric acid matrix.

Stable, gelled nitric acid compositions found especially economical and efficient as detonating explosives comprise a uniform blend of:

(a) About from 25 to 95% by weight of aqueous nitric acid having a strength of from about 70 to 99%, and preferably 75 to 97%;

(b) About from 5 to 30% of a nonexplosive fuel, preferably selected from siliceous fuels, light metals, liquid and solid hydrocarbons, carbohydrates, sulfur, mono- and dinitroaromatic hydrocarbons, and mixtures of such fuels and/or sensitizers;

(c) Up to about 40% of a self-explosive sensitizer, particularly TNT;

(d) Up to about 50% of an inorganic oxidizing salt, typically, an inorganic nitrate; and

(e) A crosslinked gelling system of the type indicated above.

Agitation of the composition during formulation is usually continued until after the composition is gelled, particularly when added fuels and sensitizers are solids which must be uniformly distributed throughout the gel matrix. Where fuels or other additives of marginal stability are to be incorporated in the compositions, all ingredients except such additives can be mixed and gelled, then such additives added to the finished gel.

In general, the unit or bulk strength of an explosive composition based on gelled nitric acid increases with increasing strength of the nitric acid gelled. Accordingly gels of nitric acid of 85% strength or higher are usually employed where high bulk strength is a requisite, e.g., in the bottom of a borehole. The bulk or unit strength of an explosive composition, its relative ease of initiation, and its minimum critical diameter can also be regulated to a large degree by the type and quantity of fuel and/or sensitizer employed. In general, a solid fuel such as ferrosilicon, sulfur or siliceous fuels is used to increase the bulk strength of a composition. Organic nitro compounds, typically mononitrotoluene, or dinitrotoluene or, in particular a self-explosive composition, especially TNT, are incorporated to provide compositions which are easily initiated, e.g., by a relatively small primer or by a blasting cap, in some cases, in small diameters. In many cases a combination of fuels will be employed within the range of proportions indicated to give a composition having the desired physical and explosive properties.

Especially preferred gelling systems comprise polymers of acrylamide, acrylonitrile, acrylic acid and copolymers of these monomers. The polyvalent metal ion preferred is chromic (Cr^{+3}). In addition to being readily available at reasonable cost, these compositions are particularly effective in providing firm cohesive gels having viscosities within the desired range of 100,000 to 5 million centipoises, high surface tension as evidenced by lack of tackiness, flexibility, water resistance and other desirable physical characteristics.

The compositions of this invention can be packaged in containers compatible with the gelled nitric acid, e.g., of polyethylene, polypropylene, or aluminum, and stored for several days without deterioration, "gassing" or separation of components.

Alternatively, the compositions can be prepared at the site of use and pumped or dumped directly into the borehole, which can be lined with a material such as polyethylene, which is both water-impervious and compatible with the gelled nitric acid. When such is the case, it is usually desirable that all components of the composition be liquid for ease of mixing and pumping the composition. Usually, the compositions to be pumped will be less viscous than those to be provided in containers and accordingly will comprise somewhat less of the polymer.

The explosive initiation system used with the gelled nitric acid-based explosive compositions of this invention naturally will be one which is compatible with nitric acid. To this end, the detonators, i.e., blasting caps, or boosters used in the explosive train, will preferably have shells of a metal such as aluminum or stainless steel or of, or coated by, a plastic such as polyethylene, polytetrafluoroethylene, polyoxymethylene, or polypropylene. Detonating fuse or electric lead wires extending to the cap and exposed to the gelled nitric acid compositions will usually be provided with a protective coating such as polyethylene, polytetrafluoroethylene, polyoxymethylene, or polypropylene, which is resistant to attack by nitric acid. The primer charge used with the charge can be a pressed pellet, e.g., of TNT or RDX, or a gelled nitric acid based explosive composition made suitably sensitive to actuation, e.g., by "Primacord," by the incorporation of such ingredients as grained TNT or by the use of acid of

with mixing continued at a temperature of about 25° C., except where otherwise indicated. Then the source of polyvalent metal ion, is added. Gelation is substantially instantaneous on addition of the source of polyvalent metal ions. None of the gel products shows visible indication of deterioration at ambient temperatures over periods of 8 hours or more.

Cap-sensitive explosive compositions are made with any of these gels by the admixture of a fuel, and optionally a self-explosive sensitizer and oxidizing salt. As indicated above, these components should preferably be admixed before the addition of the source of metal ion.

Similar results are obtained when the polymer used is a low molecular weight copolymer of acrylamide and acrylic acid commercially available from American Cyanamid as "Cyanomer" P-26. When scandium (Sc³⁺) is used as the crosslinking agent, similar products to those of Example 16 are obtained.

TABLE I

| Example | Acid strength, percent | Acrylic Polymer | Percent by wt. of aq. HNO ₃ | Polyvalent metal in ion, percent by wt. of acrylic polymer | Gel product description |
|---------|------------------------|--------------------------------------|--|--|---|
| 1..... | 70 | Polyacrylamide..... | 1.44 | Cr ³⁺ , 11.3%..... | Weak gel. |
| 2..... | 75 | do..... | 1.5 | Cr ³⁺ , 11.4%..... | Medium gel. |
| 3..... | 90 | do..... | 1.47 | Cr ³⁺ , 11.4%..... | Medium gel. |
| 4..... | 97 | do..... | 1.43 | Cr ³⁺ , 11.4%..... | Firm gel. |
| 5..... | 75 | do..... | 2.25 | Cr ³⁺ , 2.2%..... | Weak gel. |
| 6..... | 75 | do..... | 2.25 | Cr ³⁺ , 11%..... | Gel which was elastic and adhered to glass for neo. |
| 7..... | 97 | do..... | 1.6 | Cr ³⁺ , 6.5%..... | Weak gel. |
| 8..... | 97 | do..... | 2.4 | Cr ³⁺ , 7.5%..... | Medium gel. |
| 9..... | 97 | do..... | 2.35 | Cr ³⁺ , 10.8%..... | Firm gel. |
| 10..... | 70 | do..... | 2.14 | V ³⁺ , 17%..... | Medium gel, swelled by gas in 1-2 hr. |
| 11..... | 97 | Polyscrylonitrile ¹ | 1 | Cr ³⁺ , 26%..... | Weak gel. |
| 12..... | 95 | Polyacrylamide ¹ | 3 | Cr ³⁺ , 8%..... | Medium firm gel. |
| 13..... | 95 | do..... | 2.2 | Mn ²⁺ , 15%..... | Medium weak gel. |
| 14..... | 75 | do..... | 1.5 | Zr ⁴⁺ , 37%..... | Firm gel. |
| 15..... | 75 | do..... | 1.5 | Sb ³⁺ , 49%..... | Medium gel. |
| 16..... | 75 | do..... | 1.5 | Ti ⁴⁺ , 21%..... | Medium gel. |

¹ Mol. wt. 1-2 million. ² Mol. wt., ca. 500,000.

higher strength. Such primer charges of gelled nitric acid compositions typically will be in a cartridge of a high-strength plastic such as polyethylene or polypropylene, which is also compatible with nitric acid.

In the following examples which illustrate this invention, parts, percentages and ratios are by weight unless otherwise indicated. In the following examples, the terms noted below mean the following:

"Cheese-like."—Viscosity of about from 10 million to 20 million cps. (centipoises) as measured with TF¹ spindle at 0.5 r.p.m. on the Brookfield Synchro-lectric viscometer.

Very firm.—Viscosity of about from 3 million to 10 million cps. with same conditions of measurement as for "cheese-like" gels.

Firm.—Viscosity of about from 1 million to 3 million cps. measured with a TE spindle at 1.0 r.p.m.¹ on a Brookfield Synchro-lectric viscometer, model RVT, with heli-path attachment.

Medium firm.—Viscosity of about from 400,000 to 1 million cps. using the same conditions of measurement on the viscometer.

Weak.—Viscosities generally less than about 400,000 cps., generally 200,000 to 400,000 cps.

The following examples illustrate compositions of this invention containing various strengths of nitric acid and the use of various combinations of polymers and polyvalent metal ions.

Examples 1-16

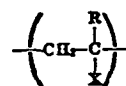
Gelled aqueous nitric acid compositions are prepared from the material noted in Table I. The polyacrylamide used in these examples is "Cyanomer" P-250, commercially available from American Cyanamid, having a molecular weight of 5-6 million. The nitric acid is charged to a mixing vessel then the polymer is added and dissolved

¹ Changes in spindle and r.p.m. necessary to obtain accurate readings.

I claim:

1. In gelled nitric acid compositions having a nitric acid strength of about from 70 to 99% and comprising nitric acid, and water, the improvement which comprises gelling said composition in situ with the reaction product of:

(1) about from 0.5 to 10% by weight based on the weight of aqueous nitric acid of a polymer having recurring units of the general formula



wherein R is selected from hydrogen, lower alkyl, and hydroxyalkyl having up to 4 carbon atoms and X is selected from



and CO₂M, wherein M is selected from ammonium and alkali metal, and

(2) about from 1 to 20% by weight based on (1) of at least one metal ion having a positive valence of from 2 to 6 and selected from chromium, vanadium, manganese, titanium, antimony, zirconium and scandium.

2. A composition of claim 1 wherein said composition comprises about from 1.0 to 5% by weight, based on the nitric acid, of the polymer and about from 2 to 12% by weight, based on the polymer, of the metal ion.

3. An explosive composition of claim 2 wherein said nitric acid composition further comprises about from 5 to 70% of nonexplosive fuel.

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4. A composition of claim 3 wherein the nitric acid composition further comprises up to 40% of a self-explosive sensitizer and up to 50% of an inorganic oxidizing salt.

5. A composition of claim 4 wherein the self-explosive sensitizer is trinitrotoluene and the inorganic oxidizing salt is an inorganic nitrate.

6. A composition of claim 3 wherein said polymer comprises polyacrylamide.

7. A composition of claim 3 wherein said polymer comprises polyacrylonitrile.

8. A composition of claim 3 wherein said polymer comprises a copolymer of acrylamide and acrylonitrile, wherein each component comprises at least 5% of said polymer.

9. A composition of claim 3 wherein said polyvalent metal ion is chromium.

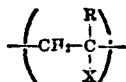
10. A composition of claim 3 wherein said polyvalent metal ion is vanadium.

11. A composition of claim 3 wherein said polyvalent metal ion is manganese.

12. A process for the production of gelled aqueous nitric acid compositions which comprises bringing into contact:

(1) a nitric acid composition having a strength of about from 70 to 99%.

(2) a polymer having recurring units of the general formula



wherein R is selected from hydrogen, lower alkyl,

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and hydrovylalkyl having up to 4 carbon atoms and X is selected from



and CO_2M , wherein M is selected from ammonium and alkali metal, and

(3) the salt of at least one metal ion having a positive valence of from 2 to 6 and selected from chromium, vanadium, manganese, titanium, antimony, zirconium and scandium.

13. A process of claim 12 wherein the nitric acid composition and the polymer are admixed and the metal ion brought into contact with the resulting mixture.

14. A process of claim 13 wherein about from 5 to 30% of a nonexplosive fuel, up to 40% of a self-explosive sensitizer and up to 50% of an inorganic oxidizing salt are admixed with the composition before the addition of the metal ion.

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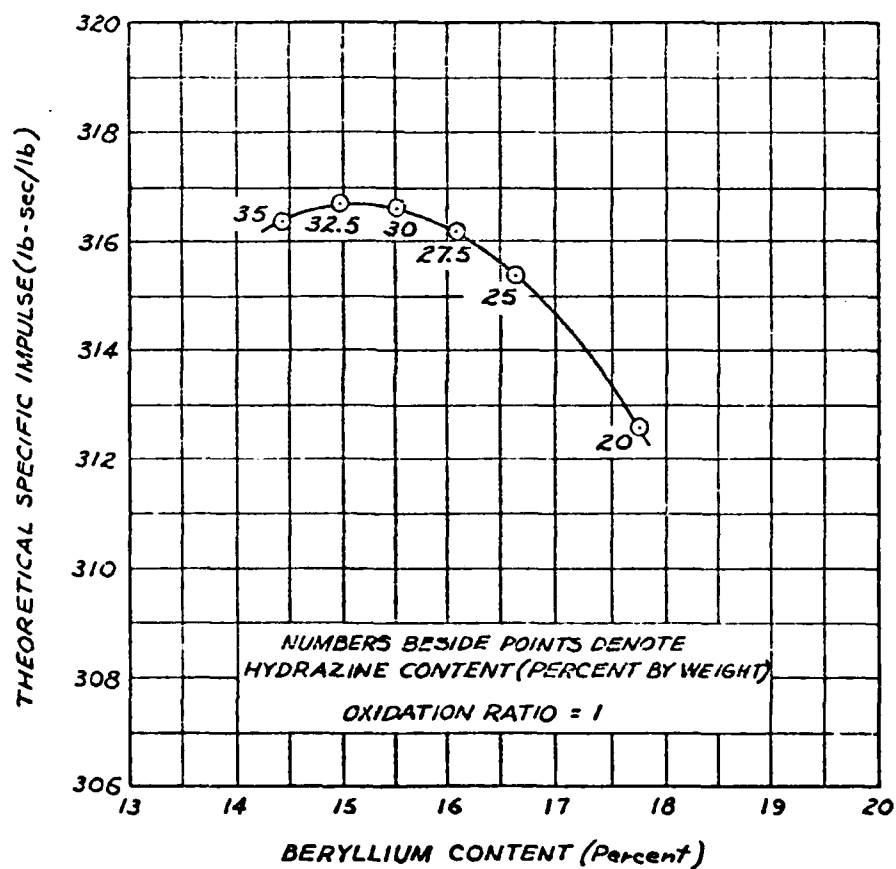
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149—39, 40, 41, 42, 43, 44, 47, 55, 56, 60, 61, 62, 69, 70, 74

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GELLED HYDRAZINE PROPELLANT COMPOSITIONS CONTAINING
HYDRAZINE NITRATE AND A FINELY DIVIDED METAL
Filed Nov. 9, 1964

3,811,970



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GELLED HYDRAZINE PROPELLANT COMPOSITIONS CONTAINING HYDRAZINE NITRATE AND A FINELY DIVIDED METAL

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9 Claims

This invention relates to heterogeneous, gelled propellant compositions.

It is an object of this invention to provide novel gelled propellant compositions. Another object is to provide gelled propellant compositions which burn to yield reaction products of low molecular weight, thereby producing increased propulsive performance. Still another object is to provide gelled propellants varying in consistency from low viscosity gels to solid rubbery gels. Other objects and advantages will be apparent from the drawing and the following detailed description.

Referring to the drawing, the figure is a graph wherein the theoretical specific impulse of compositions of this invention is plotted as a function of beryllium content.

The novel propellant compositions of this invention consist essentially of hydrazine, hydrazine nitrate, a gelling agent, and a finely divided solid metallic fuel. In addition, the compositions may contain minor amounts of burning rate modifiers such as chromic oxide, or methoxy polyethylene glycols.

Hydrazine, gelled by the addition of the gelling agent, provides the binder for the propellant composition.

The gelling agent is selected for ability to maintain a stable gel in the presence of hydrazine nitrate. Galactomannan polysaccharides and methyl vinyl ether-maleic anhydride copolymers are examples of gelling agents which do not "salt out" to break down the hydrazine gel structure in the presence of hydrazine nitrate.

The amount of gelling agent used is an important factor governing the consistency of the propellant composition. For example, compositions containing about 1.2% by weight Jaguar A-20-B (a galactomannan polysaccharide) are strong, elastic, cohesive gels which flow easily and yet keep metallic fuel particles in suspension. By increasing the concentration of this gelling agent to about 6% or greater, a solid, rubbery gel can be obtained. Thus, by varying the amount of gelling agent, the compositions of this invention can be adapted to various uses. For example a solid, rubbery gel can be utilized as a conventional solid propellant, while less viscous compositions can be pumped, injected, or extruded into reaction chambers to provide propulsive power.

The consistency of the propellant composition is also influenced by solids content. High solids content tends to produce viscous compositions and often reduces gel strength. Hydrazine nitrate is, therefore, chosen as the oxidizer, since its solubility in hydrazine reduces the dispersed solids content of the composition.

Finely divided metallic fuels such as beryllium, aluminum, magnesium, zirconium, hafnium, alloys and hydrides of such fuels, and mixtures thereof, are included in the propellant compositions of this invention. The metallic fuel is added in an amount such that the oxidation ratio of the composition is about 0.94 to 1.50 and preferably about 0.98 to 1.15. The oxidation ratio of the composition is defined by the formula:

$$\text{Oxidation ratio} = \frac{O}{C + \left(\frac{v}{2}\right)M}$$

wherein O equal the total amount of oxygen in the propellant composition; C equals the total amount of carbon; M equals the total amount of metallic fuel calculated as free metal; and v equals the valence of the metal, preferably the characteristic valence of the metal in its most stable oxide. The amounts of O, C, and M are expressed in terms of the number of gram atoms.

For an oxidation ratio of 1, there is sufficient oxygen in the composition to oxidize the carbon, which may be present in the gelling agent or burning rate modifier, to carbon monoxide and to oxidize the metallic fuel to its metal oxide. Since the oxygen reacts preferentially with the metallic fuel, it is apparent that the compositions of this invention do not contain sufficient oxygen to substantially oxidize the hydrazine. Therefore, the hydrazine, rather than being oxidized to nitrogen and water, will decompose exothermically to yield nitrogen and hydrogen when the composition is burned. The term "burned" is used, in the specification and claims, to describe decomposition as well as oxidation reactions of the propellant compositions.

The square of the specific impulse of a propellant is, approximately, directly proportional to the flame temperature and inversely proportional to the molecular weight of gaseous reaction products. Therefore, the lighter reaction products provided by the oxidation ratios specified above result in a higher specific impulse than would be obtained if sufficient oxygen were present to oxidize the hydrazine. The presence of metallic fuel also increases the flame temperature to provide a higher specific impulse.

Sufficient metallic fuel is preferably present in the composition to provide a flame temperature high enough to effect substantially complete oxidation of the metal. Otherwise, oxygen not utilized by the metal will oxidize the hydrogen of the hydrazine to form water and a lower specific impulse will be obtained. Preferably the flame temperature of the composition will be at least as high as the melting point of the metal oxide formed when the composition burns. The amount of a particular metallic fuel required to achieve a desired temperature can be readily calculated by those skilled in the art.

To obtain maximum specific impulse, there must be a balance between the metallic fuel content and hydrazine content of the composition. Increased percentages of metallic fuel produce higher flame temperatures and thus tend to increase specific impulse. However, increased percentages of metallic fuel necessarily result in lower percentages of hydrazine. Since hydrazine provides the major amount of propulsive gases, lowering the percentage of hydrazine tends to reduce specific impulse. The optimum compromise between these competing factors can be determined by calculations familiar to those skilled in the art.

The especially preferred compositions of this invention utilize finely-divided Be as the metallic fuel component since Be has the advantage of forming a highly stable oxide which does not decompose or vaporize to any substantial extent after its formation. This is advantageous because decomposition or vaporization of metal oxides absorb heat energy, thereby reducing the temperature and pressure of the thrust-producing gases.

The figure illustrates calculated specific impulses of compositions containing varying amounts of beryllium and having an oxidation ratio of 1. The high specific impulses produced by compositions of this invention are apparent from this graph, particularly within the range of 15% to 17% by weight Be.

The following are examples of compositions prepared according to this invention.

EXAMPLE 1

A gel of the following compositions was prepared:

| Ingredient: | Percent by weight |
|-------------------------|-------------------|
| Hydrazine | 24.60 |
| Hydrazine nitrate | 57.50 |
| Beryllium | 16.4 |
| Jaguar A-20-B | 1.2 |
| Chromic oxide | 0.3 |

The fluid gel was loaded into a cylindrical container and burned under pressure.

The burning rate was about .85 in./sec. at 1000 p.s.i.a. A theoretical specific impulse of about 314 lb.-sec./lb. and a theoretical flame temperature of about 3264° K. were calculated for the composition.

EXAMPLE 2

A gel of the following compositions was prepared:

| Ingredient: | Percent by weight |
|-------------------------|-------------------|
| Hydrazine | 24.20 |
| Hydrazine nitrate | 56.5 |
| Beryllium | 16.12 |
| Jaguar A-20-B | 1.13 |
| Chromic oxide | 2.0 |

Burning tests as described above were conducted. The composition burned at a rate of 1.05 in./sec. at 1000 p.s.i.a. A theoretical specific impulse of 312 lb.-sec./lb. and a theoretical flame temperature of 3230° K. were calculated for the composition.

EXAMPLE 3

A gel of the following composition was prepared:

| Ingredient: | Percent by weight |
|--|-------------------|
| Hydrazine | 24.24 |
| Hydrazine nitrate | 56.24 |
| Beryllium | 16.09 |
| Jaguar A-20-B | 0.98 |
| Chromic oxide | 0.49 |
| Carbowax 350 (a methoxy polyethylene glycol) | 1.96 |

The composition burned at a rate of 0.67 in./sec. at 1000 p.s.i.a. A theoretical specific impulse of 312 lb.-sec./lb. and a theoretical flame temperature of 3220° K. were calculated.

Many other compositions within the scope of this invention as defined in the appended claims, will be apparent to those skilled in the art.

I claim:

1. A heterogeneous propellant composition consisting essentially of hydrazine; hydrazine nitrate; finely-divided metallic fuel selected from the group consisting of beryllium, aluminium, magnesium, zirconium, hafnium, alloys of the aforesaid metals, hydrides of the aforesaid metals, and mixtures thereof; and a gelling agent capable of

maintaining a stable hydrazine gel structure in the presence of hydrazine nitrate, said composition having an oxidation ratio of about .94 to about 1.50 as defined by the formula:

$$\text{Oxidation ratio} = \frac{O}{C+M\left(\frac{v}{2}\right)}$$

wherein O equals the total amount of oxygen in said composition; C equals the total amount of carbon; M equals the total amount of metal; and v equals the valence of the metal, said O, C, and M being expressed in terms of the number of atomic equivalents, and wherein said metallic fuel is present in said composition in an amount at least sufficient to provide a flame temperature at least equal to the melting temperature of the metal oxide produced upon burning of said composition.

2. The composition of claim 1 wherein said composition has an oxidation ratio of about 0.98 to about 1.15.

3. The composition of claim 1 wherein said composition further contains a minor amount of a burning rate modifier.

4. The composition of claim 1 wherein said gelling agent is a galactomannan polysaccharide.

5. The composition of claim 1 wherein said gelling agent is a copolymer of methyl vinyl ether and maleic anhydride.

6. The composition of claim 1 wherein said metallic fuel is beryllium.

7. The composition of claim 6 wherein said composition contains from about 15% to about 17% beryllium by weight.

8. A propellant composition according to claim 7 wherein the gelling agent is a galactomannan polysaccharide and the composition contains a minor amount of a burning rate modifier.

9. The propellant composition of claim 8 wherein said burning rate modifier consists essentially of chromic oxide and a methoxy polyethylene glycol.

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U.S. Cl. X.R.

149-18, 19, 20, 43

[54] METHOD OF PROPULSION USING STABLE, HIGH ENERGY COMPOSITIONS WITH HYDRAZINE CONTAINING WORKING FLUID

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[73] Assignee: Explosives Corporation of America, Issaquah, Wash.

[22] Filed: Jan. 27, 1964

[21] Appl. No.: 340,127

[52] U.S. Cl.: 60/217, 44/7 B, 44/7 D, 149/36, 149/43, 149/114, 60/216

[51] Int. Cl.: C06d 5/10

[58] Field of Search: 60/35.4, 217, 149/36, 43; 44/7 B, 7 D

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Primary Examiner—Benjamin R. Padgett
Attorney, Agent, or Firm—Graybeal, Cole & Barnard

[57] ABSTRACT

The present invention relates to stable, high energy compositions for utilization as monopropellants in reaction engines or as explosives, depending upon proportionation of ingredients. More particularly, the present invention relates to preferably thixotropic compositions comprising a particulate metal fuel and hydrazinium nitrate as an oxidizer, coupled with one or more working fluid and desensitizer ingredients, providing high performance and high bulk density with very good physical and chemical stability. Specifically, high energy reaction systems according to the invention utilize beryllium, aluminum, and mixtures thereof as the metal fuel contributing constituent, utilize hydrazinium nitrate as the oxidizer contributing constituent, and utilize as the working fluid and desensitizer a hydrazine containing material with one or more ingredients selected from the group consisting of hydrazine, monomethylhydrazine, unsymmetrical dimethylhydrazine, and mixtures thereof with water.

34 Claims, 2 Drawing Figures

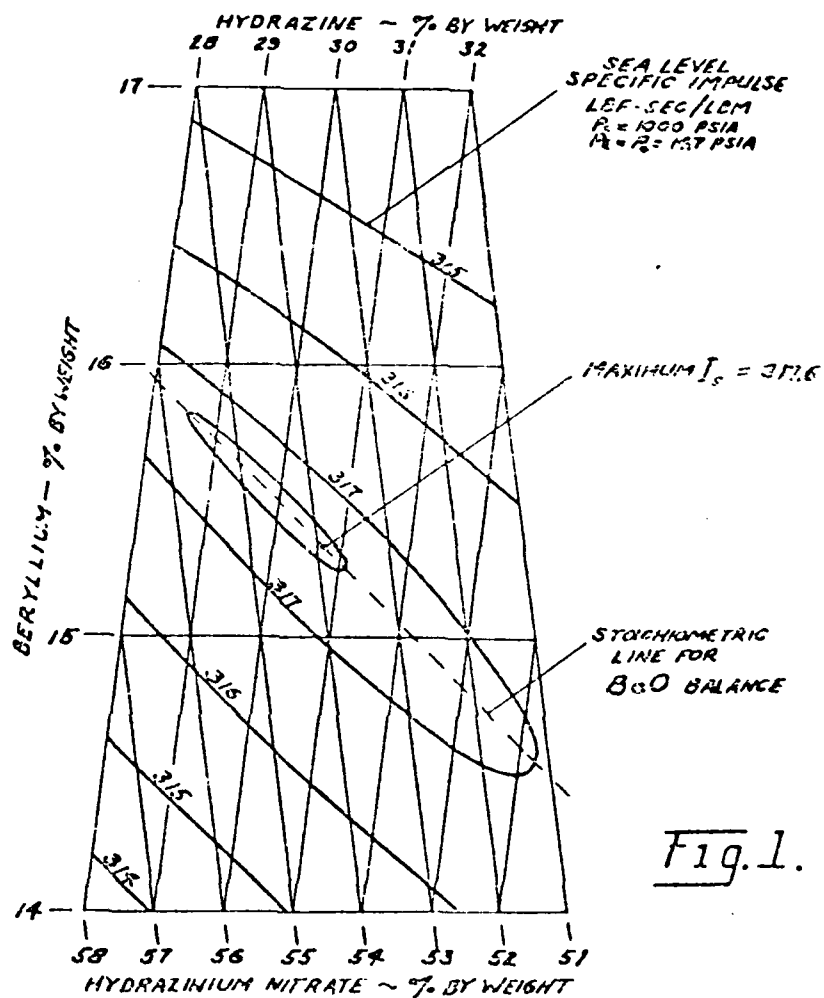


Fig. 1.

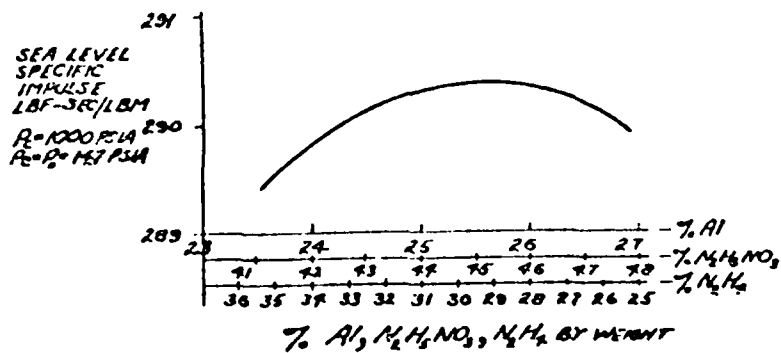


Fig. 2.

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,861,138 Dated January 21, 1975

Inventor(s) Robert M. Bridgforth, Jr., et al.

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

The term of this patent subsequent to
August 4, 1987, has been disclaimed.

Signed and Sealed this

Sixteenth Day of November 1976

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks

METHOD OF PROPULSION USING STABLE, HIGH ENERGY COMPOSITIONS WITH HYDRAZINE CONTAINING WORKING FLUID

Reaction systems involving monopropellant compositions are known to have inherent advantages as compared with bipropellant reaction systems in terms of ease of storage and handling, and in terms of greater simplicity of propellant delivering pumps, feed systems and injector components and the like. However, prior monopropellant compositions have proven to be either low in propulsion performance or so sensitive to shock detonation as to be dangerous to handle and use. In contrast, propellant compositions of the present invention combine high performance (up to about 318 seconds sea level specific impulse) with very good chemical stability and insensitivity to shock, many of the formulations characteristic of the invention being incapable of detonation. By realizing an inherent stability in terms of relative insensitivity to shock detonation, compositions of the present invention used as monopropellants can minimize and in many cases eliminate the elaborate detonation safeguards normally required when using prior high performance monopropellants.

It is a further advantage and feature of certain compositions according to the present invention that such are bi-phase, thixotropic mixtures, the compositions in this respect having present therein the metallic fuel in finely divided, solid state and having the oxidizer contributing constituent and working fluid present in liquid phase, the mixture further comprising a gelling agent giving to the composition the properties of a semi-solid insofar as storing and handling characteristics, the compositions nonetheless being pumpable and therefore compatible with known handling techniques for gelled propellants. However, in contrast to most gelled monopropellants, wherein the fuel and oxidizer are present and thoroughly intermixed in the same phase (i.e., liquid) only the surfaces of the solid phase fuel particles are exposed to the liquid phase oxidizer in the thixotropic compositions of the present invention. There is thus better segregation of the fuel and oxidizer than is the case in a monophasic fuel-oxidizer mixture, and the insensitivity to shock is consequently substantially improved.

Yet another advantage of compositions of the present invention when used as reaction engine propellants is that such compositions are compatible with most common materials employed in fabrication of reaction engine components.

Yet a further feature and advantage of compositions of the present invention is that formulations thereof compounded for use as explosives are not hypersensitive to shock yet provide very high power performance, producing more gas per unit mass than the conventional aluminum-ammonium nitrate explosive reaction. Certain typical explosive formulations thereof attain the highest performance of any known explosives, based on the Trauzl Block Test.

These and other objects, features, advantages and characteristics of compositions according to the present invention will be apparent from the following illustrative examples and discussion thereof.

In the accompanying illustrations:

FIG. 1 graphically presents sea level specific impulse data at and near optimum for the reaction system com-

posed of beryllium, hydrazinium nitrate, and hydrazine; and

FIG. 2 graphically presents sea level specific impulse data at and near optimum for the reaction system composed of aluminum, hydrazinium nitrate, and hydrazine.

EXAMPLE 1

As a first example of a propellant composition according to the present invention, the optimum formulation presented at FIG. 1 was selected, wherein the composition consists of the following ingredients, by weight:

| | |
|---|--------|
| Be | 15.32% |
| N ₂ H ₄ NO ₂ | 53.91% |
| N ₂ H ₄ | 30.77% |

Evaluation of this composition indicates that under operating conditions involving a chamber pressure of 1,000 psia and an exit pressure of 14.7 psia, the theoretical sea level specific impulse (with shifting equilibrium) is about 318 lbf-sec/lbm, and the composition has a bulk density of 0.051 lbm/in³. Further evaluation of this system indicates that the vacuum specific impulse with an exhaust nozzle area ratio of 40 is approximately 375 lbf-sec/lbm.

