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CRYSTALLINE EXPLOSIVE COMPOSED OF AN ALKYL SULFOXIDE SOLVATING A HYDRATE-FORMING SALT AND METHOD OF MAKING

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ABSTRACT OF THE DISCLOSURE

Explosives and explosive compositions, suitable for use as rocket propellants and for other explosive purposes, containing an oxidizing inorganic salt solvated with an alkyl sulfoxide and method of making such explosives and explosive compositions, whereby the solvate may be formed by heating a mixture of the hydrated salt and the alkyl sulfoxide to drive off the displaced water of crystallization or by reacting the water-free or partially hydrated salt and the alkyl sulfoxide in a solvent which dissolves both compounds and can later be removed by distillation or extraction.

SPECIFICATION

My present invention relates to a method of making a new group of explosives and explosive compositions suitable for use as rocket propellants and as substitutes for conventional explosives (e.g., nitroglycerine, trinitrotoluene) and, in fact, for any explosive purposes.

The manufacture of conventional explosives like nitroglycerine and trinitrotoluene involves the reaction of an acid (usually nitric acid) with an organic compound. Besides the explosive (ester or nitro compound) water results and has to be removed to bring the reaction to completion. An excess of water-free nitric acid or the addition of concentrated sulfuric acid usually serves this purpose. After recovery of the explosive, the excess acid has to be reconcentrated for further use. This necessitates large equipment, containing stainless or high-alloy steel, and constitutes a high percentage of the actual cost of manufacture of this kind of explosives.

Mechanical mixtures of oxidizing salts with combustible organic or inorganic materials also are used as explosives. The reconcentration of large amounts of diluted acids—as in the manufacture of nitro compounds or nitric acid esters—is not necessary in the manufacture of mechanical mixture. Therefore, they are cheaper to produce. But—since in these mixtures the distance between the oxygen atoms (in the oxidizing salts) and the hydrogen and carbon atoms of the organic compounds is much greater than in the chemical compounds like nitroglycerine and trinitrotoluene—the speed of combustion is less; they are less powerful than nitroglycerine, etc. Furthermore, the manufacture of nitric-acid-esters or nitro compounds as well as the mechanical mixture of oxidizing salts with combustible material are dangerous processes and require costly safety precautions.

It is, therefore, the principal object of the present invention to provide an explosive material and a method of making same which avoids the disadvantages of earlier systems and compositions, yet is inexpensive in cost and effective for substantially all explosive purposes. The term "explosive" as used herein is intended to refer to the substantially instantaneous release of large amounts of energy upon initiation of a reaction (usually mainly internal) by any means whereby an inherently unstable or metastable state is transformed into a thermodynamically more stable state. Explosive compositions of the type referred to here may be used in place of conventional explosives in construction and destruction, as rocket propellants, and as energy sources for any purpose.

I have found that it is possible to produce a composition having explosive properties close to those of compounds such as nitroglycerine and trinitrotoluene from inorganic salts without the costly acid regeneration and with less danger of accidental explosions.

More particularly, I have observed, that, by substituting part or all of the water of crystallizaiton in inorganic oxidizing salts with alkyl sulfoxide, well-crystallized "solvates" with explosive properties result in which the alkyl sulfoxide provides carbon and hydrogen atoms (as well as sulfur) in such close proximity to the oxidizing atoms to generate (upon detonation) energies close to those obtainable with nitroglycerine and trinitrotoluene. Furthermore, I have found that it is possible to carry out this procedure in a convenient and relatively safe manner without requiring complex and expensive apparatus.

A particularly advantageous method of operation, according to a more specific feature of this invention, is to distill a hydrated oxidizing salt in the presence of an excess of the alkyl sulfoxide and at reduced pressure so that, after distilling off the water of hydration, crystals of a salt are collected in which the sulfoxide has replaced water.

While it has been observed that dimethylsulfoxide (DMSO)[1] forms well-defined crystal structures with inorganic salts it has not heretofore been recognized—to my knowledge—that a basic explosive compound of good controllability, low cost and high explosive power can be fabricated by replacing water of hydration of a particular class of these inorganic salts with alkyl sulfoxide. While the term "oxidizing salts" as used here can refer generally to the salts of acids containing a high proportion of oxygen, nitric acid and perchloric acid salts are most desirable and, if other oxidizing and oxygen-containing acids are considered, they should have the same or greater proportions of oxygen or have greater oxidizing power.

The significance of the present invention will become apparent when it is recognized that the heat of formation of dimethylsulfoxide [DMSO or $(CH_3)_2SO$] is only 600 calories per gram but its heat of combustion (i.e., combination with oxygen is 6050 calories per gram.

Alkyl sulfoxides readily replace water of crystallization in most metal salts except for the salts of the alkali and alkaline-earth groups. The following oxidizing salts have been prepared—solvated with DMSO: aluminum perchlorate, ferrous perchlorate, chromium perchlorate, zinc perchlorate, aluminum nitrate, ferric nitrate, ferrous nitrate, chromium nitrate and zinc nitrate.

Thus, crystalline aluminum perchlorate hexahydrate, $Al(ClO_4)_3 \cdot 6H_2O$, can be solvated with alkyl sulfoxide (e.g., DMSO) to aluminum perchlorate·6DMSO which can be detonated in an explosive reaction in accordance with the following equation:

$$Al(ClO_4)_3 \cdot 6(CH_3)_2SO \rightarrow AlCl_3 + 12CO + 6H_2O + 6S + 12H_2 \quad (1)$$

When the solvate-forming reaction is carried only partially to completion, the crystal structure can be represented as

$$Al(ClO_4)_3 \cdot n(CH_3)_2SO \cdot mH_2O \quad (2)$$

where m represents the remaining moles of water of crystallization per molecule of the salt and n represents the number of alkyl sulfoxide molecules per molecule of salt; $n+m=6$.

Equation 1 demonstrates that the explosive crystal does not contain sufficient oxygen to convert all of the carbon

[1] DMSO = abbreviation for dimethylsulfoxide, $(CH_3)_2SO$.

to CO and all of the hydrogen to water. Therefore, using the method described in connection with Formula 2, the efficiency of the explosive can be increased by retaining two molecules of water in the aluminum-perchlorate-solvate which then will have the formula (m=2, n=4):

$$Al(ClO_4)_3 \cdot 4(CH_3)_2SO \cdot 2H_2O \quad (3)$$

This compound explodes—upon detonation—in accordance with the equation:

$$Al(ClO_4)_3 \cdot 4(CH_3)_2SO \cdot 2H_2O \rightarrow AlCl_3 + 8CO + 10H_2O + 4S + 4H_2 \quad (4)$$

According to a further feature of this invention, the solvate crystals are mechanically combined with oxidizing compounds to increase the energy yield of the resulting composition. In Equations 5 and 6, infra, I show the results obtained when one mole of aluminum perchlorate·6DMSO is intimately mixed with 6 moles of potassium nitrate or, respectively, with 12 moles of ammonium nitrate:

$$Al(ClO_4)_3 \cdot 6(CH_3)_2SO\ (815\ g.) + 6KNO_3\ (600\ g.) = AlCl_3 + 6CO + 6CO_2 + 18H_2O + 3K_2S + 3N_2 + 3S \quad (5)$$

$$Al(SlO_4)_3 \cdot 6(CH_3)_2SO\ (815\ g.) + 12NH_4NO_3\ (960\ g.) = 12N_2 + AlCl_3 + 42H_2O + 12CO + 6S \quad (6)$$

In the manufacturing process, it is of special interest that the addition of oxygen-rich alkali and alkaline-earth salts as well as similar ammonium salts can be accomplished during the solvatization process. The salts of the first and second main group elements of the Periodic System and the salts of ammonium do not form stable alkyl sulfoxide solvates (except beryllium salts). The coprecipitation ensures the most intimate mixtures without any of the disadvantages involved in blending unstable materials.

According to another feature of this invention, the alkyl sulfoxides which may be used effectively are those containing up to four carbon atoms per alkyl group like dimethylsulfoxide, $(CH_3)_2SO$, methylethylsulfoxide,

$$CH_3(C_2H_5)SO$$

propylethylsulfoxide, $C_3H_7(C_2H_5)SO$, and methyl-trimethyl aminosulfoxide, $CH_3—SO—CH_2N(CH_3)_2$.

The following examples represent the best mode presently known to me for carrying out the invention in practice and are, of course, only illustrative of the many variation encompassed within the invention:

EXAMPLE I

A solution of hydrated aluminum perchlorate,

$$Al(ClO_4)_3 \cdot 6H_2O$$

in dimethylsulfoxide is distilled under 10 torrs at a temperature of about 80° C. with the aid of a fractionation column. The first fraction of the distillate—pure water—is discarded. The second fraction contains substantially water-free dimethylsulfoxide. Continued distillation results in the formation of crystals (hereinafter referred to as a solvate) of aluminum perchlorate/DMSO solvate containing dimethylsulfoxide in place of the water of hydration.

Upon the appearance of solvate crystals, the concentrated solution is cooled and most of the solvate precipitates from the mother liquor.

The slurry of aluminum perchlorate solvate+dimethyl sulfoxide is subjected to vacuum filtration in order to separate the solvate crystals from the mother liquor which is returned as a cold saturated solution to the distilling vessel for further use. The recovered solvate crystals are purified with a non-polar solvent of low boiling point which is incapable of dissolving the solvate, e.g., benzene.