EXAMPLE 2

To illustrate formulation of the reaction and working fluid ingredients of the composition with a gelling agent, the composition of Example 1 was mixed with 3 percent colloidal silica, with the resulting composition being readily pumpable with an injector pressure drop of about 100 psi. Shock sensitivity tests of this composition indicate that the shock sensitivity is 15-20 Kg-cm, based on standard JANAF drop-weight test procedure. Storage tests indicate the composition to be compatible; no pressure buildup was observed in a closed sample during four week's storage under standard conditions. Theoretical sea level specific impulse of this thixotropic composition is evaluated at about 315 lbf-sec/lbm.

EXAMPLE 3

To show the effect of addition of water to the system presented in Example 1, the system investigated in Example 2 was composed of the following ingredients by weight:

| | |
|---|-----|
| Be | 17% |
| N ₂ H ₄ NO ₂ | 18% |
| N ₂ H ₄ | 40% |
| H ₂ O | 25% |

Evaluation indicated very little loss in theoretical performance providing a sea level specific impulse of about 310 lbf-sec/lbm.

EXAMPLE 4

To illustrate formulation of the reactants and working fluid and desensitizer ingredient of the composition presented in Example 3 with a gelling agent, this composition was evaluated in admixture with 6 percent by weight of colloidal silica. The shock sensitivity of this thixotropic composition was in excess of 120 kg-cm according to standard JANAF drop-weight test procedure, the shock insensitivity of this composition being markedly greater than that of the composition of Ex-

ample 2, due to the water content of the composition. This composition also proved to be fully compatible under the storage test conditions set forth in Example 2.

EXAMPLE 5

To illustrate another composition according to the invention, involving a hydrazine-rich mix (i.e., excess working fluid and desensitizer), the following composition was formulated, with proportions by weight:

| | |
|---|-----|
| Be | 10% |
| N ₂ H ₄ NO ₂ | 34% |
| N ₂ H ₄ | 56% |

Estimated sea level theoretical specific impulse was evaluated at 300 lbf-sec/lbm. This composition, compounded with 3 percent colloidal silica by weight exhibited a shock sensitivity of greater than 120 kg-cm, and the thixotropic composition proved to be fully compatible upon four week's storage of a closed sample. The superior shock insensitivity of this composition, as compared with that of Example 2, is attributed to the excess hydrazine.

EXAMPLE 6

To illustrate utilization of another hydrazine containing working fluid in a system according to the invention, the following formulation was prepared, with proportions by weight:

| | |
|---|--------|
| Be | 15.32% |
| N ₂ H ₄ NO ₂ | 52.91% |
| CH ₃ N ₂ H ₂ | 30.77% |

Estimated theoretical specific impulse under sea level conditions as set forth in Example 1 was evaluated at 308 lbf-sec/lbm. A thixotropic composition (with 3 percent colloidal silica by weight added) showed a shock sensitivity of 15-20 kg-cm, and the composition was fully compatible under the storage conditions detailed in Example 2.

EXAMPLE 7

A further formulation according to the invention was evaluated, wherein a like proportion of unsymmetrical dimethyl hydrazine was substituted for the monomethylhydrazine working fluid of the composition set forth in Example 6, with like performance characteristics.

Substitution of monomethylhydrazine or unsymmetrical dimethylhydrazine for the hydrazine as the working fluid in general involves a decrease in theoretical sea level specific performance of about 9-15 seconds.

EXAMPLE 8

To illustrate a typical and optimized composition utilizing aluminum as the metallic fuel constituent, the following composition was formulated on the basis of the data presented at FIG. 2, with proportions by weight:

| | |
|---|-------|
| Al | 25.4% |
| N ₂ H ₄ NO ₂ | 44.8% |
| N ₂ H ₄ | 29.8% |

Evaluation indicated that a maximum sea level specific impulse at a chamber pressure of 1,000 psia and an exit pressure of 14.7 psia for this composition is about 290 lbf-sec/lbm (again note FIG. 2) and that the bulk den-

sity of the composition is 0.055 lbm/in³. A somewhat different mix characterizing this three component system was tested as to sensitivity and compatibility, with the following proportions by weight:

| | |
|---|--------|
| Al | 15.32% |
| N ₂ H ₄ NO ₂ | 53.91% |
| N ₂ H ₄ | 30.77% |

This composition, compounded with 3 percent by weight of colloidal silica, demonstrated a shock sensitivity of 15-20 kg-cm, and full compatibility under the test storage conditions specified in Example 2.

EXAMPLE 9

To illustrate the utilization of an aluminum-hydrazine nitrate-hydrazine system with additional water to reduce sensitivity to shock, the following formulation with proportions by weight was evaluated:

| | |
|--|-----|
| Al | 17% |
| N ₂ H ₄ NO ₂ | 18% |
| N ₂ H ₄ | 40% |
| H ₂ O | 24% |
| (NH ₄) ₂ Cr ₂ O ₇ | 1% |

Upon compounding with 3% colloidal silica, the shock sensitivity on test proved to be in excess of 120 kg-cm and the compatibility of the mix was sufficient to permit usage thereof under conditions involving short-to-intermediate storage times (ammonium dichromate being added in the above formulation to inhibit aluminum-water reactivity and improve compatibility).

EXAMPLE 10

A formulation was evaluated involving the same proportionation as in Example 6 except that an equal weight of aluminum was substituted for the beryllium as the fuel constituent. Upon compounding with 3 percent colloidal silica, the shock sensitivity characteristics of the mix under the drop weight test procedure specified above was 110-120 kg-cm, and the composition proved to be fully compatible under the above specified storage conditions.

EXAMPLE 11

A further formulation was evaluated, involving the ingredients in the proportions specified in Example 5, with aluminum being substituted for the beryllium as the fuel constituent. The thixotropic composition proved to have a shock sensitivity in excess of 120 kg-cm and to be fully compatible under the test storage conditions specified.

EXAMPLE 12

A typical example of a composition formulation for use as an explosive is as follows:

| | |
|---|-------|
| Al | 29% |
| N ₂ H ₄ NO ₂ | 51.3% |
| N ₂ H ₄ | 19.7% |

Theoretical calculations indicate the following performance data for the above composition, in comparison with known comparable explosive systems:

| | Vol gas cc/gram | Heat cal/gm | Vol x Ht (Figure of Merit) |
|---|--------------------|----------------|----------------------------------|
| Al-N ₂ H ₄ NO ₂ -N ₂ H ₄ of Ex. 12 | 1100 | 1800 | 1980 |
| Al-NH ₄ NO ₃ | 550 | 2350 | 1290 |
| Blasting gelatine | 851 | 1422 | 1210 |
| Nitroglycerin | 721 | 1580 | 1124 |

| | -Continued | | |
|---|------------|-----|-----|
| NH ₄ NO ₃ + sawdust | 1025 | 882 | 904 |
| TNT | 730 | 925 | 675 |
| Gunpowder | 386 | 574 | 228 |

As will be noted, the Figure of Merit (a measure of the power produced) is markedly higher for the Al-N₂H₄NO₃-N₂H₄ explosive system than for the other explosive systems.

Comparative Trauzl Block Tests produced the following results:

| | Volume Difference (cc) |
|---|------------------------------|
| Al-N ₂ H ₄ NO ₃ -N ₂ H ₄ of Ex. 12 | 690 |
| Nitroglycerin | 550 |
| TNT | 295 |
| 40% dynamite | 260 |

Other explosive composition formulations characteristic of the invention are as follows, the mix in each case being compounded with about 3 percent by weight of a gelling agent:

| | | |
|-------------|---|-------|
| Example 13: | Al | 21.7% |
| | N ₂ H ₄ NO ₃ | 38.3% |
| | N ₂ H ₄ | 40% |
| EXAMPLE 14: | Al | 32.6% |
| | N ₂ H ₄ NO ₃ | 57.4% |
| | N ₂ H ₄ | 16% |
| EXAMPLE 15: | Be | 17% |
| | N ₂ H ₄ NO ₃ | 60% |
| | N ₂ H ₄ | 23% |
| EXAMPLE 16: | Be | 17% |
| | N ₂ H ₄ NO ₃ | 64% |
| | N ₂ H ₄ | 16% |
| | H ₂ O | 3% |

Our analyses and experimentations have indicated that the reducer and oxidizer constituents should be in essentially stoichiometric proportion for optimum performance, but that the proportionation may be varied substantially from stoichiometric optimum, if desired to improve other characteristics, such as sensitivity. Thus, the proportionation of the hydrazinium nitrate to the metal reducer constituent should be at least about 3.5:1 in the case where beryllium is the reducer constituent and should be at least about 1.76:1 in the case where aluminum is the reducer constituent and, in general, higher proportions of hydrazinium nitrate are to be employed in explosive formulations, as compared with propellant formulations, unless a relatively large proportion of desensitizer is used in the propellant formulation. With respect to the relative proportion of gelling agent, sufficient gelling agent is to be used to render the composition thixotropic and pumpable, with only sufficient gelling agent being employed to effect this condition, since excess gelling agent detracts from the performance characteristics of the composition in that it is a diluent insofar as the energy producing reaction is concerned. In general, it has been found that the proportion of gelling agent for these purposes should be from about 3 percent to about 6 percent of the total weight of the thixotropic composition.

Gelling agents other than colloidal silica can be employed, such as acetylene black, carboxymethylcellulose, cellulose acetate, and mixtures thereof, for example.

Ignition of propellant compositions according to the present invention can be accomplished by known techniques such as use of a pyrotechnic squib, or by injection of a small amount of hypergolic material such as red fuming nitric acid or chlorine trifluoride. Ignition

characteristics, in the case where the metallic fuel constituent is beryllium, can also be improved by admixture with the composition of relatively small amounts (e.g. less than about 5 percent by weight relative to the weight of the beryllium) of aluminum particles and/or magnesium particles, the relatively more ignitable fuel particles serving in the mix as dispersed ignition points which upon reaction in turn ignite the interspersed beryllium particles. Explosive compositions according to the invention are detonatable by known techniques, such as by use of standard commercial blasting caps.

The particulate fuel constituent should have a particle size of less than about 40 microns and preferably about 10-20 microns.

Compositions of the present invention, while intended primarily for usage as monopropellants and as explosives without addition of other reactants, can by appropriate stoichiometric compensation be used as either a fuel-rich or an oxidizer-rich ingredient in a bi-propellant propulsion reaction, or in admixture with other explosive ingredients, in the case of an explosive application.

From the foregoing, further equivalent variations of the invention as to typical formulations, as to modes of application, and as to reaction environments will be apparent to those skilled in the art to which the invention is addressed, within the scope of the following claims.

What is claimed is:

1. A stable, high energy composition for use as a propellant or as an explosive, said composition principally comprising:
 - a. as a reducing reactant, finely divided metal selected from the group consisting of aluminum, beryllium, and mixtures thereof;
 - b. as an oxidizing reactant, hydrazinium nitrate; and
 - c. a hydrazine containing working fluid.
2. The composition of claim 1, wherein the proportionation by weight of the hydrazinium nitrate to the reducing reactant is at least about 3.5:1 in the case where beryllium is the reducing reactant and is at least about 1.76:1 in the case where aluminum is the reducing reactant, and the percent by weight of the hydrazine containing working fluid is from about 20 percent to about 65 percent.
3. The composition of claim 1, wherein the reducing reactant and the oxidizing reactant are present in substantially stoichiometric relative proportions.
4. The composition of claim 1, wherein the reducing reactant essentially comprises beryllium.
5. The composition of claim 1, wherein the reducing reactant essentially comprises aluminum.
6. The composition of claim 1, wherein the finely divided reducing reactant has an average particle size of less than about 40 microns.
7. The composition of claim 1, wherein the hydrazine containing working fluid principally comprises one or more ingredients selected from the group consisting of hydrazine, monomethylhydrazine, unsymmetrical dimethylhydrazine, and mixtures thereof with water.
8. The composition of claim 7, wherein said working fluid principally comprises hydrazine.
9. The composition of claim 7, wherein said working fluid principally comprises hydrazine and water.
10. The composition of claim 9, comprising from about 20 percent to about 40 percent by weight of hydrazine and up to about 25 percent by weight of water.

11. A stable, high energy composition suitable for use as a rocket monopropellant or as an explosive depending upon proportionation, said composition principally comprising;

- a. as a fuel contributing constituent, finely divided metal selected from the group consisting of aluminum, beryllium, and mixtures thereof;
- b. hydrazinium nitrate as an oxidizer contributing constituent;
- c. a hydrazine containing working fluid and desensitizer, the said working fluid and desensitizer being present in an amount to efficiently convert a substantial portion of the thermal energy of the fuel-oxidizer reaction into kinetic energy in the case of a propellant or into work in the case of an explosive; and
- d. a gelling agent present in sufficient quantity to form a pumpable thixotropic gel in which the oxidizer contributing constituent and the working fluid contributing constituent are uniformly dispersed in liquid phase and the fuel contributing constituent is present in the form of substantially uniformly distributed solid particles.

12. The composition of claim 11, wherein the proportionation by weight of the hydrazinium nitrate to the fuel contributing constituent is at least about 3.5:1 in the case where beryllium is the fuel and is at least about 1.76:1 in the case where aluminum is the fuel, and the percent by weight of the hydrazine containing working fluid and desensitizer is from about 20 percent to about 65 percent.

13. The composition of claim 11, wherein the fuel contributing constituent and the oxidizer contributing constituent are present in substantially stoichiometric relative proportions.

14. The composition of claim 11, wherein the fuel contributing constituent essentially comprises beryllium.

15. The composition of claim 11, wherein the fuel contributing constituent essentially comprises aluminum.

16. The composition of claim 11, wherein the finely divided fuel contributing constituent has an average particle size of less than about 40 microns.

17. The composition of claim 11, wherein the hydrazine containing working fluid and desensitizer principally comprises one or more ingredients selected from the group consisting of hydrazine, monomethylhydrazine, unsymmetrical dimethylhydrazine, and mixtures thereof with water.

18. The composition of claim 17, wherein said working fluid and desensitizer principally comprises hydrazine.

19. The composition of claim 17, wherein said working fluid and desensitizer principally comprises hydrazine and water.

20. The composition of claim 19, comprising from about 20 percent to about 40 percent by weight of hydrazine and up to about 25 percent by weight of water.

21. The composition of claim 11, wherein the gelling agent is present in an amount within a range of about 3-6 percent by weight of the composition.

22. The composition of claim 11, wherein the gelling agent is selected from the group consisting of colloidal silica, acetylene black, carboxymethylcellulose, cellulose acetate, and mixtures thereof.

23. The composition of claim 11, wherein the gelling agent is colloidal silica.

24. A high energy composition wherein the energy producing constituents consist essentially of the following, in the indicated relative proportions:

- a. finely divided beryllium as a reducer constituent, present in the amount of about 15 percent by weight;
- b. hydrazinium nitrate as an oxidizer constituent, present in the amount of about 54 percent by weight; and
- c. hydrazine as a working fluid, present in the amount of about 31 percent by weight.

25. A high energy composition wherein the energy producing constituents consist essentially of the following, in the indicated relative proportions:

- a. finely divided beryllium as a reducer constituent, present in the amount of about 17 percent by weight;
- b. hydrazinium nitrate as an oxidizer constituent, present in the amount of about 18 percent by weight; and
- c. a working fluid and desensitizer, consisting essentially of hydrazine present in the amount of about 40 percent by weight and water present in the amount of about 25 percent by weight.

26. A high energy composition wherein the energy producing constituents consist essentially of the following, in the indicated relative proportions:

- a. finely divided aluminum as a reducer constituent, present in the amount of about 25 percent by weight;
- b. hydrazinium nitrate as an oxidizer constituent, present in the amount of about 45 percent by weight; and
- c. hydrazine as a working fluid, present in the amount of about 30 percent by weight.

27. A high energy composition wherein the energy producing constituents consist essentially of the following, in the indicated relative proportions:

- a. finely divided aluminum as a reducer constituent, present in the amount of about 17 percent by weight;
- b. hydrazinium nitrate as an oxidizer constituent, present in the amount of about 18 percent by weight; and
- c. a working fluid and desensitizer, consisting essentially of hydrazine present in the amount of about 40 percent by weight and water present in the amount of about 24 percent by weight.

28. The composition of claim 27, further comprising up to about 1 percent of a compound inhibiting aluminum-water reactivity during storage of the composition.

29. The composition of claim 28, wherein the compound inhibiting aluminum-water reactivity is ammonium dichromate.

30. The method of producing reaction thrust, comprising: chemically reacting in a reaction motor a fuel constituent selected from the group consisting of beryllium, aluminum and mixtures thereof and an oxidizer constituent consisting essentially of hydrazinium nitrate, the reaction occurring in the presence of an amount of hydrazine containing working fluid effective to convert a considerable portion of the thermal heat of reaction to kinetic energy; and discharging the work-

ing fluid and reaction products from the exhaust nozzle of the reaction motor to produce thrust.

31. The method of claim 30, wherein said fuel constituent consists essentially of beryllium.

32. The method of claim 30, wherein said fuel constituent consists essentially of aluminum.

33. The method of claim 30, wherein said hydrazine

containing working fluid consists essentially of hydrazine.

34. The method of claim 30, wherein said hydrazine containing working fluid comprises hydrazine and water.

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United States Patent [19]

Forrest

[11] 3,912,560

[45] Oct. 14, 1975

[54] THIN LAYER PROPAGATING SLURRY EXPLOSIVE

[75] Inventor: Charles D. Forrest, Hollister, Calif.

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Hollister, Calif.

[22] Filed: Jan. 31, 1974

[21] Appl. No.: 434,754

[52] U.S. Cl. 149/47; 149/60; 149/93

[51] Int. Cl.² C06B 31/32

[58] Field of Search 149/93, 47, 60, 38, 43,
149/62

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Primary Examiner—Stephen J. Lechert, Jr.

Attorney, Agent, or Firm—David H. Semmes

[57]

ABSTRACT

A cap-sensitive slurry explosive capable of propagating a high order detonation in thin layers and which has a high degree of safety for a cap-sensitive explosive. The slurry consists of an ultra-fine solid explosive suspended in an energetic, but non-self-explosive liquid matrix and contains no liquid explosive ingredient. The slurry resists dispersion in a variety of liquids including water and crude oil. In a preferred embodiment, the slurry includes pentaerythritol tetranitrate (PETN).

1 Claim, No Drawings

THIN LAYER PROPAGATING SLURRY EXPLOSIVE

BACKGROUND OF THE INVENTION

As is known, certain explosives such as penethaerythritol tetranitrate (PETN) for example, are hazardous when subjected to modest physical abuse from impact or friction forces. Such compounds additionally do not have desired inertness toward crude oil and brine and dilute forms of many other well environmental material. Such materials additionally are hazardous in being highly inflammable and in many formulations are toxic.

BRIEF DESCRIPTION OF THE INVENTION

The slurry of the present invention is a new type of cap-sensitive slurry explosive capable of propagating a high order detonation in thin layers. The invention provides a safe explosive in slurry form which may be used in oil well and gas well formation fracturing, rock fracturing for in situ ore leaching, non-nuclear fracturing of oil shale formations, and explosive formation of fire lanes in terrain inaccessible to motorized equipment.

The slurry of the present invention is formulated to resist accidental initiation by adiabatic compression of gas bubbles which may be introduced during loading and handling, and due to the good chemical stability of the explosive formula, the slurry gives a high degree of inertness toward crude oil and brine and dilute forms of most other well environmental materials. The material of the present invention in fires is difficult to ignite, and once ignited, burns quietly with no explosion. The ingredients comprising the slurry are non-toxic prior to detonation.

Additional advantages, objects and features of the invention will be more readily apparent from the following detailed description of an embodiment thereof.

| Example (% by weight) | |
|-------------------------------|-------------|
| Sensitive Fine Particle PETN | 20 - 50 |
| 60% Ammonium Nitrate Solution | 0 - 80 |
| Diethylene Glycol | 0 - 25 |
| Guar Gum or Polyacrylamide | 0.1 - 3.0 |
| Water | Balance |
| | 100% |
| Cross-linking Agent | As required |

The sensitive fine particle PETN is disclosed in greater detail in my co-pending application, Ser. No. 434,753, filed Jan. 31, 1974 entitled SENSITIVE FINE PARTICLE PETN.

The ammonium nitrate solution may, in certain instances, be replaced largely by potassium, barium or sodium nitrate solution. The diethylene glycol may be replaced largely by other soluble organic fuels such as formamide, diethyl formamide or other glycols and certain alcohols. Also, some portion of solid fuel may be included, i.e., fine coal, sulfur, gilsonite, or aluminum, ferro-phosphorous, ferro-silicon, etc.

A satisfactory cross-linking agent consists of Tyzor LA, which is a trademark preparation of E. I. DuPont de Nemours & Company, Inc. and which is known generally as Titanium-antimony lactate, as illustrated in U.S. Pat. No. 3,622,408.

In the above example, the concentration of ammonium nitrate solution is not critical. A 60% solution is convenient to use because the ammonium nitrate stays completely in solution above 54°F, which means that handling is simplified over, for example, an 80% solution which has a solidification temperature of about 136°F, which would require expensive heated storage. After blending with anti-freeze agent, such as diethylene glycol, the solidification temperature is decreased.

This cap-sensitive explosive is capable of propagating a high order detonation in thin layers, i.e., one-thirty second inch when confined between masonite, able to detonate completely in thin layers simultaneously exposed to a hydrostatic pressure of 10,000 psi or above and a temperature of approximately 200°F, does not cause headache during handling, and contains no liquid explosive ingredient. Further, slurry explosive is unaffected when penetrated by British 303 ammunition from a distance of 75 to 100 feet, even when backed by steel or aluminum. Slurry explosive will slowly decompose in a bonfire when unconfined, but by itself will not support combustion.

The purpose of this invention is to provide a safe explosive in slurry form which may be used in (1) the explosive fracturing of oil and gas reservoirs in order to increase formation permeability and thus increase rate of flow to wellbore; (2) the explosive fracturing of oil shale formations to permit thermal recovery of petroleum products therefrom in an economical manner; (3) various military applications; and (4) non-incendiary line charges for the rapid construction of fire lanes to fight forest fires, particularly in terrain inaccessible to mechanized equipment.

Ordinarily, PETN (penethaerythritol tetranitrate) is considered a hazardout explosive which is known to explode when subjected to modest physical abuse from impact or friction forces. For example, in a drop test apparatus in which a small (i.e., approximately one-twentieth gram) sample of sensitized small particle PETN is placed on a hard tool steel anvil and impacted by a free fall hammer, also made of hard tool steel and weighing 2.143 kg, detonations of the PETN occur when the drop height is only 2 cm. In other words, the impact sensitivity of the pure, dry PETN is 4.3 kg-cm. When this same PETN is compounded into this slurry explosive in the proportions of 40% PETN/50% of a 60% AN solution/9.5% DEG/0.5% guar and cross-linked (5 drops/100g slurry) with a 50% solution of Tyzor LA in deionized water, the resulting explosive mixture is unaffected by repeated hammer drops from a drop height of 63/5cm. Thus, in slurry form, the PETN is not exploded by an impact of 136.3 kg-cm, which is more than 30 times the energy at which the PETN alone explodes. The slurry formula given in the above example detonates completely at high velocity under a hydrostatic pressure of 10,000 psi in a layer one-sixteenth inch thick by 2-1/2 inches wide confined between two sheets of 1/4 inch thick masonite.

The consistency of the slurry can be varied to suit the needs of a particular requirement. The slurry can be provided in viscosity ranges from a thin milkshake to bread dough consistency. Rather thick slurry has the amazing property of passing readily through a small (1/32 inch diameter) orifice under low pressure and then reconsolidating with itself. This high degree of thixatropy allows it to readily adapt to a variety of applications. It has been found that the detonation rate of

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the slurry is 21,400 feet per second in a layer thickness of 0.032 inches (one-thirty second) with mild confinement. At pressures up to 10,000 psi, the slurry explosive with a thickness of 0.063 inch (one-sixteenth) detonates completely.

Manifestly, minor changes can be effected in the above-described examples without departing from the spirit and the scope of the invention as defined in and limited solely by the appended claims.

I claim:

1. A thin layer propagating slurry explosive compris-

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ing a mixture consisting of, by weight:

A. 40% sensitive fine particle pentaerythritol tetranitrate (PETN);

B. 50% of a 60% ammonium nitrate solution;

C. 9.5% diethylene glycol;

D. 0.5% guar; and

E. 5 drops/100 g slurry of a 50% solution of titanium antimonium lactate in deionized water as a cross-linking agent.

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[54] **METHOD FOR GELLING
NITROPARAFFINS IN EXPLOSIVE
COMPOSITIONS**

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149/47; 149/62; 149/76; 149/78; 149/89;
149/92; 149/105**

[58] Field of Search **149/2, 89, 38, 47, 76,
149/62, 78, 92, 105**

[56]

References Cited**U.S. PATENT DOCUMENTS**

| | | | |
|-----------|---------|----------------|----------|
| 1,217 | 4/1968 | Francis | 149/89 X |
| 3,377,218 | 4/1968 | Brown | 149/89 X |
| 3,762,970 | 10/1973 | Ballard et al. | 149/89 X |

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Attorney, Agent, or Firm—Richards, Harris & Medlock

[57]

ABSTRACT

An improved process for producing explosive gel compositions is provided wherein a polymeric thickening agent is dispersed in an aqueous medium and a nitroparaffin is added thereafter to form dispersed globules of nitroparaffin gel within the aqueous medium. Gelling agents for the aqueous medium, fuels and non-explosive sensitizing material can then be added to form an explosive gel with excellent storage and detonation capabilities.

49 Claims, No Drawings

UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 4,097,316
DATED : June 27, 1978
INVENTOR(S) : John J. Mullay

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 3, line 38, change "tne" to --the--.

Column 8, lines 37 and 38, change "2 x 8 inch" to --2" x 8"--.

Column 9, line 32, change "2 x 8 inch" to --2" x 8"--.

Signed and Sealed this

Twelfth Day of June 1979

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

DONALD W. BANNER
Commissioner of Patents and Trademarks

METHOD FOR GELLING NITROPARAFFINS IN EXPLOSIVE COMPOSITIONS

BACKGROUND OF THE INVENTION

This invention relates to gelled explosive compositions. In another aspect, this invention relates to a method for producing explosive gel compositions which result in substantial savings in production time and energy requirements. In still another aspect, this invention relates to a method of producing an improved explosive composition containing a nitroparaffin gelled with a polymeric thickening agent selected from the organic esters of cellulose, methacrylate polymers, and copolymers of vinylidene chloride and acrylonitrile.

Explosive gel compositions are well known for their reliability, economy, and ease of handling. Accordingly, the demand for explosive gel compositions is great and improved methods of manufacture are desirable. Explosive gel compositions containing gelled nitroparaffin, an inorganic nitrate, and water are used in a variety of applications. Explosive gel compositions containing inorganic nitrates and nitroparaffins are disclosed in U.S. Pat. No. 3,419,444 and in U.S. Pat. No. 3,765,966. Both of these references disclose a method for producing explosive compositions which contain a gelled nitroparaffin. According to U.S. Pat. No. 3,419,444, the nitroparaffin gel is formed first by blending nitrocellulose with the nitroparaffin. The nitroparaffin gel is then added to a mixture of an inorganic nitrate, water, a gelling agent for the water, and non-explosive sensitizer materials, such as resin balloons. The major disadvantage of this process is that in order to obtain a sensitive composition, prolonged mixing times are necessary in order to disperse the preformed nitroparaffin gel within the aqueous gel which contains the inorganic nitrates and other materials. The long mixing time required renders this process commercially undesirable.

The process disclosed in U.S. Pat. No. 3,765,966 is an attempt to overcome the disadvantages described above by setting forth a one step process whereby an explosive gel composition can be formed without the necessity of prolonged mixing to disperse a preformed nitroparaffin gel. This reference discloses that the fluid medium (water or methanol) and the liquid nitromethane should be mixed together and the solid materials, such as the inorganic nitrates, non-explosive sensitizing materials, and water gelling agents should then be added and mixed with the fluid mixture. Additionally, this reference discloses that a specific type of gelling agent must be added with the solid materials in order to gel the liquid nitromethane. The nitromethane gelling agent is a cyanoethylether of galactomannan gum. This gelling agent is presently of uncertain availability and is relatively expensive. Furthermore, it is unclear from this reference whether this specific gelling agent will sufficiently gel nitroparaffins other than nitromethane. A process for producing gelled explosives containing gelled nitroparaffin which utilizes less expensive and more readily available nitroparaffin gelling agents is therefore needed. More specifically, a method for producing an explosive gel composition containing a nitroparaffin gelled with commercially available polymeric thickeners which are easily dispersible in an aqueous phase and which thicken the nitroparaffin without the necessity of prolonged mixing is desirable.

SUMMARY OF THE INVENTION

According to the invention, explosive gel compositions containing gelled nitroparaffins are produced utilizing polymeric thickening agents selected from the organic esters of cellulose, methacrylate polymers, and copolymers of vinylidene chloride and acrylonitrile, without the necessity of prolonged periods of mixing. According to the process of the present invention, the polymeric thickening agent to be employed is dispersed in an aqueous medium by agitation. The aqueous medium can contain various oxidizers and/or inorganic nitrates in solution. A nitroparaffin is then added to the dispersion where the polymeric thickening agent preferentially migrates to it to form a nitroparaffin gel which is finely dispersed in the aqueous medium. Water gelling agents, fuels and non-explosive sensitizing materials, such as glass microballoons, for example, can then be added to form the explosive gel composition which comprises finely dispersed globules of the nitroparaffin gel. Thus, an explosive gel composition which comprises a nitroparaffin gel within an aqueous gel is formed. The resulting explosive gel has good storage capabilities and can be detonated in a conventional manner.

DETAILED DESCRIPTION OF THE INVENTION

In accordance with one embodiment of the present invention, a polymeric thickening agent is added to an aqueous medium and stirred to produce a dispersion. A nitroparaffin is then added to this dispersion while the dispersion is subjected to agitation and the nitroparaffin quickly migrates to the polymeric thickening agent to form finely divided globules of nitroparaffin gel. Optionally, the nitroparaffin can be added to the aqueous medium first and then the polymeric thickening agent is added, with agitation, to form the dispersed globules of nitroparaffin gel. After formation of the nitroparaffin gel, additional oxidizing agents, fuels and additional sensitizing material can be added to the dispersion. The aqueous phase of the dispersion is then gelled by addition of an effective amount of conventional water gelling agents. It is noted that the term "nitroparaffin gel" as used in the scope of the subject invention is used to describe the thickened material which forms as the result of admixing the polymeric thickening agent and nitroparaffin, such material having a viscosity greater than the nitroparaffin.

At this point, the aqueous medium can contain only water or it can comprise an aqueous solution of one or more oxidizing agents described in detail below. Water will comprise from about 5 to about 25 percent by weight of the explosive gel compositions of the subject invention. In one embodiment of the present invention, the oxidizing agents employed are dissolved in the water prior to formation of the nitroparaffin gel which occurs upon addition of the nitroparaffin to the aqueous medium containing the dispersed polymeric thickening agent. Alternatively, the oxidizing agents can be dissolved in the aqueous medium after the dispersed nitroparaffin gel has been formed. It is also possible to dissolve a portion of the oxidizing agents which are to be employed prior to the formation of the nitroparaffin gel with the balance of the oxidizing agents being added after the nitroparaffin gel has been formed. Regardless of the order of addition, the oxidizing agents employed herein can be dissolved in water to form an aqueous

medium at relatively low temperatures, such as room temperature to about 200° F, for example about 125°-135° F.

The explosive gel compositions of the subject invention will contain oxidizing agents in an amount ranging from about 10 to about 90 weight percent, based on the weight of the explosive gel. The oxidizing agents can include a single inorganic nitrate, mixtures of several inorganic nitrates or mixtures of inorganic nitrates with other types of oxidizing agents. Inorganic nitrates which can be employed in the subject invention include nitrates of ammonium, the alkali or alkaline earth nitrates, nitrates of Group III elements and mixtures thereof. Preferred inorganic nitrates include ammonium nitrate and sodium nitrate. Additionally, other oxidizing agents, preferably water soluble salts such as ammonium, the alkali metal or the alkaline earth metal perchlorates, perchlorates of Group III elements and mixtures thereof can be employed. Ammonium perchlorate and sodium perchlorate are preferred among this latter class of oxidizing agents. The explosive gel of the subject invention can include from about 10 to about 80 percent by weight of an inorganic nitrate or mixtures of inorganic nitrates. Other oxidizing agents, such as the aforementioned perchlorates can be present in an amount of from about 0 to about 30 percent by weight of the explosive gel provided that the total oxidizing agent content does not exceed about 90 percent by weight thereof.

The polymeric thickening agent for nitroparaffins which is added to the above described aqueous medium to form a dispersion can be selected from the organic esters of cellulose, methacrylate polymers, and copolymers of vinylidene chloride and acrylonitrile. All of the polymeric thickening agents employed in the subject invention are characterized by a high molecular weight, the ability to thicken nitroparaffins and easy dispersion in an aqueous phase. Generally the polymers employed as nitroparaffin thickening agents in the present invention have a molecular weight of about 100,000 or greater. These polymeric thickeners are commercial grade products and are utilized in powdered form so as to be easily dispersed in the aqueous phase and quickly soluble in the nitroparaffin when it is added. They can be used separately, or mixtures can be employed. The polymeric thickening agents of the subject invention can be used either alone or in conjunction with other known nitroparaffin thickening agents such as nitrocellulose or cyanoethylether derivatives of galactomannan gum. Additionally, these polymeric thickeners can be used in conjunction with emulsifying or dispersing aids such as those discussed in detail below.

The organic esters of cellulose useful in the present invention as polymeric thickening agents for nitroparaffins include cellulose acetate, cellulose acetate butyrate and cellulose acetate propionate. Mixtures of these three cellulose derivatives may be employed, or these cellulose derivatives may be employed in conjunction with the other polymeric thickening agents of the subject invention or with previously known nitroparaffin thickening agents. Examples of these polymers are those which may be purchased, in powdered form, from Eastman Kodak Company of Rochester, N.Y., under trade designations 394-60, 171-40, and 482-20.

Also useful in the present invention are methacrylate polymers and copolymers, including, methylmethacrylate polymers, ethylmethacrylate polymers and butyl methacrylate polymers. These nitroparaffin polymeric

thickening agents, as well as copolymers thereof, can likewise be employed either alone, or in conjunction with the other polymeric thickening agents disclosed herein, or with conventional nitroparaffin thickening agents. Methacrylate polymers useful in the present invention are available in powdered form from Rohm and Haas Company, Philadelphia, Pa., sold under the trade designation "Acryloid".

A third type of polymeric thickening agent which can be employed according to the present invention to thicken nitroparaffins in a one step process, thus alleviating the need for prethickening nitroparaffins or employing extended mixing times, are copolymers of vinylidene chloride and acrylonitrile. The copolymers employed in the present invention generally comprise powdered materials known as "saran" and are available in microsphere or powdered form from Dow Chemical Company, Midland, Mich. For convenience in mixing, the powdered forms are preferable. This thickening agent can also be used either alone or in conjunction with other thickening agents for the nitroparaffin.

The above described polymeric thickening agents for nitroparaffin can be added to the aqueous medium and stirring or other means of agitation can then be employed to effect relative homogeneity of the aqueous medium-nitroparaffin thickening agent dispersion. Generally, the nitroparaffin thickening agents and other dispersion aids for nitroparaffins, are added to the aqueous medium in an amount equal to from about 0.05 to about 2.0 percent by weight, based on the weight of the explosive gel composition.

Once the dispersion of the continuous aqueous medium and the discontinuous polymeric thickening agent phase, comprised of dispersed polymer particles, has been formed, the nitroparaffin is added and the mixture is stirred or otherwise agitated to produce a nitroparaffin gel dispersed within the aqueous medium. This occurs because the agitation disperses the nitroparaffin which contacts the dispersed particles of polymeric thickener to produce the dispersion of the nitroparaffin gel in the aqueous medium. Examples of nitroparaffins which can be used within the scope of this invention include mono nitrated alkanes having from about 1 to about 3 carbon atoms. Examples of these are nitromethane, nitroethane, 1-nitropropane, 2-nitropropane, and mixtures thereof. Nitromethane is the preferred nitroparaffin. The nitroparaffins can be present in the resulting explosive gel in an amount equal to from about 5 to about 30 percent by weight, based on the weight of the explosive gel. The nitroparaffins are preferably present in an amount equal to about 15 percent by weight of the explosive composition.

As discussed above, the nitroparaffin, when added to the polymeric thickening agent dispersion will migrate to the polymeric thickener particles of the dispersion to form nitroparaffin gel globules dispersed throughout the aqueous phase. Once this nitroparaffin gel has formed, gelling agents for the aqueous medium, as well as other additives, including additional oxidizers, fuels, and non-explosive sensitizing materials, for example, can be added either separately or in combination. For example, if only a portion of the oxidizing agents which are to be employed were previously dissolved in the aqueous medium, the remaining portion can be added after the nitroparaffin gel forms in the manner disclosed above.

In addition to oxidizing agents, various fuels non-explosive sensitizing materials and other auxiliary sensi-

tizing agents can also be added. Any conventional oxidizable fuel materials can be employed. Examples of suitable fuels include oxygenated organic compounds such as lower alcohols, esters, ethers, ketones, and aldehydes; and the like. Additionally, powdered or atomized aluminum can be used as a fuel. Ethylene glycol is a preferred fuel. Non-explosive sensitizing materials such as glass or resin microballoons, wood flour, cork or balsa, for example, can be employed by adding these materials along with the aqueous medium thickening agents, fuels, oxidizing agents and other additives. Preferred non-explosive sensitizing materials are glass microballoons. In addition, auxiliary sensitizing agents conventionally employed in water based explosives such as methylamine nitrate, ethylenediamine dinitrate, DNT, and TNT, and mixtures thereof, for example, can be employed. Generally, fuels, such as those described above, need not be present in the explosive gel composition but can be present in the explosive gel composition in any amount up to about 15 weight percent, based on the weight of the explosive gel. The non-explosive sensitizing materials can be present in amounts ranging from 0 to about 5 percent by weight of the explosive gel composition. The auxiliary sensitizing materials may be optionally employed in an amount of up to about 20 percent by weight. The aqueous gelling agents employed can be any conventionally known water gelling agents such as the natural gums such as guar gum or gum arabic, pregelatinized starch, carboxymethyl cellulose, ethyl and propyl ether derivatives of guar gum, polyoxy ethylene, carboxyethyl cellulose, and bi-polymeric materials such as xanthan gum, and the like. A preferred gelling agent for the aqueous medium is guar gum which is added along with an effective amount of a crosslinker such as potassium pyroantimonate, sodium dichromate, sodium borate, ferric chloride, or heavy metal ions, and the like. A polyacrylamide can be added as a secondary thickener to provide better flow characteristics depending upon whether the explosive gel composition is to be poured, pumped or applied in some other manner. Optionally a polyacrylamide can be used alone as the aqueous gelling agent and a suitable crosslinker for the polyacrylamide such as aluminum sulfate or aluminum nitrate can be used to obtain the desired consistency. The gelling agents for the aqueous phase are generally present in an amount of from about 0.2 to about 2.0 percent by weight, based on the weight of the explosive gel composition.

In another embodiment of the present invention, emulsifiers for the nitroparaffins to be employed can be added to achieve very fine dispersion of the nitroparaffin within the explosive gel composition. According to this embodiment of the invention, an emulsifying agent, such as a hydrogenated tallow amine is added to the aqueous medium along with the polymeric thickening agents. Upon addition of the nitroparaffin, very small dispersed droplets of nitroparaffin gel are formed and the emulsifier acts to keep the nitroparaffin emulsified, even in a gelled state. This fine dispersion of the globules of nitroparaffin gel within the aqueous medium results in an explosive gel composition which is more sensitive than most comparable types of aqueous explosive gels. A preferred nitroparaffin emulsifier which can be used is sold under the trade name Armeen HT, and is a hydrogenated tallow amine sold by Armac Company, Industrial Chemicals Division, Chicago, Ill. Such emulsifiers can be present in the explosive composition in an amount ranging from about 0.01 to about 0.5 weight

percent based on the weight of the explosive gel composition.

Thus, according to the present invention, an aqueous gel explosive composition can be prepared without the necessity of prolonged mixing and which utilizes readily available types of nitroparaffin gelling agents. The explosive gel compositions can be prepared by forming an aqueous medium consisting essentially of water or an aqueous solution of oxidizing agents, adding a polymeric thickening agent selected from organic esters of cellulose, methacrylate polymers, and copolymers of vinylidene chloride and acrylonitrile to the aqueous medium to form a dispersion, thereafter admixing a nitroparaffin with the dispersion to form an aqueous dispersion of nitroparaffin gel, and adding fuels, oxidizing agents, nonexplosive sensitizing materials and a water gelling agent to thereby form an explosive composition which basically comprises gelled nitroparaffin globules dispersed within an aqueous gel. The explosive gel compositions produced by this process generally will have a water content of between about 5 to about 25 weight percent based upon the weight of the explosive gel composition. The explosive gel compositions can be detonated in a known manner by conventional booster systems such as for example, Pentalite, Composition B, RDX, and other similar primers in combination with conventional blasting caps. In addition, in some cases, the explosive gel compositions of the present invention are cap sensitive and may be detonated using a No. 6 blasting cap. These cap sensitive explosive gel compositions can be prepared by employing a nitroparaffin emulsifier in the manner discussed above to thereby form more finely dispersed (and therefore more sensitive) globules of nitroparaffin gel within the explosive gel composition, and if desired, aluminum powder. Cap sensitivity can also be achieved without the use of an emulsifier by employing relatively high amounts of nitromethane and obtaining fine dispersion thereof by controlling mixing speed and temperature.

EXAMPLES

The following examples are presented to enable one skilled in the art to more fully understand the present invention. However, it is to be understood that the examples are exemplary only and do not limit the invention in any manner.

EXAMPLE 1

A mixture of 147 grams of ammonium nitrate and 56 grams of sodium nitrate were dissolved in 100 grams of water at 118° F. This aqueous medium was then added to 475 grams of ground ammonium nitrate and stirred. To this slurry-like aqueous medium was added 1 gram of Armeen HT, 3 grams of cellulose acetate sold under the trade designation of 394-60 by Eastman Kodak Company of Rochester, N.Y., along with 20 grams of ethylene glycol with continued stirring. Nitromethane in the amount of 140 grams was then added to the aqueous solution containing the polymeric thickening agent, cellulose acetate. Finely dispersed globules of nitromethane gel formed almost immediately within the aqueous medium. The following materials were then added to the aqueous medium-nitromethane gel dispersion:

B38/4000 Glass Microballoons
(Manufactured by 3M Corp.
Minneapolis, Minn.)

20 grams

-continued

| | |
|---|----------|
| Jaguar NG (Manufactured by Stein Hall & Co., Inc. New York, N.Y.) dispersed in 10 grams of nitromethane | 7 grams |
| Potassium pyroantimonate | 0.1 gram |
| Alcoa 1620A Atomized Aluminum (Manufactured by Alcoa Aluminum, Pittsburgh, Pa.) | 30 grams |

The resulting explosive gel composition was stored at 70° F for about two weeks without detrimental effect. At the end of the two week period, the explosive gel composition was found to be detonable with a 10 gram Detaprime a PETN containing mini-primer manufactured by E. I. duPont de Nemours & Co., Wilmington, Del., and a No. 6 blasting cap. Further, at the end of three months storage, at approximately 70° F, this composition was found to be detonable in 2½ inches diameter with a No. 6 blasting cap alone.

EXAMPLE 2

A mixture of 147 grams of ammonium nitrate and 56 grams of sodium nitrate were dissolved in 100 grams of water at 135° F. Ammonium nitrate in an amount of 475 grams was then added with stirring. Cellulose acetate butyrate sold under the trade designation 171-40 by Eastman Kodak Company, Rochester, N.Y., and 1 gram of Armeen HT sold by Armak Company, Chicago, Ill., was added to the aqueous medium with stirring and was found to disperse easily. Ethylene glycol in the amount of 20 grams was also added with stirring. Under agitation, 140 grams of nitromethane was added to the aqueous medium and finally dispersed globules of nitromethane gel were observed to form almost immediately within the aqueous medium. The following oxidizing agents, non-explosive sensitizing materials and water gelling agents were then added to the dispersion:

| | |
|--|----------|
| B38/4000 Glass Microballoons (Manufactured by 3M Corp. Minneapolis, Minn.) | 20 grams |
| Jaguar NG (Manufactured by Stein Hall & Co., Inc., New York, N.Y.) dispersed in 10 grams of nitromethane | 7 grams |
| Potassium pyroantimonate | 0.1 gram |
| Alcoa 1620A Atomized Aluminum (Manufactured by Alcoa Aluminum, Pittsburgh, Pa.) | 30 grams |

The explosive composition so manufactured was stored for about two weeks at about 70° F and was found to be detonable with a 10 gram Detaprime, as described in Example 1, in conjunction with a No. 6 blasting cap.

EXAMPLE 3

The procedures and materials of Examples 1 and 2 were repeated except that 3 grams of cellulose acetate propionate, sold under trade designation 482-20 by Eastman Kodak Company, Rochester, N.Y., was substituted in place of the cellulose acetate butyrate employed in Example 1 and the cellulose acetate butyrate employed in Example 2. Also, a temperature of about 160° F was employed while forming the aqueous solution of oxidizing salts. The resulting explosive composition, containing the oxidizing agents, non-explosive sensitizing materials, and fuels in the amounts listed in Examples 1 and

2 were also incorporated into the explosive composition of this Example. The resulting explosive composition was found to be detonable with a 10 gram Detaprime and a No. 6 blasting cap after approximately a two week storage period, during which temperatures averaged approximately 70° F.

EXAMPLE 4

A mixture of 147 grams of ammonium nitrate and 56 grams of sodium nitrate were dissolved in 100 grams of water at 160° F. To this solution was added 475 grams of ground ammonium nitrate with stirring. Armeen HT, a hydrogenated tallow amine emulsifying agent sold by Armak Company, Chicago, Ill., and 3 grams of dried, unexpanded saran microspheres sold under the designation XD8168 by Dow Chemical Company, Midland, Mich., were then added with continued stirring. Upon addition of 140 grams of nitromethane a nitromethane gel in the form of finely dispersed globules were observed to form almost immediately. The following materials were then added in the amount and order stated:

| | |
|---|----------|
| B38/4000 Glass Microballoons (Manufactured by 3M Corp. Minneapolis, Minn.) | 20 grams |
| Jaguar NG (Manufactured by Stein Hall & Co., Inc. New York, N.Y.) dispersed in 10 grams of nitromethane | 7 grams |
| Potassium pyroantimonate | 0.1 gram |
| Alcoa 1620A Atomized Aluminum (Manufactured by Alcoa Aluminum, Pittsburgh, Pa.) | 30 grams |

The resulting explosive gel composition exhibited good storage capabilities and after a two week period at approximately 70° F was found to be detonable with a 2 × 8 inch stick of Power Primer, a high strength gelatin dynamite manufactured by Atlas Powder Co., Tamaqua, Pa., and a No. 6 blasting cap.

EXAMPLE 5

Sodium nitrate in the amount of 56 grams and ammonium nitrate in the amount of 625 grams were dissolved in 100 grams of water and cooled to about 140° F. To this aqueous solution was added 1 gram Armeen HT, and 1 gram of Acryloid K120N, a methyl-methacrylate polymer in powder form, sold by Rohm & Hass Company, Philadelphia, Pa., with stirring. The methyl-methacrylate polymer dispersed easily in the aqueous solution. With continued stirring 140 grams of nitromethane was added and finely dispersed globules of gelled nitromethane were observed to form almost immediately. The following fuels, oxidizing agents, non-explosive sensitizing materials and water gelling agents were then added in the proportions stated:

| | |
|---|----------|
| B38/4000 Glass Microballoons (Manufactured by 3M Corp. Minneapolis, Minn.) | 20 grams |
| Ethylene Glycol | 20 grams |
| Jaguar NG (Manufactured by Stein Hall & Co., Inc., New York, N.Y.) | 7 grams |
| Alcoa 1620A Atomized Aluminum (Manufactured by Alcoa Aluminum, Pittsburgh, Pa.) | 30 grams |
| Potassium Pyroantimonate | 0.1 gram |

The resulting gel explosive composition was stored for a period of six weeks at approximately 70° F. A 2 inch diameter sample of this explosive gel composition was found to be detonable with one 10 gram Detaprime, as described in Example 1, above.

EXAMPLE 6

A mixture of 74 grams sodium nitrate, 26 grams sodium perchlorate, and 463 grams of ammonium nitrate was dissolved in 180 grams of water and heated to approximately 140° F. To this aqueous solution 5 grams of Acryloid K120N, a methyl-methacrylate polymer sold in powder form by Rohm & Hass Company, Philadelphia, Pa., was added with continued agitation. Nitromethane was then added in an amount of 140 grams and dispersed globules of gelled nitromethane were observed to form quickly within the aqueous medium. The following materials are then added in the amounts specified.

| | |
|--|-----------|
| Ethylene Glycol | 40 grams |
| B28/750 Glass Microspheres (Manufactured by 3M Corp. Minneapolis, Minn.) | 15 grams |
| Jaguar NG (Manufactured by Stein Hall & Co., Inc., New York, N.Y.) | 7 grams |
| Potassium Pyroantimonate | 0.8 grams |

The resulting explosive gel composition was found to have excellent storage characteristics and a 2 inch diameter sample of this explosive gel composition was detonable with a 2 × 8 inch Power Primer and No. 6 blasting cap after one month of storage.

EXAMPLE 7

A No. 6 cap sensitive aqueous gel explosive composition was prepared according to the subject invention in the following manner. It should be noted that because a fairly large batch was prepared (approximately 150 lbs.) the major constituents were measured in terms of pounds, while the minor constituents were weighed out in grams. First, a mixture of 22 pounds 1 ounce of flaked ammonium nitrate and 8 pounds 6 ounces of sodium nitrate were dissolved in 15 pounds of water at approximately 120° F. This aqueous medium was then added to 72 pounds of ground ammonium nitrate and stirred. To this slurry-like aqueous medium was added 68.1 grams of Armeen HT, 204.3 grams of cellulose acetate sold under the trade designation of 394-60 by Eastman Kodak Company of Rochester, N.Y., along with 3 pounds of ethylene glycol. Nitromethane in the amount of 21 pounds was then added to the aqueous solution containing the polymeric thickening agent, cellulose acetate. Finely dispersed globules of nitromethane gel formed almost immediately within the aqueous medium. The following materials were then added to the aqueous medium-nitromethane gel dispersion:

| | |
|---|-------------|
| B38/4000 Glass Microballoons (Manufactured by 3M Corp., Minneapolis, Minn.) | 3 pounds |
| Jaguar NG (Manufactured by Stein Hall & Co., Inc., New York, N.Y.) | 354.1 grams |
| Potassium pyroantimonate | 5.05 grams |
| Alcoa 1620A Atomized Aluminum (Manufactured by Alcoa Aluminum, Pittsburgh, Pa.) | 3.5 pounds |

After storage of the above composition for approximately one month, the explosive gel composition was found to be detonable with a No. 6 blasting cap in a 2 inch diameter container.

- 5 While this invention has been described in relation to its preferred embodiments, it is to be understood that various modifications thereof will now be apparent to one skilled in the art from reading this specification and it is intended to cover such modifications as fall within the scope of the appended claims.

What is claimed is:

1. A process for preparing an explosive gel composition which comprises an inorganic nitrate and a nitroparaffin comprising:

- 15 (a) forming an aqueous solution comprising an inorganic nitrate;
- (b) adding a nitroparaffin to said aqueous solution;
- (c) adding a polymeric thickening agent for nitroparaffins selected from the group consisting of cellulose acetate, cellulose acetate butyrate, cellulose acetate propionate, polymers of methyl, ethyl and butyl methacrylate, copolymers of vinylidene chloride and acrylonitrile, and mixtures thereof to said aqueous solution while agitating to form a nitroparaffin gel dispersed within said aqueous solution;
- 20 (d) gelling said aqueous solution by adding an effective amount of an aqueous gelling agent.
2. The product produced by the process of claim 1.
3. A method for producing an aqueous gel explosive composition comprising:

- 35 (a) dispersing a polymeric thickening agent for nitroparaffins selected from the group consisting of cellulose acetate, cellulose acetate butyrate, cellulose acetate propionate, polymers of methyl, ethyl and butyl methacrylate, copolymers of vinylidene chloride and acrylonitrile and mixtures thereof in an aqueous medium by agitation;
- (b) thereafter adding a nitroparaffin to said aqueous medium while agitating to form a nitroparaffin gel;
- (c) gelling said aqueous medium.
4. The process of claim 3 further comprising admixing a fuel with said aqueous medium containing the dispersed nitroparaffin gel.
- 45 5. The process of claim 4 wherein said fuel is present in an amount up to about 15 percent by weight, based on the weight of the explosive gel composition.
6. The process of claim 5 wherein said fuel is selected from the group consisting of aromatic hydrocarbons, petroleum naphthas, oxygenated organic compounds, aluminum and mixtures thereof.
- 50 7. The process of claim 6 wherein said fuel is ethylene glycol.
8. The process of claim 3 further comprising admixing a non-explosive sensitizing material with said aqueous medium containing the dispersed nitroparaffin gel.
9. The process of claim 8 wherein said non-explosive sensitizing material is present in an amount up to about 5 percent by weight based on the weight of the explosive gel composition.
- 60 10. The process of claim 9 wherein said non-explosive sensitizing material is selected from the group consisting of glass microballoons, resin microballoons, wood flour, cork, balsa and mixtures thereof.

11. The process of claim 10 wherein said non-explosive sensitizing material is glass microballoons.

12. The process of claim 3 wherein said polymeric thickening agent further comprises nitrocellulose.

13. The process of claim 3 wherein said polymeric thickening agent is in powdered form.

14. The process of claim 3 wherein said nitroparaffin is present in an amount equal to from about 5 to about 30 percent by weight, based on the weight of said explosive gel composition.

15. The process of claim 14 wherein said nitroparaffin is selected from the group consisting of nitromethane, nitroethane, 1-nitropropane, 2-nitropropane.

16. The process of claim 15 wherein said nitroparaffin is nitromethane.

17. The process of claim 3 wherein said inorganic nitrate is present in an amount of from about 10 to about 80 percent by weight, based on the weight of said explosive gel composition.

18. The process of claim 17 wherein said inorganic nitrates are selected from the group consisting of nitrates of ammonium, alkali metals, alkaline earth metals, Group III elements and mixtures thereof.

19. The process of claim 18 wherein said inorganic nitrate is a mixture of ammonium nitrate and sodium nitrate.

20. The process of claim 17, further comprising dissolving an oxidizing agent other than said inorganic nitrate in said aqueous medium in an amount up to about 30 percent by weight, based on the weight of the explosive gel composition, so that the combined total of said oxidizing agent and said inorganic nitrate is in the range of from about 10 to about 90 percent by weight of said explosive gel composition.

21. The process of claim 20 wherein said oxidizing agent is selected from the group consisting of the perchlorates of ammonium, alkali metals, alkaline earth metals, Group III elements and mixtures thereof.

22. The process of claim 21 wherein said oxidizing agent is sodium perchlorate.

23. The process of claim 21 wherein said oxidizing agent is ammonium perchlorate.

24. The process of claim 3 wherein said gelling of the aqueous medium is effected by the addition of an aqueous gelling agent in an amount of from about 0.2 to about 2.0 percent by weight, based on the weight of the explosive gel composition.

25. The process of claim 24 wherein said aqueous gelling agent is selected from the group consisting of gum arabic, guar gum, polyacrylamides, pregelatinized starch, carboxyethyl cellulose and mixtures thereof.

26. The process of claim 25 wherein said aqueous gelling agent comprises guar gum and a suitable cross linker therefor.

27. The process of claim 25 wherein said aqueous gelling agent comprises a polyacrylamide and a suitable crosslinker therefor.

28. The process of claim 3 further comprising admixing an effective amount of an emulsifier with said aqueous medium.

29. The process of claim 28 wherein said emulsifier is a hydrogenated tallow amine.

30. The process of claim 3 further comprising admixing an auxiliary sensitizing agent with said aqueous medium containing the dispersed nitroparaffin gel.

31. The process of claim 30 wherein said auxiliary sensitizing agent comprises up to about 20 percent by weight of the explosive gel composition and is selected from the group consisting of methylamine nitrate, ethylenediamine dinitrate, Dinitrotoluene, Tri-nitrotoluene and mixtures thereof.

32. The product produced by the process of claim 3.

33. In a method of making an aqueous gel explosive composition comprising a nitroparaffin gelled with a polymeric thickening agent selected from the group consisting of cellulose acetate, cellulose acetate butyrate, cellulose acetate propionate, polymers of methyl, ethyl and butyl methacrylate, copolymers of vinylidene chloride and acrylonitrile, and mixtures thereof, the improvement comprising:

dispersing said polymeric thickening agent in an aqueous medium and thereafter adding nitroparaffin to the resulting dispersion with agitation to form a nitroparaffin gel dispersed within said aqueous medium.

34. The method of claim 33 wherein said aqueous medium comprises a solution of oxidizing agents.

35. The method of claim 33 further comprising gelling said aqueous medium.

36. The product produced by the method of claim 33.

37. In a process for producing an aqueous explosive gel composition which comprises a nitroparaffin gel, the improved method of preparing said nitroparaffin gel comprising:

(a) dispersing a polymeric thickening agent for nitroparaffins selected from the group consisting of cellulose acetate, cellulose acetate butyrate, cellulose acetate propionate, polymers of methyl, ethyl and butyl methacrylate, copolymers of vinylidene chloride and acrylonitrile, and mixtures thereof in an aqueous solution by agitating;

(b) adding a nitroparaffin to said aqueous solution while agitating to thereby form dispersed globules of nitroparaffin gel.

38. The product produced by the process of claim 37.

39. A method of manufacturing a gelled explosive material consisting essentially of the following composition:

| Ingredient | % by weight |
|--|-------------|
| Inorganic nitrate | 10 - 80 |
| Oxidizing Agents (other than inorganic nitrates) | 0 - 30 |
| Water | 5 - 25 |
| Water Gelling Agent | 0.2 - 2.0 |
| Non-explosive Sensitizing Agent | 0 - 50 |
| Fuels | 0 - 15 |
| Nitroparaffin | 5 - 30 |
| Polymeric thickener of nitroparaffin selected from the group consisting of cellulose acetate, cellulose acetate butyrate, cellulose acetate propionate, polymers of methyl, ethyl and butyl methacrylate, copolymers of vinylidene chloride and acrylonitrile and mixtures thereof | 0.05 - 2.0 |

said gelled explosive material being formed by adding said polymeric thickener to an aqueous medium selected from the group consisting of water and an aqueous solution containing at least a portion of said inorganic nitrates and thereafter adding the remaining ingredients.

40. The method of claim 39 further comprising admixing an effective amount of an emulsifier with said aqueous medium.

41. The method of claim 40 wherein said emulsifier is a hydrogenated tallow amine.

42. The method of claim 41 wherein said polymeric thickening agent is in powdered form.

43. The method of claim 39 wherein said nitroparaffin is nitromethane.

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44. The method of claim 39 wherein said inorganic nitrate is selected from the group consisting of nitrates of ammonium, alkali metals, alkaline earth metals, Group III elements, and mixtures thereof.

45. The method of claim 39 wherein said oxidizing agents are selected from the group consisting of sodium perchlorates, ammonium perchlorates and mixtures thereof.

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46. The method of claim 39 wherein said water gelling agent is selected from the group consisting of guar gum, polyacrylamide and mixtures thereof.

47. The method of claim 39 wherein said fuel is selected from the group consisting of ethylene glycol, aluminum and mixtures thereof.

48. The method of claim 39 wherein said non-explosive sensitizing agent is glass microballons.

49. The product produced by the method of claim 39.

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THE BDM CORPORATION

FOREIGN FIRM PATENTS

Patent Number: 3,956,040
Author: Hiroshi Tezuka, Tokyo, Japan
Title: Explosive Slurry Composition Containing Sodium Montmorillonite
Date: May 11, 1976

Patent Number: 3,980,510
Author: John Jerold Ridgeway, Paris, France
Title: Nitroparaffin Explosive Composition Containing Hydrazine and
Diethylenetriamine
Date: September 14, 1976

Patent Number: 4,141,766
Author: Ian R. Cameron, Irvine, Scotland; John Cooper, Adrossan, Scotland
Title: Slurry Explosive Composition
Date: February 27, 1979

Patent Number: 4,221,616
Author: Collin D. McLean, Mulgrave, Australia
Title: Hydrophobic Explosive Composition and Method of Making
Date: September 9, 1980

[54] **EXPLOSIVE SLURRY COMPOSITION
CONTAINING SODIUM
MONTMORILLONITE**

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C06B 31/12; C09K 7/00

[58] **Field of Search** 149/19.1, 20, 60, 61,
149/118, 41, 38, 46, 47, 62; 252/8.5 R, 8.5
A, 8.5 B; 260/70 R

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Estabrook

[57] **ABSTRACT**

An explosive slurry composition having excellent suspension stability, good thixotropic characteristics, high detonation power and good temperature characteristics comprises as ingredients a water-swollen gel of a complex composed of sodium montmorillonite and a water-soluble organic compound having a polar group, and an oxygen supplier such as ammonium nitrate and/or a sensitizer such as aluminum powder and/or a fuel such as saccharide, fuel oil and the like. This explosive slurry composition is used for blasting hard rocks and the like in situ connected with a booster or cap.

19 Claims, No Drawings

EXPLOSIVE SLURRY COMPOSITION CONTAINING SODIUM MONTMORILLONITE

This invention relates to an explosive slurry composition comprising as an indispensable ingredient a water-swollen gel of a complex composed of montmorillonite and a water-soluble organic compound, especially an organic compound having a polar group such as $-NH_2$, $-OH$ and $-SO_3H$ (hereinafter referred to as "polar compound").

By the term "slurry explosive" is generally meant an explosive which contains water and has fluidity and which is fed into a blasting situ by means of a pump and is exploded in situ connected with a booster or cap for blasting hard rocks and the like.

Conventional slurry explosives are generally formed by incorporating and suspending an oxygen supplier, a sensitizer, a thickening agent and the like into water. As the oxygen supplier there are employed ammonium nitrate, sodium nitrate and the like, and as the sensitizer there are employed an organic sensitizer such as self-explosive T.N.T. and a metallic sensitizer such as aluminum powder and the like. Guhr gum or the like is incorporated as a thickening agent in conventional slurry explosives.

However, these conventional slurry explosives involve various defects that should be overcome. For example, the following defects and shortcomings are inevitably involved in conventional slurry explosives.

1. In conventional slurry explosives, sedimentation of the oxygen supplier, sensitizer, fuel or the like is caused to occur in the slurry with the lapse of time after preparation, and hence, reduction of the detonation power cannot be avoided.

In general, a slurry explosive may comprise 15 to 40% by weight of water and 40 to 70% by weight of ammonium nitrate, sodium nitrate or other oxygen supplier. When the oxygen supplier is contained at such a high concentration, with the lapse of storage time or if the ambient temperature is lowered below the saturated temperature of the oxygen supplier, the finely divided powers or particles of the oxygen supplier gradually cohere to form coarse crystals, which come to precipitate in the slurry.