After two washings the solvate crystals are relatively pure and can be detonated like conventional explosives. The extraction liquor (i.e., benzene containing DMSO) is separated by means of fractionated distillation with the DMSO returned to the solvate-forming stage while the benzene is reused to purify further quantities of explosive crystals.

EXAMPLE II

Using the same procedure and materials as set forth in Example I, I add an amount of ammonium nitrate equal in weight too the solvate prior to the vacuum distillation. Ammonium nitrate has good solubility in dimethylsulfoxide. After removal of most of the DMSO by vacuum distillation, intimately mixed crystals of the solvate and ammonium nitrate precipitate on cooling.

Excess DMSO is removed by vacuum filtration and solvent extracted as described in Example I. The ammonium nitrate is insoluble in benzene and does not form a DMSO solvate.

EXAMPLE III

Ferric-nitrate hexahydrate, $Fe(NO_3)_3 \cdot 6H_2O$, is dissolved in an excess of dimethylsulfoxide $(CH_3)_2SO$ and subjected to vacuum distillation as described in Examples I and II to remove the water of crystallization and an excess DMSO. Upon the recovery of the

$$Fe(NO_3)_3 \cdot 6(CH_3)_2SO$$

crystals from the mother liquor a solvent extraction with benzene is carried out to remove adherent DMSO. The ferric-nitrate/DMSO solvate is an explosive and can be readily combined with ammonium nitrate by the technique of Example II to improve the energy balance by increasing the quantity of oxidizing inorganic substances per mole of DMSO.

EXAMPLE IV

One mole of anhydrous aluminum perchlorate

$$[Al(ClO_4)_3] + 1$$

mole of hydrated aluminum perchlorate

$$[Al(ClO_4)_3 \cdot 6H_2O + 6$$

moles of $(CH_3)_2SO$ are dissolved in acetone. The solution thereafter is introduced as a fine spray into a vacuum chamber, heated to 40° C. The solvent evaporates instantly. The resulting solid explosive has the composition $Al(ClO_4)_3 \cdot 3(CH_3)_2SO \cdot 3H_2O$ and on detonation explodes according to the equation:

$$Al(ClO_4)_3 \cdot 3(CH_3)_2SO \cdot 3H_2O \rightarrow AlCl_3 + 3S + 12H_2O + 6CO$$

EXAMPLE V

An explosive composition in accordance with this invention is prepared by stirring pure dimethylsulfoxide solvate, prepared as described in Examples I and III, into an oxidizing inorganic salt molten in its own water of crystallization. Thus, aluminum perchlorate hexahydrate, $Al(ClO_4)_3 \cdot 6H_2O$, is heated to dissolve it in its water of hydration and the same weight of aluminum perchlorate/DMSO solvate, $Al(ClO_4)_3 \cdot 6(CH_3)_2SO$, is added. Upon cooling, the mixed crystals may be used as an explosive.

EXAMPLE VI

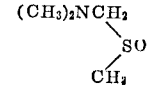
Ferric-nitrate/hexahydrate, $Fe(NO_3)_3 \cdot 6H_2O$, is dissolved in an excess of methylethylsulfoxide,

$$(CH_3)(C_2H_5)SO$$

and subjected to vacuum distillation as described in Examples I and II to remove the water of crystallization and excess sulfoxide. The solvate is purified with benzene and thereafter blended with an equal weight of ammonium nitrate. The mix serves as an explosive.

EXAMPLE VII

A substituted sulfoxide of the following formulation:



is reacted in acetone with the appropriate amount of anhydrous $Al(ClO_4)_3$. The purified solvate is used after mixing with ammonium perchlorate as an explosive.

EXAMPLE VIII

An explosive composition is prepared by blending the solvate, $Al(NO_3)_3 \cdot 4(CH_3)_2SO \cdot 2H_2O$, with nitroglycerine in proportions of two moles of the nitroglycerine per mole of solvate. The composition reacts with an energy approaching that of nitroglycerine but at lower cost. Nitroglycerine supplies part of the oxygen required by the solvate. The following reaction scheme is effective:

$$4[C_3H_5(NO_3)_3]\ (908\text{ g.}) + 2[Al(NO_3)_3 \cdot 4(CH_3)_2SO \cdot 2H_2O]\ (1122\text{ g.}) \rightarrow Al_2S_3 + 9N_2 + 5S + 28CO + 38H_2O \quad (7)$$

EXAMPLE IX

Two moles of tetranitromethane are used per mole of aluminum nitrate·6DMSO in an explosive composition which reacts in accordance with the following equation:

$$Al(NO_3)_3 \cdot 6(CH_3)_2SO\ (561\text{ g.}) + 2[C(NO_2)_4]\ (392\text{ g.}) \rightarrow \tfrac{1}{2}Al_2S_3 + 1\tfrac{1}{2}S + 5\tfrac{1}{2}N_2 + 18H_2O + 13CO + CS_2 \quad (8)$$

The solvates prepared in accordance with the foregoing examples are formed from substantially neutral noncorrosive reactants so that expensive reaction vessels are unnecessary. Moreover, the displacement of water of crystallization by the solvate molecules is not exothermic to the point that cooling of the reaction vessels is required nor are the thermal instabilities characterizing nitrate-esters or nitro compounds present. There is no need to regenerate concentrated acids from dilute acids and the recovery of solvents from the processes of the present invention are much simpler than the recovery processes of prior explosive-manufacturing systems.