Once such sedimentation occurs, pumping of the slurry explosive becomes difficult and the dispersion state of explosive ingredients becomes heterogeneous, resulting in reduction of the detonation power or in misfiring of slurry explosive.

Also the sensitizer such as aluminum powder is gradually sedimented with the lapse of time and this sedimentation has had influences on the exploding property. 2. Conventional slurry explosives are insufficient with respect to the thixotropic characteristics.

In general, it is desired that slurry explosives have so called "thixotropic" characteristics, namely they have such properties that on filling in a blasting hole the explosive is so lowly viscous and so fluid that pumping can be accomplished smoothly and after filling in a blasting hole the viscosity is recovered to an appropriate level.

In conventional slurry explosives, however, in order to improve the thixotropic characteristics it is necessary to add especially a thickening agent such as guhr gum. Moreover, in order to heighten viscosity of slurry after charging, it has been proposed to incorporate a cross-linking agent such as borax or potassium dicro-

mate into the explosive before charging or to mix such a cross-linking agent together with the explosive by means of a separate feed pump.

These means, however, involve problems as to selection of the thickening agent or cross-linking agent, adjustment of the amount used of the thickening agent or cross-linking agent, and other controls to be made depending on the ambient temperature or the like. Therefore, none of these proposals give satisfactory results. 3. Bowden et al in "Initiation and Growth of Explosion In Solids and Liquids," Cambridge University Press (1952) confirmed that microbubbles present in situ dispersed in the explosive generally give good results as regards the detonation power.

In conventional slurry explosives, however, this requirement is not satisfied and therefore, a method comprising adding such a chemical as sodium lauryl sulfate or sodium hydrogenborate or a method comprising adding glass microballoons for inseting air microbubbles has been proposed as means for overcoming this defect.

However, these methods are troublesome and high cost is necessary in order to practise them. Therefore, it cannot be said that these methods will always give satisfactory results.

It is therefore a primary object of this invention to provide a novel slurry explosive in which the above-mentioned fatal defects involved in conventional slurry explosives can be overcome and to which excellent and desirable properties are imparted.

More detailedly, the primary object of this invention is to provide a slurry explosive in which the above-mentioned undesired phenomenon of coarsening of crystals of ammonium nitrate or the like is not caused to occur even with the lapse of time or even if the ambient temperature changes in a broad range and which can retain a completely thixotropic state even without use of any particular thickening agent or cross-linking agent.

Another object of this invention is to provide an explosive slurry composition which inherently possesses a great number of microbubbles in such a dispersed state as will give good results to the detonation power.

I have conducted research on sodium montmorillonite (hereinafter referred to merely as "montmorillonite") for a long time with a view to developing effective uses of montmorillonite, and found that a macromolecule of a complex of montmorillonite and a water-soluble organic compound, especially a water-soluble organic compound having polar group such as $-NH_2$, $-OH$ and $-SO_3H$, is very suitable as a base of a slurry explosive capable of attaining the foregoing objects. Based on this finding, I have now completed this invention.

Montmorillonite is a substance containing inherently oxides of Si, Al, Mg, Ca, Na, K and the like, and its crystals are very fine (for example, a particle size of about 0.1μ). Further, montmorillonite can form complex with a variety of water-soluble organic compounds, which are inserted between crystal lattice layers of montmorillonite in such complex. Further, the complex can form swollen-gel when water is incorporated in an amount 8 to 15 times the amount of montmorillonite.

For preparing the complex of this invention, the following water-soluble organic compounds can be used.

A. Urea and urea derivatives such, for example, as urea, guanidine nitrate, guanidine carbonate and water-soluble urea-formaldehyde resins.

B. Aliphatic and aromatic amines such, for example, as ethylamine, diethylamine and p-phenylene diamine.

C. Acid amides such, for example, as formamide.

D. Amino acids and proteins such, for example, as glycine, alanine (its methyl ester), valine glutamic acid, albumin, lactoalbumin casein and water-soluble gelatin.

E. Pyridines such, for example, as pyridine, piperidine, piperazine and pyridazine.

F. Cellulose derivatives such, for example, as carboxymethyl cellulose and carboxyethyl cellulose.

G. Aliphatic and aromatic polyhydric alcohols such, for example, as ethylene glycol, glycerin and polyvinyl alcohol.

H. Lignosulfonic acid salts such, for example, as sodium lignosulfonate and ammonium lignosulfonate.

I. Methyl nitramine monohydrate, dimethyl nitramine monohydrate, nitromethane and nitroethane.

As is disclosed in literature references, for instance, Bradley; J. Am. Chem. Soc., 67, pages 975 (1945) and Sterling; J. Phys. Chem., 45, pages 65-81 (1941), montmorillonite can readily form complex with organic compounds such as mentioned above.

As result of my experiments, it has been confirmed that many polar compounds can intrude in Van der Waals spaces in clearances between crystal lattice layers of montmorillonite to form complex.

When attapulgite (palygorskite) is used instead of montmorillonite, similar complex can be formed with these polar compounds.

As the oxygen supplier to be incorporated into a water-swollen gel of a complex of montmorillonite and such polar compound, there can be mentioned, for example, ammonium nitrate, sodium nitrate, ammonium perchlorate, etc. In view of the cost and exploding property, use of ammonium nitrate is most preferred. When the oxygen balance, solubility and other factors are taken into consideration, it is preferred to substitute a part (up to 50% by weight) of ammonium nitrate by sodium nitrate.

One of most characteristic features of the explosive slurry composition of the invention is that it retains a very good stability even with the lapse of time.

As pointed above, in conventional slurry explosives fine powders or particles of the oxygen supplier such as ammonium nitrate gradually cohere to form coarse crystals with the lapse of time or if the ambient temperature changes, and these crystals sediment in the slurry system to cause heterogeneous distribution of explosive ingredients.

In contrast, in the water-swollen gel of a complex of montmorillonite and a polar compound according to this invention, ammonium nitrate and other ingredients do not cause such undesired phenomenon.

The reason has not completely been elucidated, but it is believed that the water-swollen gel of a complex of montmorillonite and a polar compound is present in the system in the form of a macromolecule and this macromolecule has an activity to prevent coarsening of crystals and causes such a strong linkage with ammonium nitrate or the like as will prevent cohesion and crystallization of ammonium nitrate or the like, with the result that a stable suspension state can be maintained for a long time.

It is surprising that also with respect to a powder of a metal to be used as a sensitizer, such as aluminum powder, the initial stable state can be retained for a

long time in a water-swollen gel of the complex of this invention.

It is believed that this feature may probably be attained by the molecular absorption of the surface of montmorillonite, though the detailed reason has not completely been elucidated.

In respect to conventional slurry explosives, various methods have been proposed as means for maintaining a good suspension stability of ingredients. There can be mentioned, for example, a method comprising incorporating carboxymethyl cellulose, a protein or the like into the slurry and a method comprising adding an acid salt of a higher alkyl amine or a salt of lauryl sulfate.

As a result of my experiments, however, it has been confirmed that none of these proposals give such excellent results as attainable according to this invention. It has also been found that a water-swollen gel of the complex of this invention gives much better results than those attained by a water-swollen gel composed merely of montmorillonite.

In the case of a water-swollen gel of the complex of this invention, it also is possible to keep a petroleum such as fuel oil in the stably dispersed state in the slurry explosive. In case detonation of a slurry explosive is effected only with a petroleum such as fuel oil, the handling safety is generally much higher than when a self-explosive sensitizer is employed, and further, the operation cost is much lower. Therefore, in the art it is generally desired that detonation of a slurry explosive is effected only with a petroleum.

However, as a result of my experiments it has been confirmed that it is impossible to retain a sufficiently stable dispersion of such fuel in conventional slurry explosives for a long time, and cohesion and phase-separation of the fuel gradually occur, resulting in reduction of the detonation power of the explosive.

In the explosive slurry composition of this invention composed of a water-swollen gel of the above-mentioned complex, the foregoing problems involved in conventional techniques are solved and it is possible to improve greatly the suspension stability of a petroleum in the explosive slurry. In this invention, the dispersibility of a petroleum can be further heightened by incorporating a lower acid amide or water-soluble alkyl amine in an amount of 0.3 to 0.7% by weight based on the total composition.

Excellent thixotropic characteristics of the explosive slurry composition of this invention will now be described. Most of colloidal systems, especially concentrated emulsions and suspensions, have a so-called thixotropic property, namely a property that when they are made fluid by application of stress, softening occurs and the viscosity is lowered but if the fluid state is caused to disappear, the viscosity is returned to the original high level.

Although a water-swollen gel composed merely of montmorillonite has such thixotropic property, a water-swollen gel of a sodium montmorillonite complex of this invention is especially excellent in thixotropic characteristics required of a slurry explosive, and it can readily be pumped into a blasting hole and the required viscosity can promptly be recovered throughout the entire composition after charging. Accordingly, there is attained an advantage that when the explosive of this invention is charged in, for instance, a downwardly inclined hole, the charged explosive does not flow down.

In the explosive slurry composition of this invention, microbubbles making a desired contribution to the blasting effect are inherently contained.

By Bowden et al supra who proposed Hot Spot Theory, it has already been confirmed that microbubbles of air or gas present in an explosive are compressed in an adiabatic state at the initial stage of detonation, whereby the blasting effect is further enhanced.

In the montmorillonite complex of this invention, since the shape of montmorillonite crystals is flat and irregular and the particle size differs greatly within a range of 100 μ to 30 μ , a space is inherently present in each crystal. Furthermore, since fine particles of montmorillonite make a contribution to enhancement of the shock interaction caused by shock waves of detonation. Thus, it is believed that by virtue of features the state desired and suitable for detonation can be attained in the explosive slurry composition of this invention.

In the case of the explosive slurry composition of this invention, any of particular means for formation of air bubbles such as indispensable in conventional slurry explosives, need not be adopted and the intended object can naturally be attained.

Embodiments of the explosive slurry composition will not be described.

The explosive slurry composition of this invention is formed by adding 50 to 70 parts by weight of ammonium nitrate or a mixture of ammonium nitrate and sodium nitrate as an oxygen supplier to 23 to 32 parts by weight of a water-swollen gel of a complex of montmorillonite and a polar compound, adding 3 to 12 parts by weight of at least one member selected from powdery metals such as aluminum powder, saccharides such as sucrose, urea and petroleum such as fuel oil as a sensitizer and/or a fuel and further adding small amounts of a viscosity adjusting agent, a dispersing agent and/or a buffer agent according to need.

According to this invention, a water-swollen gel of a complex composed of montmorillonite and a polar compound is prepared by pulverizing a bentonite ore, suspending the resulting particles in water, passing the resulting suspension-sol through a filter of about 300 mesh to remove the majority of the silt, allowing the filtered suspension-sol to stand still to sediment a silt of a fine size, decanting the resulting suspension-sol free of this silt, heating and concentrating the suspension-sol to form a water-swollen gel in which the weight ratio of montmorillonite: water is within a range of from 10 : 90 to 15 : 85, adding 1 to 5 parts by weight of a polar compound to 22 to 28 parts by weight of the so formed gel, and agitating sufficiently the resulting mixture to form a desired water-swollen gel of a complex of the polar compound and montmorillonite. In practising the above preparation process, it is possible to add an aqueous solution containing a desired amount of the polar compound to the suspension-sol before the heating step to effect concentration.

Then, 50 to 70 parts by weight of ammonium nitrate or an oxygen supplier composed of more than 50% by weight of ammonium nitrate and less than 50% by weight of sodium nitrate is incorporated into 23 to 33 parts by weight of the so formed water-swollen gel of the complex of montmorillonite and the polar compound.

Furthermore, a sensitizer or a fuel is incorporated, into the resulting admixture. Aluminum powder is most suitable as the sensitizer, and it is preferred that alumi-

num powder has a flaky form of a size of 50 to 325 mesh, which has a broad size-distribution range including very fine particles. In the explosive slurry composition of this invention, the amount incorporated of aluminum powder does not exceed 6% by weight based on the total explosive. In case aluminum powder is incorporated just before use of the explosive, deterioration or degradation of the explosive can be avoided. When aluminum powder is incorporated and then the explosive is stored for a certain period, the pH of the explosive is adjusted to 3.5 to 5.5 by addition of a buffer solution. When petroleum is incorporated, use of fuel oil having a calorific value of 10,000 to 11,000 Kcal/Kg is preferred. In addition, liquid paraffins of a low volatility composed of alkyl naphthenes can be used as the fuel. Moreover, carbonaceous materials such as sucrose and fructose can be used as the fuel. Urea is also a preferred fuel.

In addition to the foregoing ingredients, ions of humic acid, lignosulfonic acid and tannic acid are optionally incorporated in amounts not exceeding 2% by weight based on the composition as a peptizer.

In case a fuel oil is employed, in order to maintain a good dispersion state in the slurry, it is very effective to incorporate lower acid amides such as acetamide and acrylamide or water-soluble alkyl amines.

This invention will now be illustrated more detailedly by reference to Examples.

EXAMPLE 1

A bentonite ore was pulverized and suspended in water, and the majority of the silt was removed by passing the resulting suspension-sol through a filter of about 300 mesh. The filtered suspension-sol was then allowed to stand still for 20 hours to sediment a silt of a finer size. The so formed silt-free suspension-sol was subjected to decantation and concentrated under heating to obtain a water-swollen gel in which the montmorillonite : water weight ratio was 12 : 88.

Then, 3 parts by weight of urea was incorporated into 28 parts by weight of the so formed gel and the mixture was sufficiently agitated to obtain 31 parts by weight of a water-swollen gel of a complex of montmorillonite and urea.

Then, 62 parts by weight of ammonium nitrate as an oxygen supplier, 5 parts by weight of aluminum powder as a sensitizer and 2 parts by weight of urea as a fuel were added to the water-swollen gel of the complex, and a minute amount of a buffer agent was further added in order to maintain the pH of 3.5 to 5.5. Thus was obtained about 100 parts by weight of a typical instance of the explosive slurry composition of this invention.

A part of the so obtained composition was charged in a cartridge having a diameter of 50 mm and a length of 400 mm, and it was subjected to the explosion test at an ambient temperature of 20°C. or 5°C. with use of a booster (10 g of dynamite) and a cap (No. 6). In each case, the explosive completely shot and the detonation velocity was 4,200 m/sec at an ambient temperature of 20°C. and 4,100 m/sec at an ambient temperature of 5°C.

The same composition was allowed to stand still at about 20°C. for 480 hours and after this storage the explosion test was conducted under the same conditions as above. The detonation velocity was 4,100 m/sec at an ambient temperature of 20°C. and 4,000 m/sec at an ambient temperature of 5°C. Thus, it was

found that no substantial degradation of the detonation power was brought about by storage.

In the case of a comparative sample of a conventional slurry explosive composed of 18 parts by weight of water, 70 parts by weight of ammonium nitrate, 10 parts by weight of aluminum, 2 parts by weight of a thickening agent and a minute amount of a buffer agent, the detonation velocity was 4,800 m/sec at 20°C. just after preparation but it was lowered to 4,400 m/sec at 5°C. After 480 hours' storage, the sample did not shoot at the explosion test conducted at 20°C. Thus, it was confirmed that the detonation property of the sample was greatly degraded by storage.

In the case of another comparative sample composed of 30 parts by weight of a water-swollen gel composed merely of montmorillonite, 62 parts by weight of ammonium nitrate, 8 parts by weight of an aluminum powder and a minute amount of a buffer agent, the detonation velocity was 3,300 m/sec at 20°C. and 3,200 m/sec at 0°C., and after 480 hours' storage, the detonation speed was lowered to 2,900 m/sec at 20°C. Thus, it was confirmed that in the case of this comparative sample the detonation velocity was lower than in the case of the explosive slurry composition of this invention and the degree of degradation of the detonation power was rather greater than in the case of the explosive slurry composition of this invention.

EXAMPLES 2 to 5

Ammonium nitrate alone or its mixture with a minor amount of sodium nitrate was incorporated as an oxygen supplier into a water-swollen gel of a complex of montmorillonite and urea, a water-soluble urea-formaldehyde resin or a mixture thereof as a polar compound. Aluminum powder as a sensitizer and urea or sucrose as a fuel were further incorporated. The so formed explosive slurry composition was subjected to the explosion test at an ambient temperature of 20°C. The composition of each explosive and the explosion test results are shown in Table 1.

Table 1

| | Example | | | |
|--|---------------|---------------|---------------|---------------|
| | 2 | 3 | 4 | 5 |
| A. Composition (parts by weight) | | | | |
| (1) Water-swollen gel of complex of montmorillonite and polar compound: | | | | |
| (a) gel of montmorillonite and water (12.88) | 25 | 25 | 25 | 25 |
| (b) urea | | 1.2 | 1.5 | 1.5 |
| (c) water-soluble urea-formaldehyde resin | 2.5 | | | 3 |
| (2) oxygen supplier: ammonium nitrate | 60 | 60 | 60 | 62 |
| sodium nitrate | 4 | 4 | 4 | 3 |
| (3) sensitizer and fuel: aluminum powder | 4 | 4 | 2 | 1 |
| urea | | 1.3 | | 4.5 |
| sucrose | 4.5 | 4.5 | 7.5 | |
| (4) buffer agent | minute amount | minute amount | minute amount | minute amount |
| B. Detonation Velocity (m/sec) (results of the test conducted with use of cartridge of 50 mm diameter and 400 mm length, booster (10 g. of dynamite) and cap No. 6) | | | | |
| just after preparation | 4,000 | 4,200 | 3,800 | 4,100 |
| after 480 hours' storage | 3,800 | 4,000 | 3,700 | 4,100 |

From the results shown in the above Table, it is seen that when a water-swollen gel of the montmorillonite complex of this invention is employed, the properties of the explosive are hardly degraded with the lapse of time.

EXAMPLES 6 to 10

As the polar compound for formation of the complex with montmorillonite, at least two members selected from ethylene glycol, glycerol, pyridine, protein (albumin) and sodium lignosulfonate were used in addition to, or instead of, a urea type compound. Ammonium nitrate as an oxygen supplier and urea and sucrose as a fuel were employed but no sensitizer was incorporated.

The composition of each explosive sample and the results of the detonation test are shown in Table 2.

Table 2

| | Example | | | | |
|--|---------|--------|--------|-------|-------|
| | 6 | 7 | 8 | 9 | 10 |
| A. Composition of Explosive (parts by weight) | | | | | |
| (1) water-swollen gel of complex of montmorillonite and polar compound: | | | | | |
| (a) swollen gel of montmorillonite and water (12.88) | 23 | 23 | 25 | 25 | 25 |
| (b) ethylene glycol | 1.5 | 0.5 | | | |
| (c) pyridine | | 2 | 1.5 | | |
| (d) glycerol | 0.5 | | | 2 | |
| (e) protein (albumin) | | | | | 1 |
| (f) urea | 0.5 | | 0.5 | 0.5 | 0.5 |
| (g) sodium lignosulfonate | 0.5 | | | 0.5 | 1.5 |
| (2) ammonium nitrate | 65 | 65 | 65 | 65 | 65 |
| (3) fuel: urea | 5 | 5.5 | 5 | 5 | 5 |
| sucrose | 4 | 4 | 3 | 2 | 2 |
| B. Detonation Test Results (test was conducted with use of cartridge 20 mm diameter and 300 mm length and cap No. 6) | | | | | |
| at 5°C | shot | failed | failed | shot | shot |
| at 25°C | shot | shot | shot | shot | shot |
| C. Detonation Velocity (m/sec as measured at 25°C.) (results of test conducted with use of cartridge of 50 mm diameter and 400 mm length and cap No. 6) | | | | | |
| | 3,500 | 3,400 | 3,400 | 3,800 | 4,100 |

As is apparent from the test results shown in the above Table, the explosive slurry composition of this invention is characterized in that it can be completely detonated even when a sensitizer such as aluminum powder is not particularly incorporated.

It was found that an explosive having a composition of Example 10 is especially excellent in the thixotropic characteristics.

EXAMPLES 11 to 15

As the polar compound for formation of a complex with montmorillonite, carboxymethyl cellulose, polyvinyl alcohol or formamide was employed in addition to

the urea type compound. The composition of each explosive and the results of the explosion test are shown in Table 3.

Table 3

| | Example | | | | |
|--|---------------|-------|---------------|--------|-------|
| | 11 | 12 | 13 | 14 | 15 |
| A. Composition (parts by weight) | | | | | |
| (1) water-swollen gel of complex of montmorillonite and polar compound | | | | | |
| (a) swollen gel of montmorillonite and water (12.88) | 25 | 25 | 25 | 23 | 23 |
| (b) carboxy-methyl cellulose | 1.5 | | 1.5 | | 1.0 |
| (c) polyvinyl alcohol | | 1.3 | | 1.5 | |
| (d) urea | 1.5 | 1.7 | 1.3 | 1.0 | 0.5 |
| (e) sodium lignosulfonate | | | 0.5 | 0.5 | 1.0 |
| (f) formamide | | | 1.2 | | 0.5 |
| (2) oxygen supplier | | | | | |
| ammonium nitrate | 63 | 63 | 63 | 62 | 62 |
| sodium nitrate | | | | 3 | 3 |
| (3) sensitizer and fuel | | | | | |
| aluminum powder | 2 | | 2 | | |
| sucrose | | 3 | 2.5 | 3 | 4 |
| urea | 7 | 6 | 3 | 6 | 5 |
| buffer agent | minute amount | | minute amount | | |
| B. Results of Detonation Test (conducted with use of cartridge of 50 mm diameter and 400 mm length) | | | | | |
| at 0°C | shot | shot | shot | failed | shot |
| at 30°C | shot | shot | shot | shot | shot |
| detonation velocity (m/sec as measured at 0°C) | 3,700 | 3,500 | 3,900 | 3,800 | 3,800 |

From the results shown in the above Table, it is seen that the detonation property of the explosive slurry composition of this invention is not degraded at a lower temperature, and it is possible to obtain a desired detonation velocity optionally by changing the composition of the montmorillonite complex.

EXAMPLES 16 to 20

Explosives free of a metallic sensitizer, compositions of which are shown in Table 4, were prepared by employing fuel oil as a fuel. These explosives were subjected to the detonation test. The composition of each explosive and results of the detonation test are shown in Table 4.

Table 4

| | Example | | | | |
|--|---------|------|------|------|------|
| | 16 | 17 | 18 | 19 | 20 |
| A. Composition (parts by weight) | | | | | |
| (1) water-swollen gel of complex of montmorillonite and polar compound | | | | | |
| (a) swollen gel of | 23.5 | 23.5 | 23.5 | 23.5 | 23.5 |

Table 4-continued

| | Example | | | | |
|--|---------|-------|-------|-------|-------|
| | 16 | 17 | 18 | 19 | 20 |
| 5 | | | | | |
| montmorillonite and water (13.87) | | | | | |
| (b) urea | 3 | 2 | 1 | 3 | 3 |
| (c) carboxy-methyl cellulose | | 1 | 2 | | |
| 10 | | | | | |
| (2) oxygen supplier | | | | | |
| ammonium nitrate | 68 | 63 | 63 | 68 | 68 |
| sodium nitrate | | 5 | 5 | | |
| (3) fuel | | | | | |
| fuel oil | 5 | 5 | 5 | 5 | 5 |
| 15 | | | | | |
| (4) dispersing agent | | | | | |
| acetamide | 0.5 | | 0.5 | | |
| ethylamine | | 0.5 | | 0.5 | |
| 20 | | | | | |
| B. Results of Detonation Test (conducted at 20°C with use of cartridge of 50 mm diameter and 400 mm length and cap No. 6) | | | | | |
| detonation velocity (m/sec): | | | | | |
| just after preparation | 4,000 | 3,700 | 3,700 | 4,100 | 3,900 |
| after 480 hours' storage | 3,600 | 3,300 | 3,400 | 4,000 | 3,700 |

As is seen from the results shown in the above Table, in the explosive slurry composition of this invention fuel oil can be used as the fuel, and the detonation property of the explosive slurry composition of this invention is hardly degraded even if it is stored for a long time.

EXAMPLES 21 to 24

As the polar compound for formation of a complex with montmorillonite, nitromethane or methyl nitramine mono hydride was employed in addition to the ethylene glycol type compound. The composition of each explosive and the results of the explosion test are shown in Table 5.

Table 5

| | Example | | | |
|--|---------|-------|-------|-------|
| | 21 | 22 | 23 | 24 |
| A. Composition of Explosive (parts by weight) | | | | |
| (1) Water-swollen gel of complex of montmorillonite and polar compound | | | | |
| (a) swollen gel of montmorillonite and water (15.85) | 20 | 20 | 18 | 18 |
| (b) nitromethane | | | 7 | 7 |
| (c) methyl nitramine monohydrate | 8 | 8 | | |
| (d) ethylene glycol | 4 | 4 | 2 | 2 |
| 55 | | | | |
| (2) Oxygen supplier | | | | |
| ammonium nitrate | 50 | 50 | 50 | 50 |
| sodium nitrate | 8 | 6 | 6 | 6 |
| (3) Sensitizer and fuel | | | | |
| aluminum powder | 2 | | | 2 |
| urea | 6 | 8 | 10 | 8 |
| ethylene glycol | 2 | 4 | 7 | 7 |
| 60 | | | | |
| B. Results of Detonation Test (conducted cartridge of 30 mm diameter and 400 mm length) | | | | |
| at 10°C | shot | shot | shot | shot |
| at 0°C | shot | shot | shot | shot |
| detonation velocity (m/sec as measured at 10°C) and Cap No. 6 | 5,300 | 5,300 | 4,800 | 5,000 |

What is claimed is:

1. A explosive composition which comprises an aqueous slurry of:

- a. at least one inorganic oxidizing salt; and
- b. a complex of sodium montmorillonite and a water-soluble organic compound containing at least one $-NH_2$, $-OH$ or $-SO_3H$ group, said complex being in the form of a water-swollen gel in which the sodium montmorillonite: water weight ratio is between about 10:90 and 15:85.

2. An explosive slurry composition set forth in claim 1 wherein the water-soluble organic compound containing a polar group is at least one member selected from the group consisting of urea, guanidine nitrate, guanidine carbonate, water-soluble urea-formaldehyde resins, ethylamine, diethylamine, p-phenylene diamine, formamide, glycine, alanine methyl ester, valine, glutamic acid, albumin, lactalbumin, casein, water-soluble gelatin, pyridine, piperidine, piperazine, pyridazine, carboxymethyl cellulose, carboxyethyl cellulose, ethylene glycol, glycerin, polyvinyl alcohol, sodium lignosulfonate, ammonium lignosulfonate, nitromethane, nitroethane, methyl nitramine and dimethyl nitramine.

3. An explosive slurry composition set forth in claim 1 wherein ammonium nitrate or a mixture of more than 50% by weight of ammonium nitrate and less than 50% by weight of sodium nitrate is incorporated as the oxygen supplier in an amount of 50 to 70 parts by weight per 23 to 33 parts by weight of the water-swollen gel of the complex of montmorillonite and the water-soluble organic compound containing a polar group and at least one member selected from aluminum powder, urea, sucrose and petroleum such as fuel oil is incorporated as the sensitizer and/or fuel in an amount 5 to 12 parts by weight per 23 to 33 parts by weight of the water-swollen gel of the complex of montmorillonite and the water-soluble organic compound containing a polar group.

4. An explosive slurry composition set forth in claim 3 wherein 60 to 67 parts by weight of ammonium nitrate is incorporated into 23 to 33 parts by weight of a water-swollen gel of a sodium montmorillonite-urea complex prepared by adding 1 to 5 parts by weight of urea to 22 to 28 parts by weight of a swollen gel of sodium montmorillonite and water in which the sodium montmorillonite: water weight ratio is within a range of from 10:90 to 15:85, and 2 to 5 parts by weight of aluminum powder, 1 to 5 parts by weight of urea and 0 to 9 parts by weight of sucrose are further incorporated into the resulting admixture.

5. An explosive slurry composition set forth in claim 3 wherein 60 to 67 parts by weight of ammonium nitrate is incorporated into 23 to 33 parts by weight of a water-swollen gel of a complex of sodium montmorillonite, urea and sodium lignosulfonate prepared by adding 0.5 to 1.5 parts by weight of a protein, 0.5 to 2 parts by weight of urea and 0 to 1.5 parts by weight of sodium lignosulfonate to 22 to 28 parts by weight of a swollen gel of sodium montmorillonite and water in which the sodium montmorillonite: water weight ratio is within a range of from 10:90 to 15:85, and 4 to 7 parts by weight of urea and 1 to 5 parts by weight of sucrose are further incorporated in the resulting admixture.

6. An explosive slurry composition set forth in claim 3 wherein 60 to 67 parts of ammonium nitrate is incorporated into 23 to 33 parts by weight of a water-swollen gel of: complex of sodium montmorillonite and, car-

boxymethyl cellulose, urea, formamide and/or sodium lignosulfonate prepared by adding 0.5 to 2 parts by weight of carboxymethyl cellulose, 0.3 to 1.5 parts by weight of urea, 0.2 to 1.5 parts by weight of formamide and 0 to 1 part by weight of sodium lignosulfonate to 22 to 28 parts by weight of a swollen gel of sodium montmorillonite and water in which the sodium montmorillonite: water weight ratio is within a range of from 10:90 to 15:85, and 1 to 3 parts by weight of aluminum powder, 2 to 4 parts by weight of sucrose and 2 to 5 parts by weight of urea are further incorporated into the resulting admixture.

7. The explosive composition of claim 1 wherein said inorganic oxidizing salt consists of at least 50% by weight of ammonium nitrate.

8. The explosive composition of claim 7 wherein said salt consists of a mixture of at least 50% by weight ammonium nitrate with sodium nitrate.

9. The explosive composition of claim 1 wherein said water soluble organic compound is selected from the group consisting of urea, urea derivatives, aliphatic amines, aromatic amines, acid amides, amino acids, proteins, pyridines, cellulose derivatives, aliphatic polyhydric alcohols, aromatic polyhydric alcohols, lignosulfonic acid salts, methyl nitramine monohydrate, nitromethane, nitroethane and mixtures thereof.

10. The explosive composition of claim 1 which contains a sensitizer.

11. The explosive composition of claim 10 wherein said sensitizer is aluminum metal.

12. The explosive composition of claim 1 which contains a fuel.

13. The explosive composition of claim 12 wherein said fuel is petroleum oil, alkyl naphthenes, sucrose, fructose, urea or mixtures thereof.

14. The explosive composition of claim 1 which contains aluminum metal as a sensitizer and petroleum oil as a fuel.

15. The explosive composition of claim 1 which contains a peptizer.

16. The explosive composition of claim 15 wherein said peptizer is humic acid, lignosulfuric acid or tannic acid.

17. The explosive composition of claim 1 which consists essentially of ammonium nitrate, a water-swollen complex of sodium montmorillonite with urea and sucrose.

18. A process for preparing a water-swollen gel of a complex of sodium montmorillonite and a water-soluble organic compound containing at least one $-NH_2$, $-OH$ or $-SO_3H$ group which comprises pulverizing a bentonite ore, suspending the resulting particles in water, removing silt from the resulting suspension-sol, concentrating the suspension-sol to form a gel in which the sodium montmorillonite: water weight ratio is within a range of from about 10:90 to 15:85, incorporating about 1 to 5 parts by weight of said organic compound into about 22 to 28 parts by weight of said gel and then agitating the resulting mixture.

19. The process of claim 18 wherein said organic compound is selected from the group consisting of urea, guanidine nitrate, guanidine carbonate, water-soluble urea-formaldehyde resins, ethylamine, diethylamine, p-phenylene diamine, formamide, glycine, alanine methyl ester, valine, glutamic acid, albumin, lactalbumin, casein, water-soluble gelatin, pyridine, piperidine, piperazine, pyridazine, carboxymethyl cellulose, carboxyethyl cellulose, ethylene glycol, glycerin,

polyvinyl alcohol, sodium lignosulfonate, ammonium
lignosulfonate, nitromethane, nitroethane, methyl ni-

tramine and dimethyl nitramine.

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[54] NITROPARAFFIN EXPLOSIVE
COMPOSITION CONTAINING HYDRAZINE
AND DIETHYLENETRIAMINE

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[52] U.S. Cl. 149/36; 149/89

[51] Int. Cl.² C06B 25/36

[58] Field of Search 149/36, 89

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[57] ABSTRACT

A self-sterilising liquid explosive composition comprising liquid nitroparaffin, for example nitromethane, sensitised with hydrazine and containing diethylenetriamine as a delayed action sterilising agent.

6 Claims, No Drawings

NITROPARAFFIN EXPLOSIVE COMPOSITION CONTAINING HYDRAZINE AND DIETHYLENETRIAMINE

This invention relates to sensitised liquid nitroparaffin explosive compositions containing a delayed action sterilising agent to render the compositions non-detonable at a convenient time after mixing.

Nitroparaffin explosives are widely used in operations requiring a so-called 'two-component' liquid explosive which can be prepared by the on-site mixing of two non-explosive or insensitive ingredients. Generally one component, in this case nitroparaffin, is the energetic component and the second component is the sensitiser. For nitroparaffins, the sensitising components are generally amines. Such an explosive system has the advantage that the separate components can be handled and transported safely to the blasting site by normal transport, thus eliminating the requirement of the costly shipping and handling methods needed for explosives. Thus, the components can be quickly transported by air to widely distant blasting sites and mixed to provide a high quality blasting explosive. In many blasting operations only such a system could give cost-effective operation.

The mixed 'two-component' explosive is, however, a highly sensitive explosive mixture which will retain its sensitivity indefinitely and any explosive remaining after the blasting operation can be hazardous. Thus, in underwater channelling operations for oil-pipe laying, containers of explosive have been lost due to rough weather conditions and these containers constitute a continuing danger. Further, the usage sites for such explosives are generally ill-provided with magazines for explosive storage so that any explosive surplus to the blast requirements has to be detonated and it is often impractical or inconvenient to detonate surplus explosive at the mixing site. There has therefore been a demand for methods of sterilising two-component systems, and especially for delayed action sterilising agents to desensitise the compositions after a convenient period of storage. Many different compounds, for example carbonyl compounds, have been proposed for this purpose and, although effective, they have been found to impair the ease of initiation to detonation of the originally mixed explosive. It is therefore an object of this invention to provide a method of delayed sterilisation of a 'two-component' nitroparaffin explosive which does not impair the ease of initiation of the explosive when originally prepared.

I have now discovered that liquid nitroparaffin explosives sensitised with hydrazine can be rendered self-sterilising by the inclusion of diethylenetriamine in the composition. This is surprising since nitroparaffins are sensitised by amines. The use of an amine as the delayed desensitising agent ensures that initially the explosive remains as sensitive and easily initiated to detonation as the original mixture of nitroparaffin and hydrazine.

Thus, in accordance with this invention, a self-sterilising explosive composition comprises liquid nitroparaffin, sufficient hydrazine to sensitise the nitroparaffin and render it capable of detonation, and diethylenetriamine as a delayed action sterilising agent.

The time required for the initially sensitive explosive mixture to become incapable of initiation to detonation can be varied by variation of the amount of sterilising

agent in the composition. The composition conveniently contains 5 to 15% by weight of hydrazine and 2 to 10% by weight of diethylenetriamine but the amount of diethylenetriamine should preferably not be greater than the amount of hydrazine. Such mixtures will be come insensitive and incapable of detonation with a conventional initiator after 3 to 6 hours.

Suitable liquid nitroparaffins include, for example, nitromethane, dinitromethane, nitroethane, dinitroethane, nitropropane and dinitropropane.

The explosive is conveniently prepared by mixing its non-self-explosive ingredients as required at the site where it is to be used. If desired, however, the nitroparaffin and hydrazine only may be mixed together to prepare a sensitive two-component explosive mixture and the diethylenetriamine may be added at any convenient time thereafter. Accordingly, the invention also includes a method of sterilising a sensitive liquid nitroparaffin hydrazine explosive composition wherein diethylenetriamine is mixed with the composition.

The invention is further illustrated by the following Examples, in which all parts are given by weight.

EXAMPLE 1

85 parts of nitromethane and 10 parts of hydrazine were mixed to form a sensitive liquid explosive which could be detonated reliably at a velocity of more than 6.3 km per second in a 25 mm diameter column by means of a No. 8 blasting cap or a length of detonating cord having a core charge of 50 grains per foot of pentaerythritol tetranitrate (PETN).

5 parts of diethylenetriamine were mixed with 95 parts of the thus prepared explosive composition and when tested shortly after mixing, the explosive properties were the same as those of the original explosive composition and these properties were retained for about 3 to 4 hours. After 4 hours the compositions became insensitive and could not be detonated with a No. 8 blasting cap or a length of detonating cord (50 grains per foot of PETN).

EXAMPLE 2

10 parts of hydrazine were mixed with 5 parts of diethylenetriamine and the resulting mixture mixed with 85 parts of nitromethane. The resulting liquid explosive could initially be reliably detonated in a 25 mm diameter column at a velocity of more than 6.3 km per second by a No. 8 blasting cap or a length of detonating cord (50 grains per foot of PETN) but after 4 hours after the final mixing the composition could not be detonated by a No. 8 blasting cap or a length of detonating cord (50 grains per foot of PETN).

What is claimed is:

1. A self-sterilising explosive composition consisting essentially of a liquid nitroparaffin selected from the group consisting of nitromethane, dinitromethane, nitroethane, dinitroethane, nitropropane and dinitropropane, sufficient hydrazine to sensitise the nitroparaffin and render it capable of detonation, and diethylenetriamine as a delayed action sterilising agent.

2. A composition as claimed in claim 1 comprising from about 75 to about 93% by weight of nitroparaffin, from about 5 to about 15% by weight of hydrazine and from about 2 to about 10% by weight of diethylenetriamine.

3. A composition as claimed in claim 2 wherein the amount of diethylenetriamine is not more than the amount of hydrazine.

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4. A composition as claimed in claim 2 comprising about 85% by weight of nitromethane, about 10% by weight of hydrazine and about 5% by weight of diethylenetriamine.

5. A method of sterilising an explosive composition consisting essentially of a mixture of hydrazine with a nitroparaffin selected from the group consisting of

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nitromethane, dinitromethane, nitroethane, dinitroethane, nitropropane and dinitropropane in which method diethylenetriamine is mixed into the composition as a delayed action sterilising agent.

6. A composition as in claim 1 wherein the nitroparaffin is nitromethane.

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[54] SLURRY EXPLOSIVE COMPOSITION

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[58] Field of Search 149/2, 88, 21, 38, 42, 149/43, 40, 41, 44, 47, 62, 76, 78

[56]

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[57]

ABSTRACT

A slurry explosive composition comprising inorganic oxidizing salt and a liquid solvent, dispenser or carrier for the salt, which liquid is emulsified with a sensitizing liquid aliphatic mononitrate containing from 3 to 8 carbon atoms per molecule.

18 Claims, No Drawings

SLURRY EXPLOSIVE COMPOSITION

This invention relates to improved slurry explosive compositions of the kind containing a liquid alkyl nitrate as sensitiser in the liquid phase of the composition, and to a method of preparing said explosive composition.

Slurry explosives comprise inorganic oxidising salt, fuel and a liquid solvent, disperser or carrier for said salt. Although the term 'slurry' is applied to such compositions the degree of consistency may range from pourable to highly viscous extrudable gels. The oxidising salt generally comprises nitrate or perchlorate of ammonia, sodium potassium, calcium or barium, the most extensively used salt being ammonium nitrate.

The liquid content of slurry explosive is sufficient to maintain a continuous liquid phase which facilitates loading into boreholes or into paper or plastics containers to form blasting cartridges. The liquid phase may vary widely in its chemical constitution consistency and explosive sensitivity. Thus, in aqueous slurries, the liquid phase may consist mainly of an aqueous solution of inorganic oxidising salt but, non-aqueous slurry compositions are known wherein the liquid phase comprises a liquid chemical compound, which acts as fuel to contribute energy to the composition. Thickening agents, such as guar gum, dissolved in the liquid phase have been extensively used to increase the viscosity of slurry explosives, in order to prevent segregation of the ingredients and to prevent deterioration in wet conditions. Further improvements in the homogeneity and storage properties have been obtained by crosslinking the thickening agents with crosslinking agents, for example, potassium and sodium dichromates or potassium pyroantimonate. It is also common practice to improve the sensitivity of slurry explosive compositions by introducing voids to provide 'hot-spots' which are well known to facilitate initiation and propagation of detonation. Such voids may be introduced by mechanical mixing, preferably using a foaming surfactant in the composition, or by including gas filled spheres, or gas generating substances in the composition.

Fuel is included in the slurry explosive composition to combine with the oxygen from the oxidising salt and enhance the power and sensitivity of the composition. A wide variety of fuel materials have been used including coal, sugar, starch and metal powder. Whilst all fuels have a sensitising effect, some fuels have been found to be especially effective in this respect and have been widely used usually in combination with other cheaper fuel. Such sensitisers include solid materials such as finely divided metal powders and self-explosive materials such as trinitrotoluene and pentaerythritol tetranitrate. These metal powder sensitisers are difficult to disperse uniformly in the composition and the compositions tend to become less sensitive on storage. The self-explosive sensitisers are objectionable because they increase the risk of premature ignition of the explosive in handling.

Liquid non-self-explosive sensitising materials such as nitrobenzene and liquid nitrotoluene have been used but have been found to be difficult to hold in suspension in the slurry. More successful liquid sensitisers are the liquid aliphatic mononitrates containing from 3 to 8 carbon atoms, whose use is described in United Kingdom Patent Nos. 1,180,677 and 1,229,736. These liquid sensitisers, when uniformly dispersed, give well sensi-

tised slurries at high density, but tend to separate from the slurry unless they are gelled with nitrocellulose and methyl or ethyl centralite. The gelled sensitiser is less effective and is, moreover, more difficult to disperse uniformly in the composition.

It is an object of this invention to provide an improved method of using liquid aliphatic mononitrate as sensitiser in slurry explosive compositions.

In accordance with this invention a slurry explosive composition comprises at least one inorganic oxidising salt, a liquid solvent, disperser or carrier for said salt and, as sensitising fuel, a liquid aliphatic mononitrate containing from 3 to 8 carbon atoms per molecule, said liquid mononitrate being emulsified with the liquid solvent, disperser or carrier for the inorganic oxidising salt. Compositions of the invention are easier to initiate to detonation and retain the aliphatic nitrate better on storage than corresponding compositions wherein the aliphatic nitrate is not emulsified.

The liquid aliphatic mononitrates containing from 3 to 8 carbon atoms are preferably alkyl mononitrates, which are insensitive compounds with only slight explosive character, although the propyl nitrates have been reported to have been detonated with difficulty.

Preferred nitrates include n-propyl nitrate, isopropyl nitrate, amyl nitrate, hexyl nitrate and octyl nitrate.

The liquid solvent, disperser or carrier for the inorganic salt will, in the more generally used compositions, be water but useful non-aqueous compositions can be prepared wherein the liquid comprises non-aqueous liquids, for example, diethylene glycol, formamide, dimethyl formamide, dimethylsulphoxide or liquid mixtures containing one or more salts, for example, ammonium acetate, ammonium formate or an amine salt containing 1 to 6 carbon atoms, for example, methylamine nitrate or ethylene diamine dinitrate.

The emulsion may contain the liquid mononitrate either in its continuous or disperse phase depending on the emulsifier used to prepare the emulsion. Suitable oil-in-water type emulsifiers for preparing an emulsion with the mononitrate in the disperse phase include

- (a) condensates of polyalkylene oxide with a long chain alcohol containing 10 to 20 carbon atoms per molecule or with an alkyl phenol or alkyl phenol/formaldehyde resin in which phenol or resin the alkyl group contains 5 to 22 carbon atoms or with an amine or polyamine, for example, hexamethylene diamine, said condensates containing from 4 to 100 and preferably from 20 to 50 ethylene oxide groups per molecule; and
- (b) long chain amine oxides having chain lengths of 8 to 24 carbon atoms.

The long chain amine oxides cause foaming of the emulsion and are therefore advantageous for the production of sensitive low density slurry explosive.

Preferred polyalkylene oxide condensates include octylphenol or nonylphenol/polyethylene oxide condensates containing from 20 to 50 ethylene oxide groups per molecule and lauryl alcohol/polyethylene oxide condensates containing from 15 to 30 ethylene oxide groups per molecule.

Preferred amine oxides include N,N-dimethyl dodecylamine oxide, N,N-di(hydroxyethyl) dodecylamine oxide, bis(2-hydroxyethyl) cocoamine oxide and dimethyl cocoamine oxide.

Suitable water-in-oil type emulsifiers for preparing emulsions having the mononitrate in the continuous phase include alkyd condensates of polyethylene glycol with mono- or dicarboxylic acids wherein the Molecu-

lar Weight of the polyethylene glycol is in the range from 200 to 6,000. Optionally the condensates may also contain dihydric- or polyhydric alcohol.

Additional modifying surfactants may be included in the slurry explosive, for example, to control the emulsion droplet size. These surfactants include long chain amines, for example, dodecylamine, ethoxylated amines, for example, N,N-di(hydroxyethyl) dodecylamine, quaternary ammonium salts, for example, cetyl trimethyl ammonium chloride, long chain alkyl sulphate salts, for example, sodium dodecyl sulphate, alkylaryl sulphonic acid salts, for example, sodium dodecylbenzene sulphonate, long chain esters of monohydric or polyhydric alcohols, for example, sorbitan trioleate, ethoxylated esters of monohydric or polyhydric alcohols, and lignosulphonates, for example, sodium lignosulphonate.

The emulsion may also, if desired, contain an emulsion stabiliser to preserve the explosive in adverse conditions of handling and storage. Suitable emulsion stabilisers include long chain alcohols, for example, lauryl alcohol, polyalkylene oxide polymers, for example, an ethylene oxide/propylene oxide block copolymers and water-soluble cellulose or starch ethers, for example, methyl cellulose and hydroxypropyl cellulose.

Preferably the emulsion contains a thickening agent either in its continuous phase or dispersed phase or in both phases. Thus the aqueous emulsion phases may advantageously be thickened with the thickening agents normally used in aqueous slurry explosives including, for example, guar gum, hydroxypropylated guar gum, xanthan gum, starch, polyacrylamide and derivatives thereof, hydroxyethyl cellulose, polyethylene oxide or polyvinyl alcohol. These thickening agents may be crosslinked with alkali metal chromates or borates, titanium salts, potassium pyroantimonates or telluric acid. The aliphatic nitrate phase of the emulsion may be thickened by, for example, nitrocellulose, cellulose esters, polyacrylic esters or copolymers of styrene or alkyl styrene and maleic anhydride or other anhydride of an $\alpha\beta$ -unsaturated dicarboxylic acid and these thickening agents may be crosslinked with metal alkoxides, for example, titanium tetra isopropoxide.

The aforescribed emulsion is compatible with other methods of sensitising explosive slurries. Thus small voids may advantageously be included in the composition and these may be produced, for example, by including in the composition an aeration agent such as a foaming surfactant which entraps air during mixing, or a chemical gassing agent, for example, sodium nitrate, or hollow spheres. Advantageously sufficient voids are included in the composition to give the composition a density in the range 0.8 to 1.5 g/cc.

The inorganic oxidising salt may be present either as the liquid or dispersed solid phase or both phases of the slurry composition. Suitable oxidising salts include nitrates and perchlorates of ammonia, sodium, potassium, barium, magnesium or calcium and mixtures of any two or more of these salts.

The composition preferably comprises from 4 to 20% w/w of liquid alkyl mononitrate and from 5 to 25% w/w of liquid solvent, disperser or carrier, from 0.1 to 3.5% w/w of emulsifier, from 25 to 85% w/w of ammonium nitrate, from 0 to 35% w/w of other inorganic oxidising salt and optionally up to 20% of solid fuel.

The preferred solid fuel is metal powder, for example, aluminium or magnesium, although any of the commonly used solid fuels can be used.

The invention also includes a method of preparing a slurry explosive composition, which method comprises mixing inorganic oxidising salt with a liquid solvent disperser or carrier for said salt and, either before or after said mixing, emulsifying said liquid solvent, disperser or carrier with a liquid aliphatic mononitrate containing from 3 to 8 carbon atoms per molecule.

The invention is further illustrated by the following Examples in which all parts and percentages are by weight.

In the Examples the ammonium nitrate (AN) and sodium nitrate (SN) grades used have the sieve analysis given in the following Table.

TABLE

| Type | Dense Prill AN | Porous Prill AN | Fine Crystalline AN | Crystalline SN |
|---------------------------|----------------|-----------------|---------------------|----------------|
| % Passing | | | | |
| 8 Mesh BSS (2,055 μ) | 99 | 85 | 100 | 100 |
| 30 Mesh BSS (500 μ) | 24 | 5 | 98 | 30 |
| 100 Mesh BSS (150 μ) | 5 | 1.5 | 22 | 5 |
| 200 Mesh BSS (76 μ) | 2 | 2.5 | 2 | — |

The coarse aluminium powder used was atomised aluminium which all passed a 60 mesh BS sieve and 20% was retained on a 200 mesh BS sieve. The fine aluminium was atomised aluminium powder which all passed a 300 mesh BS sieve.

EXAMPLE 1

A solution was prepared from 9.6 parts of calcium nitrate and 9.8 parts of water. To this solution was added 15 parts of isopropyl nitrate and 1.5 parts of a commercial surfactant containing 70% of octyl phenoxy polyethoxy ethanol containing approximately 40 ethylene oxide groups per molecule and commercially available as Triton X405 (Registered Trade Mark). The resultant mixture was agitated vigorously for five minutes and an emulsion of the oil-in-water type formed. To this emulsion were added 61.8 parts of dense prill ammonium nitrate and a suspension of 0.7 parts guar gum and 0.2 parts zinc chromate in 1.4 parts of diethylene glycol and the emulsion was mixed for 1 minute. The resultant mixture was of pourable consistency which gelled after about 3 hours. It had density 1.33 g/cc and, when primed with 4 g pentolite (50/50 TNT/PETN), a 3 $\frac{1}{4}$ " diameter cartridge detonated at a velocity of detonation of 3.3 km/second. The minimum diameter for propagation unconfined was 3".

The same composition prepared as described in this Example but without the emulsifier exuded isopropyl nitrate.

EXAMPLE 2

The procedure of Example 1 was repeated except that the surfactant used was a lauryl alcohol/ethylene oxide condensate containing 20 ethylene oxide groups per molecule. The resulting explosive had density 1.31 g/cc and, when primed with 4 g pentolite (50/50), a 3 $\frac{1}{4}$ " diameter cartridge detonated at a velocity of detonation of 3.2 km/second.

EXAMPLE 3

A solution was prepared from 39.7 parts of ammonium nitrate, 28.8 parts of calcium nitrate, 10.0 parts of sodium nitrate, 4.0 parts ethylene glycol, 2.0 parts urea, 0.2 parts of guar gum, 0.3 parts thiourea and 15.0 parts water.

To 55.0 parts of the solution at 50° C. were added 8.0 parts isopropyl nitrate and 0.5 parts Triton X405 and the mixture was agitated to form an emulsion. 7.5 parts of coarse aluminium, 0.5 parts of starch, 28.3 parts of crushed porous prill ammonium nitrate, 0.2 parts of a 2:1 water/sodium nitrate solution and 0.01 parts of a 1:1 water/sodium dichromate solution were added to the emulsion forming an initially pourable mix which gelled after 30 minutes. The explosive had density 1.22 g/cc and, when initiated by a detonator having a base charge of 0.4 g PETN, a 1½" diameter cartridge of the mixture detonated at a velocity of detonation of 3.2 km/second.

EXAMPLE 4

A solution was prepared from 33.6 parts of ammonium nitrate, 10.4 parts calcium nitrate, 12.0 parts of water, 0.1 parts of guar gum and 0.1 parts thiourea.

To 56.2 parts of this solution at 50° C. were added 5.0 parts of isopropyl nitrate and 0.3 parts of Triton X405 and the mixture was agitated to form an emulsion. To this was added 33.59 parts of ammonium nitrate porous prills on which 3.7 parts of diesel oil had been absorbed, 0.5 parts of starch, 0.5 parts of guar gum, 0.2 parts of 1:2 sodium nitrite/water solution, and 0.01 parts 1:1 sodium dichromate/water solution.

The resulting explosive, after gelation, had density 1.25 g/cc and, when initiated with 28 g pentolite, a 3½" diameter cartridge detonated. The minimum diameter for propagation unconfined was 3" at a velocity of detonation of 3.2 km/second.

EXAMPLE 5

45.05 parts of fine crystalline ammonium nitrate, 10.0 parts of sodium nitrate, 0.15 parts zinc chromate, 0.5 parts of guar gum, 0.2 parts of polyacrylamide, 0.1 parts mannitol, and 15.0 parts coarse aluminium powder were mixed. To this mixture were added 15.0 parts water, 10.0 parts isopropyl nitrate and 1.0 parts of Triton X405 and mixing was continued to emulsify the isopropyl nitrate. 3.0 parts of silane coated hollow glass microspheres ranging in particle size from 20 to 400 microns were added and incorporated by gentle mixing. The pH of the mixture was adjusted to 5.5 by zinc nitrate addition and the slurry was allowed to gel.

The gelled slurry had density 1.21 g/cc and, when initiated with 4 g pentolite at 15° C., a 2" diameter cartridge detonated at a velocity of detonation of 3.5 km/second. The minimum diameter for propagation unconfined was 1½".

A sample of the gelled slurry was confined in a 2" diameter 30" length steel tube and primed with 84 g pentolite under a hydrostatic pressure of 500 psi. On initiation of the primer the slurry detonated, as evidenced by complete rupture of the steel tube.

EXAMPLE 6

7.0 parts of isopropyl nitrate was added to a solution of 0.3 parts Triton X405 and 0.15 parts of sodium dodecylbenzene sulphonate in 6 parts of water, and mixed for 5 minutes. The resulting emulsion was mixed (for 5 minutes) with a pre-mix of 39.34 part of fine crystalline ammonium nitrate, 5.0 parts of sodium nitrate, 11.0 parts of coarse aluminium powder, 0.4 parts of hydroxypropylated guar gum and 0.3 parts of polyacrylamide and the mixture was allowed to stand for a further 5 minutes. A solution of 0.01 parts of chromic nitrate in 0.5 parts water was then added and mixed for 1 minute to give an extrudable composition. The white appear-

ance of the mix and its low density 1.28 g/cc (whereas density 1.6 g/cc would be expected for the non-aerated composition) indicated the presence of small air bubbles in the mix.

When initiated by a detonator having a base charge of 0.4 g PETN, a 3½" diameter cartridge detonated at a velocity of detonation 3.3 km/second. The minimum diameter for propagation unconfined was 1½".

EXAMPLE 7

To a liquid prepared from 45.0 parts of ammonium nitrate, 20.0 parts sodium nitrate, 15.0 parts of ammonium acetate and 20.0 parts formamide heated sufficiently to prevent any crystal precipitation, were added 0.4 parts of hydroxypropylated guar gum which was allowed to solvate.

7.0 parts of isopropyl nitrate and 1.0 part Triton X405 were added to 30 parts of the liquid and mixed to form an oil-in-water type emulsion. A pre-mix of 52.5 parts of fine crystalline ammonium nitrate, 5.0 parts of sodium nitrate and 4.0 parts of coarse aluminium was then mixed with the emulsion. A crosslinker consisting of 0.1 parts zinc chromate was added to the mixture. The mixture had gelled after 24 hours. The density was 1.44 g/cc and, when initiated with 8 g pentolite (50/50) a 3½" diameter cartridge detonated at a velocity of detonation of 3.4 km/second.

EXAMPLE 8

A liquid (for the slurry liquid phase) was prepared from 45.0 parts of ammonium nitrate, 20.0 parts of formamide, 10.0 parts of urea and 20.0 parts of ammonium formate.

To 33.3 parts of this liquid maintained above its crystallisation temperature were added 0.4 parts of hydroxypropylated guar gum which was allowed to solvate. To the resulting solution was then added 7.0 parts of isopropyl nitrate and 1.0 part Triton X405 and the mixture was agitated to form an emulsion. To this emulsion was added 26.0 parts of fine crystalline ammonium nitrate, 30.0 parts of sodium nitrate, 2.0 parts of coarse aluminium powder and 0.3 parts of zinc chromate. After the resulting explosive had gelled it had a density of 1.30 g/cc and, when initiated with 15 g pentolite (50/50), a 3½" diameter cartridge detonated at a velocity of detonation of 3.2 km/second.

EXAMPLE 9

A liquid was prepared from 50.0 parts of ammonium nitrate, 20.0 parts of aluminium nitrate, 10.0 parts of calcium nitrate and 20.0 parts of formamide. An explosive was prepared in a manner similar to that described in Example 8 from 33.3 parts of the liquid, 54.0 parts of fine crystalline ammonium nitrate, 6.0 parts of isopropyl nitrate, 1.0 part of Triton X405, 0.5 parts of hydroxypropylated guar gum, 5.0 parts of coarse aluminium powder and 0.2 parts of zinc chromate. After gelation the explosive had density 1.40 g/cc and, when initiated with 8 g pentolite (50/50), 3½" diameter cartridge detonated.

EXAMPLE 10

A liquid was prepared from 40.0 parts of ammonium nitrate, 20.0 parts of calcium nitrate, 20.0 parts formamide and 20.0 parts ethylene glycol.

An explosive was prepared in a manner similar to that described in Example 8 from 25.0 parts of the liquid, 53.1 parts of fine crystalline ammonium nitrate, 6.0 parts

of isopropyl nitrate, 1.0 part of Triton X405, 3.0 parts of coarse aluminium powder, 0.5 parts of hydroxypropylated guar gum, 0.2 parts of zinc chromate and 11.2 parts of sodium nitrate. The density of this slurry explosive was 1.36 g/cc and, when initiated with 4 g pentolite (50/50), a 3¼" diameter cartridge detonated at 3.3 km/second.

EXAMPLE 11

A composition was prepared from 35.0 parts of the solution prepared in Example 3, 35.10 parts of fine crystalline ammonium nitrate, 10.0 parts of sodium nitrate, 1.0 part of starch, 0.5 parts of hydroxypropylated guar gum, 10.0 parts of isopropyl nitrate, 0.50 parts of bis(2-hydroxyethyl) cocoamine oxide, 7.89 parts of fine aluminium powder and 0.01 parts of 1:1 sodium dichromate/water solution. The mixing procedure was similar to that described in Example 3.

The composition after gelation had a density of 1.28 g/cc and, when initiated by a detonator having a base charge of 0.6 g PETN, a ¼" diameter cartridge detonated at a velocity of detonation of 3.8 km/second.

The emulsifier used in this Example also acted as a foaming agent and entrapped air bubbles into the composition during mixing thereby enhancing the sensitivity.

EXAMPLE 12

The procedure described in Example 11 was repeated except that the emulsifier used was dimethyl cocoamine oxide instead of bis(2-hydroxyethyl) cocoamine oxide, and the resulting explosive composition had the same properties as that prepared in Example 11.

EXAMPLE 13

A solution was prepared from 48.7 parts ammonium nitrate, 17.0 parts sodium nitrate and 17.0 parts water, and, while being maintained at a temperature above its crystallisation temperature, was slowly added with stirring to a mixture of 11.0 parts isopropyl nitrate and 3.0 parts of an alkyd condensate of 1 part pentaerythritol, 1 part glycerol, 2 parts polyethylene glycol (MW 600), 5 parts C₁₈ fatty acid and 2 parts trimellitic anhydride alkyd condensate. To the resultant water-in-oil type emulsion, in which isopropyl nitrate was the continuous phase, were added 3.0 parts of hollow glass microspheres and 0.3 parts of a copolymer of 30 parts t-butylstyrene, 4 parts methyl methacrylate and 3 parts methacrylic acid.

After gelation the resulting explosive had density 1:1 g/cc and, when initiated by a detonator having a base charge of 0.8 g PETN, a 3¼" diameter cartridge detonated at 4.5 km/second.

EXAMPLE 14

8 parts of amyl nitrate were added to 10 parts of water and 0.5 parts of N,N-dimethyl dodecylamine oxide and mixed to form an emulsion. A pre-mix of 6 parts of coarse aluminium powder, 0.7 parts of guar gum, 0.02 parts of potassium pyroantimonate, 5.0 parts of sodium nitrate and 69.78 parts of fine crystalline ammonium nitrate was mixed with the emulsion, and the resulting slurry explosive, after gelation, had density 1.34 g/cc. When initiated with 12 g pentolite (50/50), a 3" diameter cartridge detonated. Separation of amyl nitrate occurred when the same composition was prepared without the emulsifier.

EXAMPLE 15

A slurry was prepared by the mixing procedure described in Example 14 from 8 parts n-propyl nitrate, 10.3 parts of water, 0.5 parts of N,N-di(hydroxyethyl) dodecylamine oxide, 9 parts of coarse aluminium powder, 0.7 parts of guar gum, 0.2 parts of zinc chromate, 5.0 parts of sodium nitrate and 66.3 parts of fine crystalline ammonium nitrate.

The resulting slurry explosive, after gelation, had density 1.30 g/cc and, when initiated with a detonator having a base charge of 0.8 g PETN, a 2¼" diameter cartridge detonated.

The same composition but without the emulsifier exuded n-propyl nitrate.

EXAMPLE 16

A slurry was prepared by the mixing procedure described in Example 14 from 7 parts of isopropyl nitrate, 10 parts of water, 0.5 parts of an ethoxylated octyl phenol/formaldehyde resin (the base resin of which had a Molecular Weight of approximately 900 and was ethoxylated with 4 molecules of ethylene oxide), 10 parts of coarse aluminium powder, 0.7 parts of guar gum, 0.2 parts of zinc chromate, 5 parts of sodium nitrate and 66.6 parts of fine ammonium nitrate. The resulting slurry had density 1.40 g/cc and, when initiated with 4 g of pentolite (50/50), a 3¼" diameter cartridge detonated.

EXAMPLE 17

The procedure described in Example 16 was repeated except that the ethoxylated octyl phenol/formaldehyde resin was replaced by hexamethylene diamine propoxylate of Molecular Weight Approximately 3,500 which had been condensed with 30% of its weight of ethylene oxide. The explosive properties of the resulting composition were the same as those of the composition prepared in Example 16.

EXAMPLE 18

The procedure described in Example 16 was repeated except that the ethoxylated phenol/formaldehyde resin was replaced by 0.1 parts of sodium dodecyl benzene sulphonate and 0.4 parts of a block copolymer containing 20% ethylene oxide and 80% propylene oxide and having a Molecular Weight of 2,500. The explosive properties of the resulting composition were the same as those of the composition prepared in Example 16.

EXAMPLE 19

The procedure described in Example 18 was repeated except that the sodium dodecyl benzene sulphonate was replaced by 0.1 parts of cetyl trimethyl ammonium chloride. The explosive properties of the resulting composition were the same as those of the composition prepared in Example 18.

EXAMPLE 20

The procedure described in Example 18 was repeated except that the sodium dodecyl benzene sulphonate was replaced by 0.1 parts of dodecylamine. The explosive properties of the resulting composition were the same as those of the composition prepared in Example 18.

EXAMPLE 21

The procedure described in Example 18 was repeated except that the sodium dodecyl benzene sulphonate was

replaced by 0.1 parts of N,N-di(hydroxyethyl) dodecylamine. The explosive properties of the resulting composition were the same as those of the composition prepared in Example 18.