Highly concentrated solutions of metal nitrates or perchlorates—manufactured in places with cheap energy (coal, oil or electricity)—can be transported at low cost to the solvation plant (even by pipe line since these solutions do not corrode metals as acids do).

Since explosives usually contain over 70% oxygen (derived from the oxygen-rich acid), the actual cost of the combustible organic portion of the molecule is of minor importance; the price of the acid and the manufacturing cost are the major cost factors.

I claim:

1. An explosive composition composed of a crystalline explosive consisting essentially of at least one hydrate-forming inorganic oxidizing salt of perchloric or nitric acid and an alkyl sulfoxide at least partly solvating said salt.

2. An explosive composition containing a crystalline explosive consisting of at least one hydrate-forming inorganic oxidizing salt of an oxygen-rich acid and an alkyl sulfoxide at least partly solvating said salt and wherein:

said salt is selected from the group which consists of aluminum perchlorate, ferrous perchlorate, ferric perchlorate, chromium perchlorate, zinc perchlorate, aluminum nitrate, ferrous nitrate, ferric nitrate, chromium nitrate, and zinc nitrate; and

said alkyl sulfoxide is a dialkyl sulfoxide or a mono- or di-substituted dialkyl sulfoxide, selected from the group consisting of dimethylsulfoxide, methylethylsulfoxide, propylethylsulfoxide and methyltrimethylaminosulfoxide.

3. The explosive composition defined in claim 2, further comprising at least one solid oxidizing ammonium salt or oxidizing salt of a metal from Groups I and II of the Periodic Table in combination with the alkyl sulfoxide solvate.

4. The explosive composition defined in claim 2, further comprising an explosive organic nitric-acid ester or an organic nitro compound in admixture with the crystalline salt solvated with said alkyl sulfoxide.

5. The explosive composition defined in claim 2, further comprising a combustion-retarding compound admixed with the crystalline salt solvated with said alkyl sulfoxide.

6. A method of making an explosive, comprising the steps of:

heating a hydrated inorganic salt in the presence of an alkyl sulfoxide at a temperature sufficient to drive off at least part of the water of hydration of said salt but less than that at which solvation of the salt by said alkyl sulfoxide is precluded to form crystals of said salt at least partially solvated by said alkyl sulfoxide, said salt and said alkyl sulfoxide being subjected to distillation in vacuo to remove at least part of the water of hydration and form crystals of the salt solvated with the alkyl sulfoxide;

collecting the crystals of the salt solvated with alkyl sulfoxide; and

extracting the crystals so collected with a solvent incapable of dissolving the solvated crystals, said alkyl sulfoxide being a dialkyl sulfoxide or a mono- or di-substituted dialkyl sulfoxide selected from the group consisting of dimethylsulfoxide, methylethylesulfoxide, propyl-ethylsulfoxide and methyl-trimethylaminosulfoxide, said salt being selected from the group which consists of aluminum perchlorate, ferrous perchlorate, ferric perchlorate, chromium perchlorate, zinc perchlorate, aluminum nitrate, ferrous nitrate, ferric nitrate, chromium nitrate, and zinc nitrate.

7. The method defined in claim 6 wherein said crystals are admixed with an explosive substance from the group which consists of nitroglycerine and trinitrotoluol or an oxygen-containing ammonium salt or salt of an element of Groups I and II of the Periodic Table.

8. A method of making an explosive, comprising the step of:

heating a hydrated inorganic salt of perchloric or nitric acid in the presence of an alkyl sulfoxide at a temperature sufficient to drive off at least part of the water of hydration of said salt but less than that at which solvation of the salt by said alkyl sulfoxide is precluded to form crystals of said salt at least partially solvated by said alkyl sulfoxide.

9. The method defined in claim 8 wherein said salt and said alkyl sulfoxide are subjected to distillation in vacuo to remove at least part of the water of hydration and form crystals of the salt solvated with the alkyl sulfoxide, said method further comprising the steps of:

collecting the crystals of the salt solvated with alkyl sulfoxide; and

extracting the crystals so collected with a solvent incapable of dissolving the solvated crystals.

10. The method defined in claim 8 wherein said crystals are admixed with an explosive substance from the group which consists of nitroglycerine and trinitrotoluol or an oxygen-containing ammonium salt or salt of an element of Groups I and II of the Periodic Table.

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