EXAMPLE 22

The procedure described in Example 6 was repeated except that the sodium dodecyl benzene sulphonate was replaced by 0.1 parts of sodium lignosulphonate. The explosive properties of the resulting slurry composition were the same as those of the composition prepared in Example 6.

EXAMPLE 23

A slurry was prepared by the mixing procedure described in Example 14 from 6 parts of isopropyl nitrate, 17 parts of methylamine nitrate solution (10 parts methylamine nitrate to 7 parts of water), 0.5 parts of an octyl phenoxy polyethoxy ethanol containing 40 ethylene oxide groups per molecule, 7 parts of coarse aluminium, 0.7 parts of guar gum, 0.2 parts of zinc chromate, 5 parts of sodium nitrate and 63.6 parts of fine ammonium nitrate. The resulting slurry explosive had density 1.35 g/cc and, when initiated with a detonation having a base charge of 0.8 g PETN, a 3/4" diameter cartridge detonated.

EXAMPLE 24

The procedure described in Example 3 was repeated except that the 0.2 parts of guar gum was replaced by a mixture of 0.2 parts guar gum and 0.15 parts of a xanthan gum "Biopolymer" XB 23 (Registered Trade Mark) commercially available from General Mills Inc. The resulting solution was thixotropic and gave improved emulsion stability compared with Example 3.

The resultant explosive had density 1.2 g/cc and when a 1 1/4" diameter cartridge was initiated by a detonator having a base charge of 0.3 g PETN it detonated at a velocity of detonation of 3.3 km/second.

What we claim is:

1. A slurry explosive composition comprising at least one inorganic oxidising salt, a liquid selected from the group consisting of solvents, dispersers and carriers for said salt and, as sensitising fuel, a liquid aliphatic mononitrate containing from 3 to 8 carbon atoms per molecule, said liquid mononitrate being emulsified with the said liquid by means of an emulsifier.

2. A composition as claimed in claim 1 wherein the liquid aliphatic mononitrate comprises an alkyl mononitrate.

3. A composition as claimed in claim 1 wherein the liquid aliphatic mononitrate is selected from the group consisting of n-propyl nitrate, isopropyl nitrate, amyl nitrate, hexyl nitrate and octyl nitrate.

4. A composition as claimed in claim 1 wherein the said liquid solvent, disperser or carrier is selected from the group consisting of water, diethylene glycol, formamide, dimethyl formamide, dimethylsulphoxide and liquid mixtures containing at least one salt.

5. A composition as claimed in claim 4 wherein the said liquid mixtures each contain a salt selected from the group consisting of ammonium acetate, ammonium formate, methylamine nitrate and ethylenediamine dinitrate.

6. A composition as claimed in claim 1 wherein the emulsifier is selected from the group consisting of (a) condensates of polyalkylene oxide with a compound selected from the group consisting of long chain alcohols

containing 10 to 20 carbon atoms per molecule, alkyl phenols and alkyl phenol/formaldehyde resins in which phenols and resins the alkyl group contains 5 to 22 carbon atoms, amines and polyamines, said condensates containing from 4 to 100 alkylene oxide groups per molecule, (b) long chain amine oxides having a chain length of 8 to 24 carbon atoms and (c) alkyl condensates of polyethylene glycol with an acid selected from the group consisting of monocarboxylic acids and dicarboxylic acids in which condensates the Molecular Weight of the polyethylene glycol is in the range from 200 to 6,000.

7. A composition as claimed in claim 6 wherein the emulsifier is selected from the group consisting of condensates of polyethylene oxide with a compound selected from the group consisting of octylphenol and nonylphenol said condensates containing from 20 to 50 ethylene oxide groups per molecule, condensates of polyethylene oxide with lauryl alcohol containing from 15 to 30 ethylene oxide groups per molecule, N,N-dimethyl dodecylamine oxide, N,N-di(hydroxyethyl) dodecylamine oxide, bis(2-hydroxyethyl) cocoamine oxide, dimethyl cocoamine oxide and alkyl condensates of polyethylene glycol, an acid and an alcohol selected from the group consisting of dihydric- and polyhydric alcohols.

8. A composition as claimed in claim 6 comprising additionally a modifying surfactant to control the emulsion droplet size, said modifying surfactant being selected from the group consisting of long chain amines, ethoxylated amines, quaternary ammonium salts, long chain alkyl sulphate salts, alkylaryl sulphonic acid salts, lignosulphonates and long chain esters of alcohols selected from the group consisting of monohydric and polyhydric alcohols, and ethoxylated esters of alcohols selected from the group consisting of monohydric and polyhydric alcohols.

9. A composition as claimed in claim 8 wherein the modifying surfactant is selected from the group consisting of dodecylamine, N,N-di(hydroxyethyl) dodecylamine, cetyl trimethyl ammonium chloride, sodium dodecyl sulphate, sodium dodecylbenzene sulphonate, sorbitan trioleate and sodium lignosulphonate.

10. A composition as claimed in claim 6 comprising additionally an emulsion stabiliser selected from the group consisting of long chain alcohols, polyalkylene oxide polymers, water-soluble cellulose ethers and starch ethers.

11. A composition as claimed in claim 10 wherein the emulsion stabiliser is selected from the group consisting of lauryl alcohol, ethylene oxide/propylene oxide block copolymers, methyl cellulose and hydroxypropyl cellulose.

12. A composition as claimed in claim 1 comprising additionally a thickening agent selected from the group consisting of guar gum, hydroxypropylated guar gum, xanthan gum, starch, polyacrylamide and derivatives thereof, hydroxyethyl cellulose, polyethylene oxide, polyvinyl alcohol, nitrocellulose, cellulose esters, polyacrylic esters, and copolymers of styrene and alkyl styrene with $\alpha\beta$ -unsaturated dicarboxylic acids.

13. A composition as claimed in claim 12 wherein the thickening agent is crosslinked with a compound selected from the group consisting of alkali metal chromates, alkali metal borates, titanium salts, potassium pyroantimonate, telluric acid and metal alkoxides.

14. A composition as claimed in claim 1 comprising an aeration agent selected from the group consisting of

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foaming surfactants, chemical gassing agents and hollow spheres.

15. A composition as claimed in claim 14 comprising sufficient voids to give the composition a density in the range 0.8 to 1.5 g/cc.

16. A composition as claimed in claim 1 wherein the oxidising salt is selected from the group consisting of nitrates and perchlorates of ammonia, sodium, potassium, barium, magnesium and calcium and mixtures containing at least two of the said salts.

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17. A composition as claimed in claim 1 comprising from 4 to 20% by weight of liquid mononitrate, from 5 to 25% by weight of the said liquid, from 0.1 to 3.5% by weight of emulsifier, from 25 to 85% by weight of ammonium nitrate, from 0 to 35% by weight of oxidising salt other than ammonium nitrate and from 0 to 20% of solid fuel.

18. A composition as claimed in claim 17 wherein the solid fuel comprises metal powder.

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[54] **HYDROPHOBIC EXPLOSIVE
COMPOSITION AND METHOD OF MAKING**

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[57] ABSTRACT

A slurry explosive composition comprising at least one inorganic oxidizing salt, an aqueous liquid phase, fuel material and a sensitizing agent which agent comprises a combination of hydrophobic particles of high explosive material and gas bubbles.

14 Claims, No Drawings

HYDROPHOBIC EXPLOSIVE COMPOSITION AND METHOD OF MAKING

This invention relates to explosive compositions of matter and more particularly it relates to slurry explosive compositions of matter.

Slurry explosives comprise inorganic oxidizing salt, fuel, a liquid solvent, disperser or carrier for said salt and, optionally, at least one thickening agent. Although the term "slurry" is applied to such compositions the degree of consistency may range from pourable or pumpable fluids of varying viscosity, through viscous extrudable gels up to friable materials such as are described in Australian Pat. No. 483,568 and which may be packaged in the form of cartridges. The oxidizing salt component usually comprises nitrate, chlorate or perchlorate of ammonia, sodium, potassium, calcium or barium, the most extensively used salt being ammonium nitrate. The liquid phase may vary widely in its chemical constitution, consistency, and explosive sensitivity but commonly slurry explosives are aqueous. Thus, the liquid phase may consist mainly of an aqueous solution of inorganic oxidizing salt. So as to increase the viscosity of slurry explosives of the kind described thickening agents for example gums such as guar gum or xanthan gums, or synthetic polymers such as polyacrylamide or copolymers thereof have been used in an attempt to prevent segregation of the ingredients or to prevent deterioration in wet conditions. It has also been proposed that improved homogeneity and storage properties could be obtained by crosslinking the thickening agents with crosslinking agents, for example potassium pyroantimonate, sodium dichromate, potassium dichromate or rare earth salts, or a redox system for example a mixture of an arsenious compound and sodium dichromate. It has also been proposed to use agents which are capable of sensitizing the explosive compositions to the action of detonating materials, and typically such sensitizing agents have included metallic materials such as finely divided aluminium often referred to as "paint-fine" aluminium optionally in the presence of a gas located within the composition. It has also been proposed to use high explosive materials, such as trinitrotoluene (TNT), in the form of large flakes or pellets as sensitizing agents for slurry explosive compositions. It has also been proposed in the specification of U.S. Pat. No. 3,216,872 to use in an aqueous slurry explosive containing as an essential oxygen-releasing salt component a mixture of inorganic nitrates, from about 10 to 30% w/w of a high explosive material as a sensitizing agent, the agent having a sufficiently small particle size that it passes through a standard 30 mesh sieve, and typical examples of such an agent are exemplified as being trinitrotoluene of which only about 0.25% w/w passes a 120 mesh sieve, or pentaerythritol tetranitrate (PETN) (50 mesh), or cyclonite (30 or 40 mesh).

Surprisingly, and in contradistinction to the teachings of the prior art that finely divided high explosive sensitizing agents having a particle size finer than would be retained on a 30 mesh sieve are prone to desensitization by water unless they are used in the presence of at least two inorganic nitrates, it has now been found that slurry explosive compositions containing one or more oxygen-releasing salts may be rendered very sensitive to detonation if there is present in the composition a sensitizing agent comprising finely divided hydrophobic high explosive material in combination with gaseous material.

Accordingly the present invention provides a slurry explosive composition which comprises at least one inorganic oxidizing salt, a liquid phase, fuel material, and optionally at least one thickening agent which optionally may be crosslinked, characterised in that said slurry explosive comprises, as a sensitizing agent, first, hydrophobic, as hereinafter defined, particles of a high explosive material which are capable of passing through a screen of 120 BS mesh, and secondly, bubbles of gaseous material.

By sensitizing agent we mean a material which when added to an explosive composition of fixed dimensions reduces the minimum primer necessary to initiate that explosive composition.

Although we wish in no way to be bound by this theory, we believe that the mode of action of the sensitizers of this invention is to surround the gas bubbles and consequently to decompose rapidly at the temperature of the hot spot formed when the shock wave interacts with a gas bubble, thereby increasing the temperature of the hotspot to a value where the bulk of the explosive will decompose explosively.

We base this theory on the observations that the particles of the high explosive must be hydrophobic, hence they will tend to collect at the interface of the gaseous bubbles and the slurry composition, and that they must be smaller than those retained on a 120 BS mesh screen implying that this small size is necessary to allow them to collect at the interface.

By hydrophobic we mean that the particles of the high explosive component are not wetted by the liquid which provides the liquid phase in the slurry explosive composition. The particles are deemed to be not wetted by a liquid when, if they are scattered on the surface of the said liquid as it is agitated, they float and remain in that state for at least one hour in the absence of any further agitation of the said liquid.

A high explosive is an explosive composition characterized by very high rates of reaction (1.6 to 10 kilometers/sec.) and high pressures (3 to 300 kbars) during detonation—(Engineering and Mining Journal October 1976, p 81).

Trinitrotoluene is a very convenient high explosive material for use in the invention. Other explosive materials which give good results include dinitrotoluene, pentaerythritol tetranitrate, pentolite which is a mixture of equal weights of pentaerythritol tetranitrate and TNT, tetryl, cyclonite and various mixtures of TNT and cyclonite such as composition B and cyclotol.

Conveniently the high explosive component constitutes up to 10% w/w of the composition and for many compositions adequate sensitivity to detonation is acquired when the high explosive component constitutes from 1 to 5% w/w of the composition.

In some cases the particles of the high explosive material are hydrophobic with respect to the liquid phase in their own right but in others they have to be treated to render them hydrophobic. For example, if the high explosive material used is pentaerythritol tetranitrate and the liquid phase is aqueous, then the pentaerythritol tetranitrate particles require to be treated with an agent, such as di-iso-octylphthalate and other water resisting agents as listed in copending Australian Pat. No. 35094/78, to prevent them being wetted by the aqueous phase.

The gaseous component of the bubbles of the sensitizing agent may be for example air, oxygen, nitrogen or an oxide of nitrogen. The gaseous component such as

air may be entrained into the composition by agitation of the composition for example by stirring, or alternatively it may be fed into the composition in the form of a compressed gas, or yet again it may be formed in situ in the composition by the decomposition of a gas-forming material present in the composition. Thus for example small amounts of sodium nitrite may be used as a decomposable component of the composition.

In general, except for the sensitizing agent, the compositions of our invention are of conventional types. Thus the oxygen releasing salts used as ingredients in our compositions may be, for example, inorganic nitrates, chlorates and perchlorates and mixtures thereof. We prefer that the oxygen releasing salt material be chosen from the perchlorates or nitrates of the alkali and alkaline earth metals or ammonium and of these we prefer sodium nitrate, calcium nitrate, ammonium perchlorate and particularly ammonium nitrate. The amount of oxygen releasing salt in such compositions is not narrowly critical; we have found that compositions containing amounts of oxygen releasing salts from 50% w/w to 90% w/w of the total composition are satisfactory and amounts from 60% w/w to 85% w/w are preferred. The particle size and shape of the oxygen releasing salt is not critical and is well known from the art of ammonium nitrate manufacture; powders and prilled particles are satisfactory.

The liquid phase comprises an aqueous solution. The amount of water in this aqueous liquid phase should be sufficient to dissolve at least part of the oxygen releasing inorganic salt and at least part of any water soluble fuel which may be present, and also be sufficient to hydrate at least part, preferably all, of any gummy gelling agent present. Suitably the amount of water when present may constitute from 3% w/w to 35% w/w of the total composition, but the amount present should not be in excess of the explosive limit of the composition. We prefer that the water be in the range from 3% w/w to 25% w/w of the total composition. In the instance where the explosive composition is of the pourable or pumpable type it is more preferred that water constitutes from 12% w/w to 17% w/w of the composition; where the composition is of a friable type a very suitable range for the water content is from 3% w/w to 14% w/w and a range from 4% w/w to 10% w/w is especially preferred.

When referring to fuels or fuel materials in this specification we mean substances which are stable in such explosive compositions, that is prior to detonation, and during preparation and storage the substance is chemically inert to the system. The said substances must be combustible and their physical nature should be such that they may be incorporated in our compositions in a manner so as to be uniformly distributed throughout the compositions. Such fuels are well known in the art and they may be organic or inorganic and may also be derived from animals and plants.

The fuels when employed in the compositions of this invention can be, for example, non-explosive carbonaceous, non-metallic and metallic fuels or mixtures of the aforementioned types of fuels. They can be varied widely.

Suitable fuels include organic water soluble substances for example urea, carbohydrates such as sugars or molasses, water soluble alcohols or glycols, glues or mixtures of these. Suitably the proportion of water soluble fuel in our compositions is in the range from

0.5% w/w to 10% w/w, preferably from 4 to 7% w/w, of the total composition.

Other suitable fuels include water insoluble or sparingly water soluble materials which may be chosen from inorganic materials for example sulphur, aluminium, silicon, ferrosilicon, ferrophosphorus, magnesium, titanium, boron, mixtures thereof for example mixtures of aluminium with ferrosilicon, or organic materials for example finely divided charcoal, anthracite, gilsonite, asphalt, cellulosic materials such as sawdust, or cereal products for example flours, dextrins or starches. When the inorganic fuel is a metal it is preferably in granulated or powdered form. Such granulated or powdered metal may be in the form of discrete particles, but metal powders wherein the metal is in the form of flakes or in the form of aggregates of particles or flakes are also satisfactory. Preferred fuels are the metallic powders. The most preferred metallic fuel is aluminium. The proportion of water insoluble or sparingly water soluble non-metallic fuels in such compositions may suitably be in the range from 1% w/w to 10% w/w of the total composition and amounts from 4% w/w to 7% w/w of the total composition are preferred. The proportion of metallic water insoluble fuels when present in such compositions may be as high as 25% w/w and amounts in the range from 0.5% w/w to 20% w/w of the total compositions are preferred.

Where desirable there may be included as a component of our compositions one or more conventional thickening agents, for example gums such as the galactomannan or xanthan gums. Typical examples of galactomannan gums are guar gum or derivatives thereof and locust bean gum whilst the xanthan gums may be typified by reference to biopolymeric materials which are produced by processes comprising the transformation of carbohydrate material by means of micro-organisms such as those of the species of *Xanthomonas*. A very useful biopolymeric material is that available under the trade name of "Biopolymer" XB23 which is derived from a polymer which has been reacted with *Xanthomonas campestris*. Preferably such gums, when used in our compositions are in a crosslinked form. When such gums are used in our compositions it is convenient to use amounts such that the gum component comprises from 0.1 to 5% w/w, more usually from 0.3 to 3% w/w, of the composition.

In general the explosive compositions of our invention may be prepared by the conventional formulating techniques used for preparing slurry explosives. Thus for example a part or all of the oxygen releasing salt may be in the form of a solution of the salt or part may be incorporated in powdered or prilled form. Fuel materials when used may also be incorporated in a dry form or alternatively in the form of a dispersion or solution in part of the liquid component. It has been found convenient to incorporate the high explosive component of the sensitizing agent to the composition by adding it to a composition which comprises the gaseous component of the sensitizing agent. Suitably such incorporation may be effected by adding the high explosive component by itself or as a dispersion in a part of the liquid component of the composition.

When guar gum is used as a component of the compositions of the invention it is preferred that there is present in the composition a sufficiency of liquid to ensure that the gum component is at least partially solvated. When agents are used to crosslink such gum it is preferred that such an agent be added as one of the final

ingredients. In instances where such a crosslinking agent is a system comprising two or more components it is desirable that whilst some of the components may be incorporated at any stage of the preparation of the mixture, the last ingredient added is a component of the crosslinking system. Thus for example when such a crosslinking system is a redox system it is desirable that the oxidizer component of that system be added to the composition as the final ingredient. Other thickening agents such as synthetic polymers and copolymers may also be used; for example polymers derived from acrylamide, and especially copolymers derived from acrylamide and containing mer units which bear bidentate groups are satisfactory. Typical examples of such copolymers are those derived from a major proportion of acrylamide and a minor proportion of 2-acetoxyethyl methacrylate or methacryloylacetone optionally with mer units derived from acrylonitrile.

The invention also includes a method of preparing a slurry explosive composition, which method comprises mixing inorganic oxidizing salt and fuel material with a liquid solvent disperser or carrier for said salt, optionally mixing therewith at least one thickening agent which optionally may be crosslinked, to form a mixture and modifying the sensitivity characteristics of said mixture by incorporating therein an amount of sensitizing agent as hereinbefore described.

The compositions of the invention are advantageous over similar compositions of the prior art in that their enhanced sensitivity characteristics may be achieved by the use of a relatively small amount of the high explosive component of the sensitizing agent. Thus their cost is reduced and furthermore the use of the smaller amounts of high explosive has the attendant advantage of reducing hazards of manufacture.

The invention is now illustrated by, but is not limited to, the following examples wherein all parts and percentages are expressed on a weight basis unless otherwise specified. Examples 7 to 11 inclusive and 14 do not lie within the invention and are included for the purposes of comparison.

EXAMPLE 1

An explosive composition containing 3% TNT as a high explosive component of a sensitizing agent was made by preparing a first composition by mixing 4450 parts of ammonium nitrate powder, 1300 parts of sodium nitrate powder and 1000 parts of water. A second composition was prepared by mixing 30 parts of thio-urea, 15 parts of guar gum, 34 parts of ethylene glycol, 1350 parts of crushed ammonium nitrate, 250 parts of pregelled starch, 50 parts of sodium carboxymethylcellulose, 580 parts of urea and 700 parts of a coarse atomized aluminium powder. This second composition was added to and mixed with the first composition referred to above to form a homogeneous mixture which was slightly acidic. This homogeneous mixture was stirred still further whilst there was added thereto 40 parts of sodium nitrite, 300 parts of finely divided trinitrotoluene and 1 part of zinc chromate. (The trinitrotoluene referred to above was prepared by dissolving trinitrotoluene in hot methanol to form a solution, pouring this solution into water to effect a rapid precipitation of trinitrotoluene, classifying the precipitate so formed and recovering for use in the composition of the invention that portion of the particulate trinitrotoluene which passed through a 120 mesh sieve). The composition so obtained which had a density of 1.04 grams/cubic centi-

meters was packed into cylindrical cardboard tubes which were 35 centimeters long and had a diameter of 2.5 centimeters. The composition was detonated in this unconfined state at a temperature of 22° C. by means of two No. 8 detonators each of which contained approximately 0.45 gram of PETN.

EXAMPLES 2 TO 6 INCLUSIVE

The general procedure of Example 1 was repeated except that each of the amounts of TNT, the diameter of the cardboard tube, and the temperature of detonation was varied as shown in Table 1. The amount of gaseous component in the composition was charged in Examples 3 to 6 inclusive and these changes are illustrated by the values of the density shown in Table 1. The greater the density value, the less was the amount of gaseous component in the composition.

TABLE 1

| Ex-ample No | TNT (parts) | Diameter of tube (cm) | Temperature of detonation (°C.) | Density (gm/cc) | Minimum Primer for detonation |
|-------------|-------------|-----------------------|---------------------------------|-----------------|-------------------------------|
| 2 | 1000 | 2.5 | 26 | 1.04 | 1 × No6 (0.22 gm PETN) |
| 3 | 1000 | 2.5 | 22 | 1.23 | 2 × No8 |
| 4 | 300 | 5.0 | 22 | 1.20 | 3 × No8 |
| 5 | 300 | 5.0 | 27 | 1.10 | 1 × No8 |
| 6 | 300 | 5.0 | 27 | 1.40 | 5 gm Pentolite |

EXAMPLE 7

In this comparative Example the general procedure of Example 3 was repeated except that the finely divided trinitrotoluene of that Example was replaced by 1000 parts of granular trinitrotoluene which was retained on a 60 mesh sieve. The minimum primer for detonation of this composition was 10 grams of pentolite.

EXAMPLES 8 TO 10 INCLUSIVE

For the purposes of comparison these examples record the sensitivity of prior art compositions set out in Examples 1 to 4 inclusive of the specification of U.S. Pat. No. 3,216,872 and reproduced in Table 2. Table 2 also shows the density of the composition and the amount of pentolite required to detonate the composition under confined conditions in a steel pipe having a diameter of 1.25 inches (3.2 centimeters). The TNT used as the sensitizing agent in these examples had the following screen analysis.

| US Standard Screen Mesh size | Screen Analysis of TNT % by Weight |
|------------------------------|------------------------------------|
| -30 + 40 mesh | 0.25 |
| -40 + 50 mesh | 26.25 |
| -50 + 70 mesh | 59.00 |
| -70 + 100 mesh | 12.25 |
| -100 + 120 mesh | 2.00 |
| -120 + 200 mesh | 0.25 |
| -200 + 230 mesh | Trace |
| -230 | Trace |
| | 100.00 |

TABLE 2

| Example No | 8 | 9 | 10 | 11 |
|------------------------|-----------------|------|------|------|
| USA Patent | | | | |
| Example No | 1 | 2 | 3 | 4 |
| Component | Parts by weight | | | |
| Fine TNT | 20.0 | 20.0 | 20.0 | 20.0 |
| Mill ammonium nitrate | 56.5 | 47.2 | 39.5 | 20.7 |
| Mill sodium nitrate | 5.0 | 15.0 | 24.2 | 40.0 |
| Zinc oxide | 0.3 | 0.3 | 0.3 | 0.3 |
| Bagasse | 1.0 | 1.0 | 1.0 | 1.0 |
| Cornstarch | 3.2 | 2.5 | 0.0 | 0.0 |
| Hydrosol 3B | 2.0 | 2.0 | 3.0 | 3.0 |
| Water | 16.0 | 16.0 | 16.0 | 18.0 |
| Oil No 5 | 0.0 | 0.0 | 0.0 | 1.0 |
| Sea coal | 0.0 | 0.0 | 0.0 | 1.0 |
| Total | 104 | 104 | 104 | 105 |
| % TNT | 19.2 | 19.2 | 19.2 | 19.2 |
| Pentolite used (grams) | 10 | 10 | 3 | 30 |
| Density (gm/cc) | 1.36 | 1.44 | 1.47 | 1.48 |

EXAMPLE 12

5240 Parts of powdered ammonium nitrate were added to and mixed with 100 parts of water to form a first composition. A second composition was prepared by mixing together 30 parts of thiourea, 15 parts of guar gum, 34 parts of ethylene glycol, 2000 parts of crushed ammonium nitrate prills, 250 parts of pregelled starch, 50 parts of sodium carboxymethylcellulose and 340 parts of urea. The first composition and the second composition were mixed with stirring to form a third composition and to this third composition there was added with stirring 40 parts of sodium nitrite, 1000 parts of finely divided trinitrotoluene of the type described in Example 1 and 1 part of zinc chromate. There was thus obtained an explosive composition having a density of 1.12 grams per cubic centimeter. This explosive composition was packed into cylindrical cardboard tubes which were 35 centimeters long and had a diameter of 5 centimeters. The explosive cartridges so obtained were detonated at a temperature of 26° C. using three No. 8 detonators.

EXAMPLE 13

An explosive composition containing 5% of hydrophobic PETN as a high explosive component of a sensitizing agent was made by preparing a first composition by mixing 7210 parts of ammonium nitrate powder, 598 parts of sodium nitrate powder and 1522 parts of water at 70° C. A second composition was prepared by mixing 30 parts of thiourea, 15 parts of guar gum, 35 parts of ethylene glycol, 1355 parts of crushed ammonium nitrate, 580 parts of urea, 250 parts of pregelled starch, 50 parts of sodium carboxymethylcellulose, 500 parts of a coarse atomized aluminium powder, 32.4 parts of sodium acetate and 8.7 parts of glacial acetic acid. This second composition was added to and mixed with 6650 parts of the first composition referred to above to form a homogeneous mixture which was slightly acid. This mixture was stirred further whilst there was added thereto 25 parts of sodium nitrite, 500 parts of treated PETN and 2 parts of potassium antimony tartrate. (The PETN referred to above was prepared by dissolving PETN in acetone and rapidly precipitating the PETN by adding water. Diisooctylphthalate—1% based on the weight of PETN—was added, the mixture stirred for 15 minutes, filtered and dried. This gave hydrophobic PETN particles of size range 2 to 10 microns). The composition so obtained which had a density of 1.13 grams/cubic centimeter was packed into cylindrical cardboard tubes which were 22 centimeters long and

had a diameter of 2.5 centimeters. The composition was detonated in this unconfined state at a temperature of 21° C. by means of two No. 8 detonators.

EXAMPLE 14

This is a comparative example illustrating the necessity for the high explosive particles to be hydrophobic.

The general procedure of Example 13 was repeated except that untreated PETN powder was used. This composition of density 1.18 grams/cubic centimeter could not be detonated in a cardboard tube of diameter 2.5 centimeters by three No. 8 detonators.

I claim:

1. A slurry explosive composition comprising at least one inorganic oxidizing salt, a liquid phase, and fuel material wherein said slurry explosive composition comprises, as a sensitizing agent, (i) hydrophobic particles of a high explosive material which are capable of passing through a screen of 120 B.S. mesh and (ii) bubbles of gaseous material.
2. A composition according to claim 1 wherein said slurry explosive composition comprises a thickening agent.
3. A composition according to claim 2 wherein said thickening agent has been crosslinked.
4. A composition according to claim 1 wherein said high explosive material comprises at least one compound selected from the group consisting of trinitrotoluene, dinitrotoluene, pentaerythritol tetranitrate, pentolite, cyclonite, cyclotol and tetryl.
5. A composition according to claim 4 wherein said high explosive material is trinitrotoluene.
6. A composition according to claim 1 wherein said high explosive material has been treated with a compound to render it hydrophobic.
7. A composition according to claim 6 wherein the said compound used to render the high explosive material hydrophobic is di-iso-octylphthalate.
8. A composition according to claim 1 wherein said high explosive material comprises an amount in the range of 0.1% to 10% w/w inclusive of the said slurry explosive composition.
9. A composition according to claim 8 wherein said high explosive material comprises an amount in the range of 1% to 5% w/w inclusive of the said slurry explosive composition.
10. A composition according to claim 1 wherein said gaseous material comprises at least one gas selected from the group consisting of air, oxygen, nitrogen and oxides of nitrogen.
11. A process for the preparation of a slurry explosive compositions as defined in claim 1 in which hydrophobic particles of a high explosive material which are capable of passing a screen of 120 B.S. mesh are mixed with the other solid and liquid components of the said slurry explosive composition and wherein bubbles of gaseous material are generated within said slurry explosive composition.
12. A process according to claim 11 wherein the bubbles of gaseous material are generated within said slurry explosive composition by agitation.
13. A process according to claim 11 wherein the bubbles of gaseous material are generated within said slurry explosive composition by injection a compressed gas into the said composition.
14. A process according to claim 11 wherein the bubbles of gaseous material are generated within said slurry explosive composition by the addition of a material which will decompose to form gaseous products.

THE BDM CORPORATION

UNASSIGNED PATENTS

Patent Number: 4,132,574
Author: Charles D. Forrest, Asheville, NC
Title: Superfine PETN Thin Layer Slurry Explosive
Date: January 2, 1979

Patent Number: 4,221,618
Author: Melvin A. Cook, Salt Lake City, UT
Title: Slurry Explosives
Date: September 9, 1980

[54] SUPERFINE PETN THIN LAYER SLURRY
EXPLOSIVE

[76] Inventor: Charles D. Forrest, 151 La Mancha
Dr., Asheville, N.C. 28805

[21] Appl. No.: 777,315

[22] Filed: Mar. 14, 1977

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 622,319, Jan. 31, 1974,
Pat. No. 3,912,560.

[51] Int. Cl.² C06B 45/00

[52] U.S. Cl. 149/2; 149/47;
149/60; 149/62; 149/93; 149/111

[58] Field of Search 149/2, 47, 60, 62, 93,
149/111

[56]

References Cited

U.S. PATENT DOCUMENTS

3,912,560 10/1975 Forrest 149/47

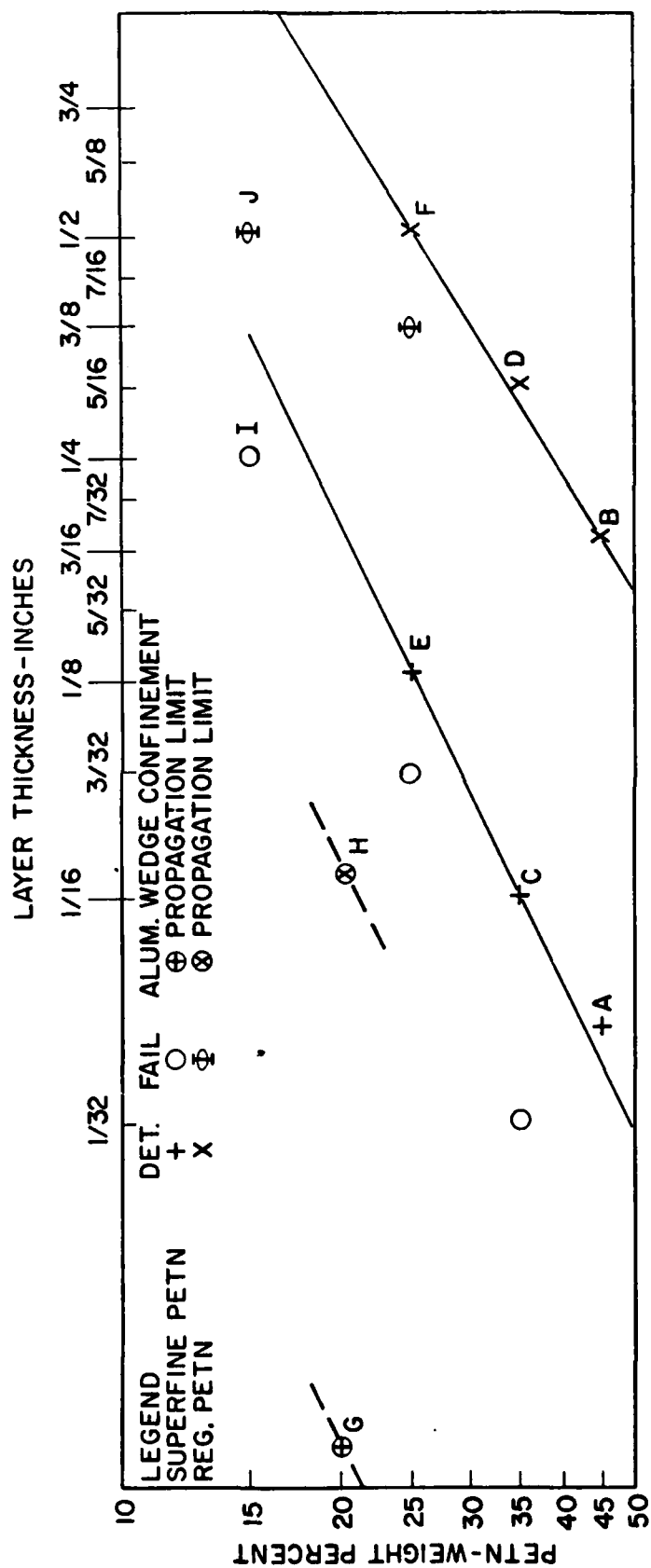
Primary Examiner—Stephen J. Lechert, Jr.
Attorney, Agent, or Firm—Tom R. Vestal

[57]

ABSTRACT

A cap-sensitive slurry explosive capable of propagating a high order detonation in thin layers and which has a high degree of safety for a cap-sensitive explosive. The slurry consists of a super-fine grained explosive, suspended in an energetic, but non-self-explosive liquid matrix and contains no liquid explosive ingredient. The slurry resists dispersion in a variety of liquids including water and crude oil. In the preferred embodiments the slurries include penetaerythritol tetranitrate (PETN) in super fine particles, having an average particle size of about 6.5 microns.

11 Claims, 1 Drawing Figure



SUPERFINE PETN THIN LAYER SLURRY EXPLOSIVE

CROSS-REFERENCE TO RELATED APPLICATIONS

This is a continuation-in-part of my application THIN LAYER PROPAGATING SLURRY EXPLOSIVE, Ser. No. 622,319 filed Jan. 31, 1974, now U.S. Pat. No. 3,912,560 issued Oct. 14, 1975.

BACKGROUND OF THE INVENTION

As is known, certain explosives such as pentaerythritol tetranitrate (PETN) for example, are hazardous when subjected to modest physical abuse from impact or friction forces. Such compounds additionally do not have desired inertness toward crude oil and brine and dilute forms of many other well environmental material. Such materials additionally are hazardous in being highly inflammable.

BRIEF DESCRIPTION OF THE INVENTION

The slurry of the present invention is a new type of cap-sensitive slurry explosive capable of propagating a higher order detonation in thin layers. The invention provides a relatively safe explosive in a slurry form which may be used in oil well and gas well formation fracturing, rock fracturing for in situ ore leaching, non-nuclear fracturing of oil shale formations, and explosive formation of fire lanes in terrain inaccessible to motorized equipment.

The slurry of the present invention is formulated to resist accidental initiation by adiabatic compression of gas bubbles which may be introduced during loading and handling, and due to the good chemical stability of the explosive formula, the slurry gives a high degree of inertness toward crude oil and brine and dilute forms of most other well environmental materials. The material of the present invention in fires is difficult to ignite, and once ignited, burns quietly with no explosion in the absence of confinement. The ingredients comprising the slurry are non-toxic prior to detonation.

According to the instant invention there is disclosed a relationship between the composition of a slurry comprising superfine particles of PETN in the slurry as compared and contrasted to a completely analogous slurry comprised of fine particle PETN, as is conventionally available. According to the particular improvements taught herein, a study was conducted to clearly differentiate the performance characteristics between superfine PETN and are regular PETN to obtain the effect of using PETN explosive which has an average particle size of approximately 6.5 microns. As is taught herein, both sets of formulations are made with identical ingredients and mixed in identical procedures except for the type of PETN used. As used herein, regular PETN can be described as that available in military grade, Class IV, having a particle size by test on screens as follows:

SCREEN TEST

| | |
|-------------------|-------------------------|
| On 50 U.S. Std., | 1.6 percent |
| On 100 U.S. Std., | 20.9 percent cumulative |
| On 200 U.S. Std., | 61.9 percent cumulative |

In distinction, the superfine PETN used in the instant slurry compositions for contrast with the regular PETN has an average particle size of about 6.5 microns in

diameter. Such superfine PETN is available from such manufacturers as DuPont, and will hereinafter be referred to as superfine PETN.

It has been found that by employing superfine PETN in the slurry formulations, the propagating thickness is from three to six times smaller than that obtainable with a slurry using regular PETN as a constituent part. This decrease in thin layer propagating thickness is particularly advantageous in applications of oil and gas well stimulation, solution mining, coal and oil shale fracturing and any other application seeking successful explosive stimulation with very thin layers of explosive slurries.

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 is schematic representation of the propagation layer thickness versus PETN content for formulations using both the regular and superfine PETN explosive.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In order to correlate the reduction in slurry thickness that could be achieved with the superfine PETN substitution for regular fine particle PETN, the following mixtures were prepared:

| MIX NO. | | A | B | C | D | E | F | G | H | I | J |
|-----------------------|---|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Superfine PETN (Wt) | % | 45 | | 35 | | 25 | | 20 | | 15 | |
| Regular PETN | % | | 45 | | 35 | | 25 | | 20 | | 15 |
| Ammonium Nitrate | % | 27 | 27 | 33 | 33 | 39 | 39 | 42 | 42 | 45 | 45 |
| Water | % | 18 | 18 | 22 | 22 | 26 | 26 | 28 | 28 | 30 | 30 |
| Diethylene Glycol | % | 9.5 | 9.5 | 9.4 | 9.4 | 9.4 | 9.4 | 9.3 | 9.3 | 9.3 | 9.3 |
| Jaguar HP-8 (GuarGum) | % | 0.5 | 0.5 | 0.6 | 0.6 | 0.6 | 0.6 | 0.7 | 0.7 | 0.7 | 0.7 |

The formulations were detonated on test fixtures which were the same for both the superfine and the regular PETN slurries. Since the only purpose of this test was to determine the propagation layer thickness versus the PETN content, as between the regular and superfine PETN, the results shown in FIG. 1 are illustrated for comparison purposes only and not as absolute values for propagation layer thicknesses.

As illustrated in FIG. 1, the uniform detonation, for example, of 25 percent superfine PETN slurry was 0.125 inches while an exactly analogous slurry with larger size particle PETN exhibited a uniform detonation layer thickness of 0.500 inches. As can be seen readily from inspection of FIG. 1, which is a logarithmic plot of propagation layer thickness versus PETN content for the two categories of PETN, the fine particle regular PETN slurries represented a uniform detonation layer thickness as shown by lines B, D and F in the text fixture, while the superfine particle PETN slurries exhibited a minimum uniform detonation layer thickness as represented by lines A, C and E.

The formulations B, D, and F and also the formulations A, C, and E were tested on a fixture known as a Benelex 41 in a uniform layer with the fixture having a masonite confining layer. The slurries G and H were tested with an aluminum confinement. The tapered aluminum wedges for compositions G and H provided for an explosive 2 1/4 inches wide by 20 inches long. The wedge was constructed of 6061-T6 aluminum with a milled slot tapered uniformly over the 20-inch length, the aluminum being approximately 3/4 inch thick on the

bottom and the sides with a $\frac{1}{4}$ inch aluminum top cover. The slurry formulations were detonated with a number 6 aluminum blasting cap, readily available from DuPont, together with a 7.2 gm sheet explosive primer. The sheet explosive primer was used only for convenience in sealing the end of the test fixture in the shots which employed superfine PETN. The sheet explosive primer also insured sufficient primer to detonate the compositions which employed regular PETN, and provided identical initiation for all compositions.

With the wedge configuration the slurry comprising 20 percent of a superfine PETN exhibited a propagation limit of 0.011 inches while the same composition with regular fine PETN exhibited a propagation limit of .068 inches. Therefore, as can be seen from an inspection of the data points of FIG. 1, the employment of a superfine PETN, having an average particle size of about 6.5 microns, resulted in a propagating thickness from three to six times smaller than that obtainable with the regular PETN.

In preparing the formulations, the approximate weight percentages also included a minute amount of cross-linking agent. A satisfactory cross-linking agent was found to be TYZOR LA, a trademark product of the E. I. DuPont de Nemours and Company, Inc., which is generically known as titanium-antimony lactate. A ten percent solution of this cross-linking agent was added in the concentration of about five drops per 100 gram of slurry just prior to loading into the test assembly. The amount of cross-linking agent may be varied to accommodate greater or lesser amounts of gelling agent, and also to effect a greater or lesser degree of cross-linking, if desired. Likewise, the concentration of cross-linking solution may be varied from about 5% to about 50%. Additionally, the mixtures G and H were partly settled and stirred just prior to the cross-linking operation. In the above examples, the concentration of the ammonium nitrate solution is not critical. A 60 percent solution is convenient to use because the ammonium nitrate stays completely in solution above 54° F, which means that handling is simplified over, for example, an 80 percent solution which has a solidification temperature of about 136° F; thus requiring expensive heated storage. After blending with an anti-freeze agent, such as diethylene glycol, the solidification temperature is decreased. In the above mixes A-J, the sample weight percentages for each individual constituent part are as shown prior to adding the cross-linking agent.

These formulations are then cap-sensitive explosives capable of propagating a high order detonation in thin layers, i.e., one thirty-second of an inch when confined between masonite. More significantly, there is shown herein a relationship between the use of superfine particle PETN, where the 6.5 micron diameter particles allow for reduction of three to six times in the thin layer propagation layer thickness as a function of PETN content. These formulations are able to detonate completely in thin layers at temperatures of approximately 200° F while simultaneously exposed to a hydrostatic pressure of 10,000 psi or above and do not cause handling problems since there is no liquid explosive ingredient. It has been found that the slurry explosives are not detonated by British 303 ammunition from a distance of 75 to 100 feet even when backed by steel or aluminum. Such slurry explosives will slowly decompose in a bon fire when unconfined, but by themselves will not support combustion. Therefore, the purpose of this inven-

tion is to teach a relationship between the use of superfine [extremely small] particle PETN for the reduction of detonating layer thicknesses for particular applications. This control of detonation layer thickness as a function of the composition constituents allows the explosive to be tailored to explosive fracturing of oil and gas reservoirs in order to increase formation permeability and other such controlled applications. In such applications it is critical that the explosive propagate in thin layers to be effective to stimulating oil and gas wells, solution mining and coal and oil shale fracturing operations.

Ordinarily PETN (penethaerythritol tetranitrate) is considered a hazardous explosive which is known to explode when subjected to modest physical abuse from impact or friction forces. For example, in a test apparatus a small (approximately 1/20 of a gram) sample of sensitized small particle PETN when placed on a hard tool steel anvil and impacted by a free fall hammer (or hard tool steel and weighing 2.143 kg), a detonation of the PETN will occur when the drop of the hammer is only 2 cm. In other words, the impact sensitivity of the pure dry PETN is 4.3 kg-cm. However, when this same PETN is compounded into a slurry explosive form where the PETN comprises upwards to 45 percent of the total weight of the mixture, the resulting explosive mixtures as shown herein are unaffected by repeated hammer drops, even from a drop height of 63.5 centimeters. Thus, in slurry form PETN has been found to be not exploded by an impact of 136.3 kg-cm. This is more than thirty times the energy at which the PETN alone explodes. As taught herein, by particularly using a slurry wherein the PETN particles have an average diameter of about 6.5 microns, the advantages of a slurry can be further maximized for very thin layer applications. It has been found that the superfine PETN can be shown to have a significant effect on the propagation thickness of the slurry. As particularly illustrated in FIG. 1, for the same composition the use of superfine PETN particles results in a three to six times reduction in the propagating layer thickness. As has also been shown, this reduction in thickness of layer capable of supporting detonation occurs over a wide range of formulations, anywhere from 15 to 50 percent by weight of PETN in slurries.

The sensitized superfine PETN as employed herein may be made according to the method taught in my copending application Ser. No. 434,753, filed Jan. 31, 1974. While we do not in anyway wish to be limited by theory, it is presently believed that it is a unique structure and not particle size alone which imparts significantly improved detonation properties to the Superfine PETN and thus to the slurry explosives prepared therefrom, and described in the instant invention.

When viewed under an optical microscope the particles of Superfine PETN can be seen to contain a high density of optical barriers. Furthermore, when examined under very high magnification by electron microscope techniques the Superfine PETN particles are seen to contain a large number of apparent void spaces, estimated at exceeding 1000 voids and even exceeding 2000 voids for the average diameter -particle of about 6.5 microns. These voids have an apparent diameter of about 0.18 to 0.2 micron.

It is theorized that these microvoids or crystal imperfections are in large part responsible for the improved detonation properties evidenced for Superfine PETN, in that they serve as reflection sites for an incident

shock wave, and that the resultant collisions of the reflected shock waves pump heat energy into and thus shorten the detonation reaction zone, and at the same time reduce the cross-sectional area of explosive required to sustain a stable detonation.

The improved slurry of the invention herein may also be used to produce a low detonation flame temperature composition by deleting the oxidizer components - i.e. the solid crystalline nitrates of Groups I and II of the Periodic Chart of the Elements. Additional antifreeze agents such as diethylene glycol may be needed to compensate for the additional water.

Additional compositions were prepared in which the oxidizer component was omitted and therefore comprised PETN, gelling agent, diethylene glycol, and water, along with Tyzor® LA cross-linking agent. The amount of PETN was varied from 25 per-cent to 40 per-cent and the diethylene glycol from 9.5 to 25 per-cent. The amounts of gelling agent and cross-linking agent were similar to their compositions described above.

These compositions were loaded into plastic tubing having inside diameters of from three-eighth inch to five-eighth inch with a wall thickness of one thirty-second inch to one-sixteenth inch and the loaded assemblies were found to detonate when initiated by an electric blasting cap. When laid out among dry brush and pine duff type fuels, these assemblies did not cause fires when detonated, whereas the oxidizer containing compositions cited above did start fires in every instance.

It has now been demonstrated that the Superfine PETN remains effective whether it has been dried or whether it has not been dried prior to incorporation into the slurry explosive formulation, and thus it must be assumed that the void spaces are effective in their function whether they define a gas phase or a liquid phase.

Within these slurries it is contemplated that the ammonium nitrate may be replaced by any of potassium, barium and sodium nitrate, and diethylene glycol may be substituted by formamide, dimethyl formamide or other glycols and alcohols provided their vapor pressure with temperature is substantially no greater than the aforementioned compounds of water, and further provided that these glycols or alcohols are at least partly miscible with water in combination with other ingredients in the formulation. Further the guar gum or Jaguar HP-8 may be replaced by polyacrylamide or other gelling agent such as familiar to those skilled in the art.

Manifestly, minor changes can be effected in the above-described compositions without departing from the spirit and scope of the invention as defines and are limited solely by the appended claims.

I claim:

1. An improved slurry explosive able to propagate in very thin layers comprising of, by weight:

- A. approximately 15% to 45% by weight of sensitized superfine particle penetaerythritol tetranitrate (PETN) said sensitized particles having at least 1000 interstitial voids of apparent diameter of approximately 0.18 to 0.2 micron uniformly distributed in an average diameter particle of about 6.5 microns; and
- B. approximately 45% to 27% by weight of a material selected from the group consisting of ammonium nitrate, potassium, barium, and sodium nitrate; and
- C. approximately 10% by weight of a material selected from the group consisting of diethylene

glycol, formamide, dimethyl formamide, glycols and alcohols; and

D. approximately 0.5% to 0.7% of a material selected from the group consisting of guar gum and polyacrylamide; and

E. a cross-linking agent; and

F. the balance water.

2. The improved slurry of claim 1, wherein said sensitized particles have at least about 2000 interstitial voids having an apparent diameter of approximately 0.18 to 0.2 microns uniformly distributed in an average diameter particle of about 6.5 microns.

3. The improved slurry explosive of claim 1, wherein said voids define a gaseous phase.

4. The improved slurry explosive of claim 1, wherein said voids define a liquid phase.

5. An improved slurry explosive as in claim 1, wherein said mixture comprises by weight:

A. 45% of said sensitized superfine penetaerythritol tetranitrate (PETN); and

B. 27% of said material selected from the group consisting of ammonium nitrate, potassium, barium, and sodium nitrate.

6. An improved slurry explosive as in claim 1, wherein said mixture comprises by weight:

A. 35% of said sensitized superfine penetaerythritol tetranitrate (PETN); and

B. 33% of said material selected from the group consisting of ammonium nitrate, potassium, barium and sodium nitrate.

7. An improved slurry explosive as in claim 1, wherein said mixture comprises by weight:

A. 20% of said sensitized superfine penetaerythritol tetranitrate (PETN); and

B. 42% of said material selected from the group consisting of ammonium nitrate, potassium, barium and sodium nitrate.

8. An improved slurry explosive as in claim 1, wherein said mixture comprises by weight:

A. 15% of said sensitized penetaerythritol tetranitrate (PETN); and

B. 45% of said material selected from the group consisting of ammonium nitrate, potassium, barium and sodium nitrate.

9. An improved slurry explosive as in claim 1, wherein said mixture comprises by weight, five drops per 100 grams of slurry of a 50% solution of titanium and antimony lactate as said cross-linking agent.

10. An improved slurry explosive able to propagate in very thin layers comprising, by weight:

A. Approximately 15% to 45% of sensitized superfine particle penetaerythritol tetranitrate (PETN), said sensitized particles having at least 1000 interstitial voids of apparent diameter of approximately 0.18 to 0.2 micron uniformly distributed in an average diameter particle of about 6.5 microns; and

B. Approximately 10% by weight of a material selected from the group consisting of diethylene glycol, formamide, glycols and alcohols; and

C. Approximately 0.5% to 0.7% of a material selected from the group consisting of guar gum and polyacrylamide; and

D. A cross linking agent; and

E. The balance water.

11. The improved slurry of claim 10 where in the material in group (b) is diethylene glycol in a percent, by weight, of the composition of approximately 25%.

• • • • •

United States Patent [19]

Cook

[11] 4,221,618

[45] Sep. 9, 1980

[54] SLURRY EXPLOSIVES

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149/76, 112, 105, 113

[56]

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| | | | |
|-----------|--------|--------------------|-----------|
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| 3,892,610 | 7/1975 | Huzinec | 149/113 X |
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[57]

ABSTRACT

This invention relates to Cold-Formulated Slurry Explosives with Ultra-Fine Oxidizer Solids and including perchlorates.

15 Claims, No Drawings

SLURRY EXPLOSIVES

The present invention relates to new and improved cold-formulated slurry explosives containing colloidal ammonium perchlorate, and/or other colloidal (ultra-fine) oxidizers.

The invention may be more readily understood by considering the following definitions and abbreviations to be used throughout the specification and claims.

DEFINITIONS AND ABBREVIATIONS

Slurry: A state of matter comprising a dispersion and a disperse phase. The dispersion phase is a continuous liquid, and the disperse phase comprises suspended solids and in some cases insoluble liquids. The dispersion phase of slurry explosives is in general a thickened and gelled aqueous oxidizer solution saturated with ammonium nitrate and usually sodium nitrate, often also containing other solutes. The disperse phase is generally rich in AN and usually contains other particulate solids and in some cases insoluble liquids.

Slurry Explosive: Here called "Explosive Slurry" abbreviated "ES" to emphasize that this invention pertains largely to the slurry state. Specific types are abbreviated:

CFES: Cold-formulated explosive slurry (formulated at ambient temperatures AT).

HFES: Hot-formulated explosive slurry of prior art (formulated by adding all ingredients to a hot oxidizer solution).

To designate a particular type, the sensitizer is affixed as follows: FO-CFES means fuel oil-sensitized CFES; gil-CFES means gilsonite-sensitized CFES, etc. FO-HFES means fuel oil-sensitized HFES, etc.

AN: Ammonium nitrate; $\text{AN}_2(\text{aq})$: saturated aqueous solution of AN; **CAN:** coarse AN; **FAN:** fine AN; **UFAN:** ultra-fine AN; **AP:** ammonium perchlorate; **UFAP:** ultra-fine AP; (AP is essentially "salted out" of the cold dispersion phase by the common ion effect); **FO:** fuel oil; **MA:** methyl alcohol; **NaP:** sodium perchlorate; **NaP(aq):** aqueous NaP solution; **60 NaP(aq):** 60% NaP(aq); **SN:** sodium nitrate; **SN(aq):** aqueous solution of SN; **$\text{AN}_2/\text{SN}(\text{aq})$:** aqueous solution saturated with AN but not SN; **$\text{AN}_2/\text{SN}_2(\text{aq})$:** aqueous solution saturated with AN and SN; **FSN:** fine SN; **UFSN:** ultra-fine SN.

CFOS and HFOS are unsensitized oxidizer slurries made in the cold-formulation and hot-formulation methods, respectively.

Slurry Point: (Designated V_o) the minimum dispersion phase required to maintain the slurry state, i.e., to maintain continuity of the dispersion phase. (Slurry point is discussed on pages 280-285, *The Science of Industrial Explosives*, IRECO, Slat Lake City, 1974.)

V_1 : volume percent dispersion phase; V_2 : volume percent disperse phase ($V_1 + V_2 = 100$).

Sensitiveness Test: This is a propagation ("go, no go") test used herein to compare the cold-formulated products of this invention with the hot-formulated ones of prior art and thus the relative sensitiveness by the criterion of critical density at constant charge diameter and temperature. It consists of firing (usually) a 30-pound charge packaged in 5" diameter (d) polyethylene (thus having a length [L] of 35 ± 5 ") with a "booster" after measuring charge density (ρ -g/cc by weighing in and out of water) and temperature ($^{\circ}\text{C}$). The result is recorded as " $D - \rho(t, \text{age in days})$ " if the charge propa-

gates the detonation wave completely, or as $F - \rho(t, \text{age})$ if part of the charge is left undetonated.

The booster used in this sensitiveness test was a commercial 2"(d) \times 4"(L) cast pentolite booster for blasting agents, i.e., explosives such as the CFES of this invention that will not detonate with a blasting cap alone and which contain no explosive ingredients per se.

Critical Density (ρ_c): The maximum ρ for consistent detonations at or below which no F's are observed. (Some D's may be observed at $\rho > \rho_c$.) If ρ_c has not been determined, or to illustrate whether or not a particular charge has a sensitiveness above or below a particular level, a result of only one or two sensitiveness tests may be shown by listing an observed " $D - \rho(t, \text{age})$ ", of " $F - \rho(t, \text{age})$." In examples where critical diameter has been determined by a sufficient number of tests, the sensitiveness-test results are summarized by a $\rho_c(t)$, ρ_c being approximately a linear function of the temperature of the charge at the time of firing, i.e., $\rho_c = \rho(0^{\circ}) + 0.007t$ for ρ_c in grams/cc and t in $^{\circ}\text{C}$.

PRIOR ART

NaP and AP are often mentioned in patent literature as oxidizers for slurry explosives along with AN, SN, and "other inorganic oxidizers." To be sure, NaP(aq) has been used with AN solutions but in smaller amounts and in different ways than dictated by the metathesis method of this invention, as described below. The first HFES patent to mention perchlorates was U.S. Pat. No. 3,096,223 (present inventor a patentee). NaP and AN were not used together in this case. U.S. Pat. No. 3,249,476 shows NaP, NaP/SN, and AP/SN as examples of salts useful in lowering fudge points of hot solutions but nothing to indicate the use of NaP(aq)/AN in the composition and manner to accomplish the purposes of this invention. U.S. Pat. No. 3,282,753 (present inventor a patentee) not only does not contemplate the metathesis reaction but has a water limitation inconsistent with the present invention. Slurry explosive patents often list many oxidizers including perchlorates and AN but with no evidence of contemplation of the NaP/AN metathesis for CFES. Examples include U.S. Pat. Nos. 3,318,740; 3,431,155; 3,485,686; 3,507,718; 3,522,117; 3,695,950; 3,727,350; and 3,985,593. U.S. Pat. No. 3,465,675 made allowance for AN-chlorate and perchlorate reactions by specifying that the nitrates on the one hand and chlorates and perchlorates on the other be used separately. The patent and other literature of public domain do not address the important problem of formulating the disperse phase to maximize sensitiveness in the ways described herein, i.e., using colloidal or ultra-fine oxidizer salts.

"OXIDIZER SLURRY" OR "OS" COMPONENTS OF CFES AND HFES

$\text{AN}_2/\text{SN}_2(\text{aq})$ and $\text{AN}_2/\text{SN}(\text{aq})$ are preferred oxidizer solutions for the disperse phase of both CFES and HFES. They have been used extensively since the beginning of the slurry explosives industry being claimed in the first patent of this era (U.S. Pat. No. 2,930,685). They are generally thickened by guar gum and gelled with a suitable cross-linking agent. Hydroxypropyl guar gum cross-linked with potassium (pyro)antimonate at 20/1 gum/cross-linker is a preferred thickening and cross-linking system and the one used in examples given herein.

An object of the present invention is improved and cold-formulated slurry explosives with ultra-fine oxidizer solids.

Further objects will be appreciated from the following description of the invention:

This invention relates to improved slurry explosives with the solids (or disperse) phase consisting of ultra-fine (colloidal) ammonium perchlorate, (usually) a small amount of ultra-fine sodium nitrate, ammonium nitrate which may be coarse, fine, or ultra-fine, or combinations thereof. The ultra-fine ammonium perchlorate and sodium nitrate are made by a metathesis reaction and ultra-fine ammonium nitrate by (colloid) milling. The fine ammonium nitrate is made by grinding or by recrystallization from a hot concentrated solution fortified with crystal-growth inhibitors. What combination of ultra-fine, fine and coarse ammonium nitrate is used depends on the sensitiveness level desired. The metathesis here used is between aqueous sodium perchlorate and solid ammonium nitrate prills using enough excess of the latter to saturate the water of the reactant solution and, in case only coarse ammonium nitrate is needed, to provide all the undissolved ammonium nitrate. In the metathesis reaction the sensitizer fuel, thickener, and other ingredients except the gelling and density-control agents may be added along with the solid ammonium nitrate. The products of the metathesis are a dispersion phase made from the water of the reactant solution saturated with ammonium nitrate and sodium nitrate, with some, though very little, ammonium perchlorate and a disperse phase of ultra-fine ammonium perchlorate, usually a small amount of ultra-fine sodium nitrate, and a major portion of ammonium nitrate. When the ammonium perchlorate is present in an amount above about 18%, the ammonium nitrate of the disperse phase may be all coarse; but at lower amounts of ammonium perchlorate, from part to all of the solid ammonium nitrate constituent should be fine depending on the sensitiveness level desired which, of course, depends also on the sensitizer used.

Slurry explosives cold-formulated by the above metathesis reaction and containing coarse, fine, or ultra-fine ammonium nitrate have significant advantages over those of prior art including faster detonation reactions with a corresponding appreciable increase in sensitiveness (which generally means appreciably better blasting action), lower production and sensitizer costs, greater ease of mixing and packaged slurry quality. Lower costs of production are associated with simplicity of mixing and no need for the conventional hot-formulation and hot-storage facilities generally used in the slurry explosives of prior art. Lower sensitizer costs are associated with the ability of the cold-formulated slurry explosives of this invention to use economical and technically desirable sensitizers either not applicable at all or only marginally effective as sensitizers for the slurry explosives of prior art. By packaged slurry quality is meant not only adequate, time-independent sensitiveness but also high-quality physical properties (softness, stable and tight gel structure, water resistance, high enough density to sink in water-filled boreholes, and long "shelf life").

SN is a preferred constituent of the dispersion phase, not because it is a better oxidizer than AN (it is actually not as good and is more expensive), but because it contributes important qualities: (a) For a given amount of water, $SN_2(aq)$ adds (approximately) 0.27 times the volume of the water component at 0° C. and 0.36 times

that at 30° C. in addition to (approximately) 0.75 and 1.54 times the volume of the water component contributed by AN at 0° and 30° C., respectively. Thus $AN_2/SN_2(aq)$ has a volume (approximately) 2.02 times as great as that of its water constituent at 0° C. and 2.93 times as great at 30° C. The corresponding weight ratios are (approximately) 0.73 and 0.88 for SN, and 2.91 and 4.38 for $(AN+SN+water)/water$ at 0° C. and 30° C., respectively, with approximately a linear variation between. These values were computed using the (evidently good) approximation that each salt has the same saturation concentration in $AN_2/SN_2(aq)$ as in $AN_2(aq)$ and $SN_2(aq)$ separately. The effective (saturation) densities assumed in these approximations were 1.57 g/cc for AN, 2.7 g/cc for SN, 2.5 for calcium nitrate (CN), and 0.8 for methanol in $AN_2/SN_2(aq)$ based on the saturated $AN(aq)$ and $SN_2(aq)$ solutions. Densities in the disperse phase were those listed for the pure substances, namely, 1.725 g/cc for AN (1.69 g/cc for $t > 32^\circ C.$), 1.95 for AP, 2.26 for SN, and 1.08 for gilsonite. (b) $SN(aq)$ and $SN_2(aq)$ inhibit crystal growth of AN in the disperse phase of CFES and HFES but appear to do so best with some SN in the disperse phase. (c) SN increases the density of the dispersion phase making it easier to disperse the solids (mostly AN) than in $AN_2(aq)$ alone.

Slurry point is an important quantity in CFES design. V_0 usually falls in the range $40 < V_0 < 60$ often at or near the lower limit. It varies with temperature, so a CFES having, for example, $V_1(20^\circ) = 60$ may have $V_1(0^\circ)$ as low as 50; or with $V_1(20^\circ) = 50$, the $V_1(0^\circ)$ may be as low as 42. Minimizing V_0 also minimizes the water requirements. Enough leeway should be provided in the difference $V_1 - V_0$ so it will always be positive and CFES will retain the slurry state at all AT's. To minimize V_0 , experience in casting "amatols" may be used wherein molten TNT is the dispersion phase and AN comprises the disperse phase. (This slurry state undergoes a transition to a "cast" when the TNT solidifies.) With an optimally blended AN, particle size distribution V_0 is about 40 in the AN/molten TNT slurry making it possible to cast a 60/40 (AN/TNT) "amatol." With less than ideal blending, a 50/50 amatol is obtained, but with very poor blending the AN/TNT ratio may go as low as 40/60. The situation is essentially the same in CFES and HFES; when the disperse phase has the proper particle size distribution and the densities of the two phases are close together, as in the AN/molten TNT slurry, V_1 may be as low as 40. But in less favorable circumstances it may go as high as 60. When $AN_2/SN_2(aq)$ is used as the dispersion phase and UFAP (with some UFSN) together with CAN or a combination of CAN and FAN in the disperse phase, V_1 may be as low as 40.

How low in V_1 the slurry explosive should be formulated depends on the difference in AT between that at which the CFES is formed and the lowest AT anticipated in storage and use. It would be proper to make CFES only slightly greater than V_1 if the formulation and use or storage ATs are the same or if the former AT is below the use or storage temperature. If the difference $V_1 - V_1^0$ is permitted to become negative, the slurry state will be destroyed and with it the gel stability which may not be restored when $V_1 - V_1^0$ again becomes positive.

SLURRY FEATURES OF "OXIDIZER SLURRIES"

The essential physical properties of CFES of this invention as well as the HFES of prior art are determined largely by the oxidizer slurry or "OS" component. Four types of OS are thus considered before examples of CFES are given:

CFOS: This designation pertains to the OS of this invention most easily formulated with nearly all the desired properties ready for sensitization, namely, the product of the $60\text{NaP(aq)}/\text{AN}$ metathesis. At the 30/70 ratio CFOS is easily formed at say 20°C . (and is still in the slurry state at zero $^\circ\text{C}$.) simply by stirring AN prills into the NaP(aq) . The computed properties of this CFOS at the 30/70 ratio [taking AP(aq) as negligible, as seems to be the case] were: $V_1(20^\circ)=50.4$ and $V_1(0^\circ)=40.2$, $\text{AN}_2/\text{SN}_2(\text{aq})=23.0/10.6/12$ and $14.3/8.8/12/\text{AN}/\text{SN}/\text{water}$ at 20° and 0° , respectively, and the disperse phase is about $17.3/1.9/35.2$ UFAP-/UFSN/CAN and $17.3/1.9/35.2/1.8/8.8$ UFAP-/UFSN/CAN/FAN at 20° and 0°C ., respectively for the product formed at 20°C . This is an ideal OS system for several reasons: (a) The 60NaP(aq) is the product available at the lowest (contained NaP) cost. (The 60-64% product is the one that is shipped but for standardization purposes solutions above 60% might be diluted to say 60%, or possibly to as low as 58% in order to produce $\text{AN}_2/\text{SN}_2(\text{aq})$ with a minimum UFSN.) (b) The density of both the reactant and the product solutions are ideal for the use of AN prills (immersion density about 1.45 g/cc due to locked-in aeration released when AN dissolves) so the prills will float to make easy mixing of the $60\text{NaP(aq)}/\text{AN}$ reactants. (c) The product (CFOS) is as easy to form (as is the corresponding CFES) as an HFOS (or corresponding HFES) but has the advantage of being at or very near to AT when formulation is complete because the sensitizer, thickener, and other ingredients may easily be added right along with the AN prills. In HFES, on the other hand, an appreciable cooling period is required to drop from the formulation temperature to AT. Gel stability, AN crystal growth, and intimacy of the "redox" (oxidation-reduction) admixture responsible for detonability are all adversely affected by this slow cooling. Even the 32° transition temperature of AN (where the crystal habit changes from the β [below] to the γ structure [above]) has an influence on sensitiveness, i.e., it hampers stability, when the disperse phase has in it an insoluble liquid sensitizer, in passing through this phase transition.

(d) On the negative side is the fact that CAN is the form of the undissolved AN in the disperse phase when AN prills are used in the metathesis reaction. This could be cured by using FAN or even UFAN in place of prills in the final stages of CFOS, but it adds an extra step, namely, that of forming the FAN or UFAN. A replacement of CAN by FAN is unnecessary in CFES when sensitized with insoluble fuels because the limitation is then not the sensitiveness but rather V_1° .

(e) When insoluble solid or liquid sensitizers are used, the V_1° limitation imposes a lower limit on UFAP (in order to remain within the slurry state) amounting to about $20\pm 2\%$ in the final CFES. The UFAP has considerable sensitizing quality and is thus very desirable but still the most costly ingredient in many preferred CFES's. In some applications a lower sensitiveness would be desirable if greater economy could be real-

ized. It is not as simple as just diluting the NaP(aq) with water and making up the Sn deficiency to produce the preferred $\text{AN}_2/\text{SN}_2(\text{aq})$ because this incurs excessive cooling in the metathesis with excess AN. That is, AN and SN both dissolve endothermically in water at -77 and -60 cal/gram , respectively, and exothermicity of the $60\text{NaP(aq)}/\text{AN}$ metathesis nearly balances the endothermicity of $\text{AN}_2/\text{SN}_2(\text{aq})$ formulation when the 60NaP(aq) is used in this metathesis solution formation. This is not so at lower NaP(aq) concentrations. The CFES would be impractical were it not for the favorable heat balance of the $60\text{NaP(aq)}/\text{AN}$ metathesis with excess AN. Therefore (except for an indicated small water dilution to about 58% in some climates) the $60\text{NaP(aq)}/\text{AN}$ system is preferred, and other methods to reduce UFAP and cost besides diluting the system with water should be used.

CFOS-CN: A simple way to lower the NaP(aq) within the limitation imposed by V_1° is to use a soluble fuel or oxidizer to extend the dispersion phase. Examples of such fuels are given later in connection with CFES products. Here calcium nitrate (CN) is considered for this purpose. The use of a commercial CN prills (Norsk Hydro or NHCN) by adding it along with the AN in the $60\text{NaP(aq)}/\text{AN}$ metathesis has a two-fold advantage: It lowers the 60NaP(aq) requirement and accomplishes a small water dilution without incurring excessive endothermicity (by reason of the exothermicity of the CN dissolution). But it also has a disadvantage of introducing a bivalent ion which tends to lower gel stability. NHCN has approximately the composition $77.5/7.5/15$ (CN/AN/ H_2O). The $60\text{NaP(aq)}/\text{AN}$ prills/NHCN prills at the ratio $25.5/59.5/15$ lowered the 60NaP(aq) requirement from 31 to 20 percent corresponding to a UFAP minimum of 11.5.

CFOS-M: This is an OS with the preferred $\text{AN}_2/\text{SN}_2(\text{aq})$ dispersion phase and FAN, UFAN, or both comprising the disperse phase. (With CAN alone as the AN constituent of the disperse phase, this OS would be of little value because, as a diluent for the CFOS, it cuts sensitiveness excessively.) This may be corrected either by adding FAN (made by simply grinding AN prills) or by milling or colloidizing the AN. The simplest and apparently the best way to do this is by homogenizing the $\text{AN}_2/\text{SN}_2(\text{aq})$ -CAN system, e.g., using a "Greenco" grinder or homogenizer. This was done with this system at 20° and $V_1=50$, namely, 46.4% $\text{AN}_2/\text{SN}_2(\text{aq})$ and 53.6% AN prills. This product remained in the slurry state at 0°C . [with 12.2% water $V_1(0^\circ)=39.9$]. This CFOS-M had a (computed) dispersion phase of $23.42/10.7/12.2$ AN/SN/ H_2O and $14.4/8.9/12.2$ and a disperse phase of 53.6 UFAN and $53.6/9/1.8$ UFAN-/FAN/FAN at 20° and 0°C ., respectively. With a system such as this, no NaP(aq) at all is needed to achieve a good level of sensitiveness, but its advantage must be weight against the cost of the CFOS on a purely economical basis, i.e., the extra cost of homogenizing against that of 18% or more UFAP. The system $\text{AN}_2/\text{SN}_2(\text{aq})$ -FAN/SAN is likewise good (but not as good) and less costly because grinding to FAN is less costly than grinding to UFAN size.

CFOS-H: A surprising result in the application of this invention was that hot, concentrated AN solutions with fudge points from 50° to 85°C . and to which SN had been added in the correct amount to give $\text{AN}_2/\text{SN}_2(\text{aq})$ at 20°C . together with 0.1 ± 0.1 (zero to 0.2%) "Petro Ag Special" (surfactant sodium methylnaphthalene sulfonate) could be cooled with stirring or air-"sparg-

ing" all the way from the fudge point to 20° C. or below to give an OS having $45 < V_1 < 55$, i.e., having essentially the same composition except for the Petro Ag Special (PAS) as in the above CFOS-M. For example, to an 86% AN solution at 90° was added 12 parts of SN and 0.1 parts PAS. The mixture was then cooled with stirring to near AT (below the 32° transition temperature where fluidity increased sharply) to produce a thick (but not too thick to pump) OS. This demonstrated the feasibility of this method of producing a cold AN/SN slurry from hot AN solution. The practical advantage of this system is that hot AN solution is often the most economical source of AN, and the fudge-cooling yields storable CFOS-H without the need for hot-storage facilities. Moreover, the CFES products made therefrom are more sensitive than the corresponding HFES products, i.e., with a given fuel sensitizer, as shown in examples given below. For practical purposes, CFOS-H products with up to 15% rather than the low 12.2% water of the above example may be preferred. For example, to 100 parts of the 83% AN solution was added 16 parts SN and 0.1 parts PAS, and the product cooled with sparging to 20° C. to give a CFOS-H having a dispersion phase of $V_1 = 59.3$ and a disperse phase of 43.5/0.9/0.86 FAN/FSN/PAS. This example utilized the 83% AN solution most generally available and is more readily cooled to ambient temperatures (AT). CFOS-H with 16.3% water, 16.3% SN, and 0.1% PAS have been fudge-cooled in this manner to below 10° C. with nothing but simple, relatively slow stirring.

EXAMPLES OF CFES AND COMPARISONS WITH HFES

Fuel oil (FO) has been used as the sensitizer for the popular dry blasting agent ANFO since 1955. FO-HFES has also been in commercial use since the early 1960's, but it was not until the early 1970's that it began to be used in large quantities. The initial bulk product (FO-HFES does not have packaged slurry quality) was too insensitive and unstable in sensitiveness to be able to "sleep" in the borehole for more than a few hours. Charges were thus loaded and fired within hours of each other. In spite of many developments directed toward stabilizing FO and other insoluble liquid fuels in HFES (U.S. Pat. Nos. 3,318,740; 3,431,155; 3,485,686; 3,507,718; 3,522,117; 3,695,950; 3,727,350; 3,985,593 and 4,059,449), even yet the "sleeping" quality is only a few days.

EXAMPLE S-1

As a standard by which to compare the cold-formulated explosive slurries of this invention with hot-formulated (commercial) products of prior art, a system with the lowest sensitiveness for a commercially viable HFES was selected, namely, the FO-HFES. Several 5"(d), 30-lb charges were made as follows: To 22 pounds of 64/18/18 AN/SN/H₂O solution at 55° C. was added 50 grams hydroxypropyl guar gum mixed with 6 pounds of AN prills. Then 15 grams PAS and 1000 milliliters FO were incorporated, the product gassed with sodium nitrite/acetic acid and then packaged for sensitiveness tests. The sensitiveness tests gave $p_c = 1.08(20^\circ, 1)$ (meaning a critical density of 1.08 g/cc at 20° C. after one day) and $F-1.0(0^\circ, 1)$ (meaning a failure at a density of 1.0 g/cc, 0° C., and after one day storage). Sensitiveness deterioration in this FO-HFES was observed after five days normal (AT) storage.

Example S-2:

To 22 pounds of the 78% AN solution having about the same fudge point as the above 64/18/18 solution (about 50° C.) was added six pounds AN prills into which 50 grams guar gum had been mixed. After thickening, 15 grams PAS and 935 milliliters FO were incorporated, and the product cross-linked and gassed with sodium nitrite/acetic acid as before. The sensitiveness test gave the result $F-1.05(20^\circ, 1)$. (Other studies showed it had a critical density of 1.06 g/cc in 6" diameter charges of 36" in length). These results, together with computed composition and V_1 data, are summarized in Table I along with similar types of data for nine examples of CFES products of this invention.

Example A

The FO-CFES of this invention was easily made with 31.5% (the minimum imposed by the V_1 limitation) to 35% and more 60NaP(aq), 61.5 to 58% or less AN prills, 6.6 ± 0.2 FO, 0.1 PAS, 0.4 ± 0.1 hydroxypropyl guar gum cross-linked with $0.02 \pm 0.005\%$ potassium (pyro)antimonate, and density controlled. (The density-controlling for the results shown in Table I was effected with sodium nitrite/acetic acid at from 0.8 to 1.2 mol ratio. CO₂, expanded perlite ["Ryolex"] and foamed polystyrene were also studied in this system. U.S. Pat. No. 3,382,117; 3,390,030, '031, and '032; 3,449,181, and 3,453,158 are examples of patents describing density control in HFES.)

TABLE I

| Computed Product Data for CFES Examples A-H and (Standard) FO-HFES Products | | Dispersion | | | | | | | | | |
|---|----------|------------|----|----------------|----------------|------------------|------|------|------|-----|-------------------------|
| t° C. | | Phase | | Disperse Phase | | Sensitiveness | | | | | [p _c (g/cc)] |
| Example | ES Type | a | b | % | V ₁ | V ₁ ' | UF | F | C | L | |
| S-1 | FO-HF | 45 | 20 | 50.7 | 49 | (40) | — | 23.3 | 20.0 | 6.0 | 1.08 |
| | | | 0 | 38.5 | 41 | | — | 35.5 | 20.0 | 6.0 | (0.94 est.) |
| S-2 | FO-HF | 45 | 20 | 47.7 | 55 | | | 26.7 | 20.0 | 5.6 | <1.05 |
| A | FO-CF | AT | 20 | 50.4 | 52 | 40 | 21.1 | — | 21.9 | 6.6 | 1.34 |
| | | | 0 | 38.6 | 42 | | 21.1 | 11.8 | 21.9 | 6.6 | 1.20 |
| B | GII-CF | AT | 16 | 54.8 | 58 | 42 | 24.2 | 7.3 | 13.7 | — | 1.24 |
| C | FO-CF-CN | AT | 12 | 58.1 | 52 | (42) | 14.4 | 1.1 | 19.3 | 7.1 | ≥1.24 |
| D | MA-CF | AT | 26 | 54.5 | 64 | 50 | 15.5 | — | 30.0 | — | 1.38 |
| | | | 1 | 42.8 | 54 | | 15.5 | 11.7 | 30.0 | — | 1.20 |
| E | MA-CF-M | 20 | 20 | 48.5 | 60 | | 7.2 | 31.0 | 13.3 | — | ≥1.26 |
| F | MA-CF-M | AT | 20 | 43.6 | 53 | | 35.0 | 21.4 | — | — | ≥1.14 |
| G | MA-CF-H | AT | 17 | 48.8 | 58 | | 6.5 | 32.5 | 12.2 | — | ≥1.31 |
| H | FO-CF-H | 20 | 11 | 55.4 | 60 | | — | 38.6 | — | 6.0 | ≥1.18 |

TABLE I-continued

| Computed Product Data for CFES Examples A-H and (Standard) FO-HFES Products | | Dispersion | | | | | | | | | |
|---|---------|------------|-------|------|----------------|----------------|------------------|---------------|-----|---|-------|
| Example | ES Type | t° C. | Phase | | Disperse Phase | | | Sensitiveness | | | |
| | | | a | b | % | V ₁ | V ₁ ' | UF | F | C | L |
| 1 | TO-CF | AT | 20 | 46.0 | 48 | 18.4 | — | 23.0 | 7.0 | — | ±1.30 |

*Formulation temperature (AT - ambient temperature not recorded).

†Temperature of sensitiveness test.

Values in () are estimates from OS studies.

UF - ultra-fine AP and SN in all cases except F where it was UFAN.

F - Fine AN and SN except in B where it was all fine gilsonite.

C - Coarse AN.

L - FO containing 0.1% PAS or "red" tall oil (Example I).

Example A is represented by at least half of more than a hundred sensitiveness tests, this example being based on the 33.5/60 ratio for 60NaP(aq)/AN. (The V₁' was based on the 31.5% lower limit and on the corresponding OS studies.) Certain of these products had packaged-slurry quality and nearly all of them had bulk-slurry quality based on studies covering more than five months AT (hot-summer to cold-winter) storage, $\rho(t, \text{age})$ sensitiveness tests, density-stability studies, water resistance and thermal-cycling tests. Packaged-slurry quality was observed in the FO-CFES made with chromate-free (NaP(aq) and density-controlled with sodium nitrite acetic acid. Products made with CO₂ density control retained their sensitiveness but gradually increased in density because CO₂ dissolved in FO (such that density-lowering from the ungasied state was lost at 5±2% per day). Products made with 60 NaP(aq) containing "0.1 max" sodium dichromate had bulk slurry quality but not packaged slurry quality. That is, they were essentially normal in water resistance, density and sensitiveness, but the gel texture was less than desirable for long-time storage involving thermal fluctuations.

Sensitiveness of FO-CFES followed, as nearly as could be determined, the linear plot $\rho_c(0^\circ)$ being 1.20, 1.28, and 1.18 g/cc for nitrite gassing, baking soda gassing, and Ryolex, respectively, and the temperature coefficient being about 0.007 g/cc per °C. This was based on the best dividing line between all D's (below) and F's with some D's (above). No loss in sensitiveness was seen in sensitiveness tests up to 150 days of midsummer to winter storage.

While 0.1% Petro Ag Special disperses FO in the FO-CFES, aliphatic alcohols in amounts above about 0.5% do likewise. Using the 5.5/2.0 FO/MA sensitizer and Ryolex 18 density control, for example, duplicate charges formulated at the 60 NaP(aq)/AN ratio of 33.5/60 gave 2D—1.19 (11°, 104), even though the MA had probably all evaporated before the end of the 104 days' storage, as seen in studies mentioned below. These and V₁' data show that FO is held in dispersion by the UFAP and thickened CFES, not necessarily by the dispersing agent, although the latter is needed for rapid dispersion of FO.

EXAMPLE B

Gilsonite has been used extensively in HFES but never as a sensitizer, rather only as an energizing fuel. This economically attractive, fine-grained solid hydrocarbon has too little sensitizing value to sensitize HFOS to detonability in the sensitiveness test here used or even in 6" diameter charges at any $\rho(t) > 1.0(20^\circ)$. Gilsonite has accordingly been used only in conjunction

with other sensitizers in the HFES of prior art (U.S. Pat. Nos. 3,882,752; 3,367,805, and 3,713,914). On the other hand, results of a dozen sensitiveness tests with all-gilsonite-sensitized CFES (gil-CFES) gave $\rho_c = 1.24(16^\circ)$ at the 60 NaP/AN ratio = 37/55, 7.3% gilsonite, 0.4% guar gum, CO₂ density control, and a CAN constituent of 13.7%. The product made with chromate-free NaP(aq) had packaged slurry quality, but that with the usual "0.1 max" sodium dichromate was not far behind in quality. The minimum 60 NaP(aq) in this example was 33% corresponding to V₁(0°) = 42, and two charges were unchanged in quality after 104 days of normal AT storage. Another advantage of the NaP(aq)/AN metathesis for this gil-CFES was that the gilsonite could be added right along with the AN prills going readily into the slurry. In the HFES products of prior art, gilsonite had to be used in a "premix."

Example C

Five FO-CFES-CN charges were tested using the 25/52.5/15 ratio for 60 NaP(aq)/AN/NHCN, 7.0 FO, 0.1 PAS, 0.45% guar gum, and density controlled with sodium/nitrite/acetic acid. Results were D—1.18(1°, 6), F—1.3(1° 6), 2D—1.24(12°, 115), and F—1.33(12°, 115). This product did not have packaged-slurry quality (but had good bulk-slurry quality) by reason of only fair gel quality caused by Ca⁺⁺. The lower limit imposed by V₁' was about 20% 60 NaP(aq) to give 11.5 UFAP but no UFSN by reason of the 2.25% water introduction in the NHCN. (CN does not inhibit AN crystal growth.)

Example D

This is a MA-CFES for which over 30 sensitiveness tests were made and MA evaporation studied. MA is an economical fuel sensitizer considered in the prior art for MA-HFES (U.S. Pat. Nos. 3,465,675 and 3,765,967) which has not enjoyed commercial success because of the high volatility and low flashpoint of MA. In fact, if MA is to be used at all as a sensitizer for slurry explosives, the safe way to do so would seem to be in cold formulations such as MA-CFES. These products were found to have excellent properties except for slow MA evaporation (too fast for packaged slurry but not for bulk slurry applications). The minimum 60 NaP(aq) required with MA sensitizer was 23% (imposed again by the V₁' limitation). In this example 60 NaP(aq)/AN prills at the 25/60.5 ratio was used together with 13.5% MA and 0.6±0.3% guar gum. The sensitiveness test gave $\rho_c = 1.38(26^\circ, 2)$ with only the slight aeration with (variable) guar gum content needed for density control and $\rho_c = 1.20(1^\circ, 2)$ using CO₂ density control. An anomalous result [F—1.25(15°, 8)] was obtained leading to MA and isopropyl alcohol-evaporation studies showing

that MA evaporates at (summer) AT at a high enough rate to account for this failure below the previously established $\rho_c(t)$ line. Approximately the same evaporation loss and effectively the same sensitiveness were observed using 10% isopropyl alcohol and 29.8/58.6 for the 60 NaP(aq)/AN. When 8.1% n-butanol was used as the sensitizer, the result (again with no density control necessary) was D—1.38(20°, 10), but NaP(aq)/AN ratio then had to be higher (33.3/57.6). At any rate, n-butanol did not evaporate in these hot-summer tests.

MA was difficult to use in CFOS because (a) the guar gum thickened the dispersion phase very slowly in the cold, approximately half polar dispersion phase, and (b) the density difference between the dispersion and disperse phases was excessively great. FO-CFES has a favorable density difference between the two phases because the low-density sensitizer (FO) expands the disperse rather than the dispersion phase. MA does just the opposite; it lowers the density of the dispersion phase to 1.1 to 1.2 g/cc (from 1.44 to 1.51 g/cc) for AN₂/SN₂(aq) at 0° to 30° C., respectively, without changing appreciably the average density of the disperse phase from that of CFOS. The former difficulty is considerably improved by using less 60 NaP/AN and adding CFOS-M or CFOS-H. $V_1 - V_1^0$ remained high in the MA-CFES-M and MA-CFES-H, but because H₂O/MA was higher they thickened more readily in the cold slurries. Ethylene glycol, sugars, formamide, monomethylamine nitrate, and many others are better sensitizers than MA in this system but all more costly. Furthermore, NA is a marginal sensitizer for HFES and thus well suited to bring out the advantages of the CFES of this invention. It was therefore used in three additional examples presented below as a constant factor to show certain features of CFOS-M and CFOS-H.

Example E

The 60 NaP(aq)/AN metathesis system at the 11.3/26.4 ratio was added along with 19.8% AN₂/AN₂(aq) at 20°, 32 (ground) FAN, 0.8 guar gum, and 11.5% MA. The product was then gelled and density controlled with CO₂ to give the MA-CFES-M of Table I based on one sensitiveness test: D—1.26(20°, 1). This single charge was made with chromate-free NaP(aq) and appeared to have excellent quality except for the found slow evaporation of MA in storage.

Example F

Two MA-CFES-M charges were made with no UFAP (as an example of UFAN) using the OS 51.9/8.3/8.3 AN/SN/H₂O (homogenized in a Greenco grinder), 19.4 FAN, 11.5 MA, and 0.8 guar gum. The products were then gassed with CO₂. The results of the sensitiveness test were 2D—1.14(20°, 7).

Example G

To the 60 NaP(aq)/AN metathesis product at the 10/23.3 ratio and 20° C. was added a CFOS-H having the composition 42/4.4/6.4/0.1 AN/SN/H₂O/PAS which had been fudge-cooled with stirring to 28° C. (after which it was permitted to stand unstirred) along with 13% MA and 0.8% guar gum. The charge was then gelled and density controlled with sodium nitrite/acetic acid. The total water content was thus only 10.4. The sensitiveness test gave D—1.31(17°, 1).

Example H

To check FO dispersion stability in CFOS-H, a 27½-pound charge of this OS was made using the 67.3/16.3/16.3/0.1 AN/SN/H₂O/PAS composition by starting with an 80.5% AN solution, adding the SN and PAS at 65° C. and fudge-cooling to 10° C. At this point it was still pumpable, indeed, no thicker than it was at 32° just before the AN underwent the γ - β transition point. The CFOS-H was then permitted to stand overnight in a room at 20° C. Then the settled FAN was (easily) stirred back into suspension in the AN₂/SN₂(aq), 50 grams guar gum, and 820 grams FO dispersed (requiring no longer than the time required for the guar gum to thicken the solution) and the charges gelled with K-(pyro)antimonate and density-controlled with sodium nitrite/acetic acid (two examples) and Ryolex 40-1 in a third. The results were: D—1.18(11°, 6), F—1.36(11°, 6), and D—1.10(12°, 6), respectively.

Example I

A low-melting tall oil (TO) was used to make TO-CFES. Tall oil is of interest in this invention because it offers several valuable alternatives of application and promotes gassing with sodium nitrite or baking soda. It may either be used as such, as in this example, or to form a solid fuel by making it into an alkali metal salt where it is only partly soluble to distribute itself in both phases, or a Ca-salt by precipitating it in ultrafine form by introducing the sodium-salt into a solution containing the stoichiometric amount of CN (to avoid appreciable Ca++ in solution to reduce the quality of the gel. Other saturated and unsaturated fatty acids, some of the aliphatic acids, and sodium phenoxide should also be useful in the same ways. In this example the 60NaP(aq)/AN metathesis was carried out at the 30/62.6 ratio and 7% "red" tall oil added along with 0.4% guar gum. The product was then gelled and gassed with sodium nitrite to give a TO-CFES with the sensitiveness-test result: D—1.30(20°, 8).

Examples A to I (summarized in Table I) are all based on marginal (FO, TO, MA) and submarginal (gilsonite) fuel sensitizers as far as the HFES of prior art is concerned. These examples, however, show that none of these sensitizers is marginal in the CFES of this invention. Obviously ρ_c will be increased appreciably or the critical diameter at $\rho = 1.1$ g/cc lowered appreciably by employing a CFOS having primarily UFAP and FAN in the disperse phase in combination with a high-quality sensitizer, e.g., dinitrotoluene (DNT), nitrobenzene, or an explosive sensitizer like monomethylaminenitrate, TNT, or the like. As a final example, therefore, a DNT-CFES-H was made using essentially the same composition as was used in preparing a DNT-CFES-H for which a sensitiveness test result was D—1.51(20°, 2) and a propagation test had been made by the method of U.S. Pat. No. 4,084,993 showing a complete detonation of a 1.5" diameter charge at 1.1 g/cc using a 30-gram cast 50/50 pentolite booster.

Example J

A fuel-rich emulsion of DNT was first prepared by dispersing 18 parts molten DNT in 18.5 parts of a 78% AN solution at 58° C. containing 0.1 parts guar gum and 0.1 parts acetic acid. (The melting point of the DNT here used was 56° and the fudge point of the solution about 50°.) This product was then quench-cooled with a CFOS made from the product of the 64NaP(aq)/AN

metathesis at the 30/33.1 ratio and at 15° C. along with 0.4% additional guar gum. The product was then gelled but no density-control agent used. Essentially the same result was obtained in the sensitiveness test as for the DNT-HFES, i.e., D—1.52(20°,5) in this case. While this did not provide a basis for showing any sensitiveness advantage of the DNT-CFES over the corresponding HFES, the former was easier to formulate and had a better gel texture. It also had a theoretically better disperse phase constitution. Both had a computed $V_1(20^\circ)=56$, but, by reason of the use of 63.5% cold material to quench-cool 36.5% hot emulsion in the CFES compared with 20% AN prills to quench-cool 80% of the DNT emulsion in the HFES, the disperse phase should have had an average particle size appreciably less than in the HFES case. The disperse phase comprised approximately the 15.8/10/18 UFAP/FAN/DNT composition in the CFES, but water content (14.8%) was sufficient in both cases that all the AN prills added to the HFES should have gone into solution at the quench temperature (about 48° C.) in the HFES. The DNT was noticeably finer in the CFES.

Having described my invention, what is claimed and desired to be secured by Letters Patent is:

1. Aqueous explosive slurries formulated at ambient temperatures comprising:

- (a) A dispersion phase having a minimum volume in the range 40 to 60% of the slurry consisting of an aqueous solution saturated with ammonium nitrate and containing sodium nitrate at or near saturation, with or without other soluble fuel, soluble oxidizer, or both,
- (b) A disperse phase having a maximum volume of 60 to 40% of the total slurry consisting of from zero to 50% ultra-fine (colloidal size) ammonium perchlorate, from zero to 5% ultra-fine or fine recrystallized sodium nitrate, and from 50 to 100% ammonium nitrate in colloidal (milled), fine ground, fine recrystallized or coarse form, or combinations thereof, at least 30% of the disperse phase being ultra-fine (colloidal) oxidizer solids,
- (c) Soluble insoluble, partially soluble, or combinations thereof of fuel sensitizer(s) sufficient to oxygen-balance the explosive slurry at zero to negative oxygen percentage (based on CO_2 and H_2O as the products of detonation) and to sensitize it at or above a level of detonability whereby it propagates completely in an unconfined 5" diameter polyethylene-packaged charge at least six diameters in length with a 2" diameter \times 4" long case 50/50 pentolite booster or its equivalent with the explosive slurry having a density above 1.10 g/cc at 20° C. or above 1.0 at zero ° C.
- (d) Thickened and gelled with guar gum, a cross-linking agent therefor and density controlled to the desired density by gas generated chemically or introduced mechanically by aeration using varia-

tions in the guar gum content, or by incorporation of a low-density porous or aerated solid.

2. The explosive slurry of claim 1 in which the ultra-fine component of the disperse phase is either predominately or entirely ultra-fine ammonium perchlorate produced by a metathesis reaction of aqueous sodium perchlorate with solid ammonium nitrate with the latter in sufficient excess to saturate the resulting ammonium nitrate/sodium nitrate solution, and contribute from zero to all of the undissolved ammonium nitrate of the disperse phase in the form of coarse, prill-size ammonium nitrate, or from all to none fine ground or recrystallized ammonium nitrate.

3. An explosive slurry of claim 1 in which from zero to all of the solids of the disperse phase and from zero to all of the aqueous solution of the dispersion phase comprise fine, recrystallized ammonium nitrate and the corresponding mother liquor, respectively, prepared by fudge-cooling with stirring at 30° C. or below starting with a hot, concentrated ammonium nitrate solution having a fudge point of 50° C. or higher to which sodium nitrate has been added in an amount up to the water content of the solution.

4. An explosive slurry of claim 1 in which from zero to all of the ammonium nitrate of the disperse phase is fine, ground or ultra-fine, milled ammonium nitrate.

5. An explosive slurry of claim 1 in which a part to all the ammonium nitrate of the disperse phase and part to all of the dispersion phase comprises a cold-milled or homogenized slurry of ammonium nitrate and sodium nitrate.

6. An explosive slurry of claim 3 in which up to 0.2% solution methylnaphthalene sulfonate has been added to assist sodium nitrate as a crystal-growth inhibitor for ammonium nitrate.

7. An explosive slurry of claim 2 in which calcium nitrate prills in an amount up to 20% is added with the ammonium nitrate prills.

8. An explosive slurry of claim 1 in which the sensitizer is an insoluble liquid fuel.

9. An explosive slurry of claim 1 in which the sensitizer is fuel oil dispersed with up to 0.2% sodium methylnaphthalene sulfonate.

10. An explosive slurry of claim 1 in which the sensitizer is a solid, granular fuel.

11. An explosive slurry of claim 1 in which the sensitizer is gilsonite.

12. An explosive slurry of claim 1 in which the sensitizer is a lower aliphatic acid alcohol.

13. An explosion slurry of claim 1 in which the sensitizer is ethylene glycol.

14. An explosive slurry of claim 1 in which the sensitizer is an explosive per se such as coarse TNT or monomethylamine nitrate.

15. An explosive slurry of claim 1 in which the sensitizer is a saturated or unsaturated fatty acid, the sodium, salt, or the calcium salt thereof.

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