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OXIDIZING AGENT

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This invention relates to an oxidizing agent characterized by high oxidizing activity at low temperature and by a low freezing point.

A number of hypergolic fuels have recently been developed for use in thrust engines. A hypergolic fuel comprises an oxidizing component and a reducing component which, upon being mixed together, undergo rapid spontaneous ignition. The oxidizing component is a powerful oxidizing agent such as hydrogen peroxide, liquid oxygen, or nitric acid and the reducing component is ordinarily an organic material which undergoes spontaneous ignition when mixed with the oxidizing agent.

Of the several powerful oxidizing agents capable of being used as the oxidizing component of the hypergolic fuel, nitric acid has advantages over the others based on its relative stability, its relative ease of handling, and its cost. Nitric acid, however, has two disadvantages which have tended to limit its uses in hypergolic fuels: First, it has a relatively high freezing point, about —40° F., which makes it unsuitable for use as the oxidizing component of a hypergolic fuel charged to a jet or thrust engine operating at very high altitudes and, second, it has a relatively low activity as indicated by relatively long ignition delay period, i. e., the time elapsing between the mixing of the oxidizing and reducing components of the hypergolic fuel and the occurrence of spontaneous ignition.

Some improvement of the deficiencies of nitric acid in respect to freezing point and activity has been effected by dissolving about 7.5% by weight of nitrogen dioxide in the nitric acid to form a material referred to in the art as red fuming nitric acid. The improvement in activity is not great and many potentially good reducing components of hypergolic fuels do not ignite with sufficient rapidity when mixed with red fuming nitric acid, and further, the substitution of red fuming nitric acid for nitric acid increases the hazards incident to storage failure. Considerable improvement in the activity of nitric acid is also obtained by mixing 12 to 15% by weight of concentrated sulfuric acid with the nitric acid. The resulting mixture, however, forms sludge when stored in any of the usual metallic containers and the presence of the sludge causes frequent plugging of lines and spray nozzles leading from the storage tank to the combustion chamber, thus imposing an operational hazard which cannot be tolerated.

It has now been found that a mixture of a major proportion of fuming nitric acid and a minor proportion of an alkane sulfonic acid containing 1 to 5 carbon atoms constitutes an oxidizing agent having a freezing point much lower than that of the nitric acid alone and having an oxidizing activity at low temperaturess which greatly exceeds that of fuming nitric acid alone. Suitable mixtures of fuming nitric acid and alkane sulfonic acid ordinarily contain from 2 to 30 volume per cent of alkane sulfonic acid.

The fuming nitric acid component of this oxidizing composition is predominantly fuming nitric acid, that is, nitric acid having a purity in the range from 95% to 100% HNO_3 and 0 to 5% by weight of water is satisfactory. Commercial fuming nitric acid contains about 98.5% HNO_3. A small amount of N_2O_5 may be added to commercial fuming nitric acid to render it substantially completely anhydrous. Red fuming nitric acid, i. e., nitric acid containing up to about 20% NO_2 may also be used as the nitric acid component of the composition. Methane sulfonic acid, ethane sulfonic acid, propane sulfonic acid, butane sulfonic acid, pentane sulfonic acid, and mixtures of these acids, are added to fuming nitric acid in amounts ranging ordinarily from 2 to 30% by weight to constitute the oxidizing agent of the invention. Methane sulfonic acid and ethane sulfonic acid are preferred for use as the oxidizing component of the fuel because of their great solubility in fuming nitric acid. Commercially available mixtures of alkane sulfonic acids containing methane sulfonic acid, ethane sulfonic acid, propane sulfonic acid and butane sulfonic acid can be mixed with fuming nitric acid in amounts ranging from 2 to 30% by volume to produce a highly active oxidizing agent characterized by a low freezing point. Pentane sulfonic acid is operable, but less desirable, because of lower solubility in the nitric acid.

Anhydrous fuming nitric acid freezes at —42° F. A mixture of 85% by volume of anhydrous fuming nitric acid and 15% by volume of ethane sulfonic acid has a freezing point of —73° F. A mixture of 79% by volume of anhydrous fuming nitric acid and 21% by volume of ethane sulfonic acid has a freezing point of —93° F. A mixture of 84% by volume of anhydrous fuming nitric acid and 16% by volume of methane sulfonic acid has a freezing point of —76° F. Mixtures of anhydrous fuming nitric acid with mixed alkane sulfonic acids containing 1 to 4 carbon atoms, the mixed alkane sulfonic acids being present in amounts from 5 to 20% by volume, shows freezing points below —50° F.

The oxidizing agent of the invention does not form sludge when in contact with metals. Aluminum strips were exposed to a mixture of 85 volume per cent HNO_3 and 15 volume per cent methane sulfonic acid at 140° F. The oxidizing agent remained clear after 500 hours exposure. Under the same conditions a mixture of nitric acid and sulfuric acid containing 12% sulfuric acid sludged and became opaque in 3 hours.

Ignition delay tests were carried out using the oxidizing agents of the invention and a mixture of mercaptans as a reducing component. The mercaptans boiled in the range 136° F. to 250° F. and contained approximately 1% isopropyl mercaptan, 23% normal propyl mercaptan, 37% secondary butyl mercaptan, 7% isobutyl mercaptan, 11% normal butyl mercaptan and 21% amyl mercaptans. In the tests 3 volumes of the oxidizing agent were mixed with one volume of the mercaptans at —40° F. The ignition delays are measured by mixing the mercaptan and the acid in an especially constructed oxidizing cylinder so arranged that at the instant of mixing the mercaptans and the acid, an electrode is grounded initiating a pulse to an electric timer to commence the measurement of the delay. Soon after the acid contacts the mercaptans, ignition takes place. Ionization caused by the flame grounds a tubular electrode to the walls of the oxidizer cylinder, furnishing the terminating pulse to the electric timer to complete the delay measurement.

Results using mixtures of anhydrous fuming nitric acid and methane sulfonic acid are set out in the following table:

Ignition delay at —40° F.

[3 cc. acid/1 cc. mixed mercaptans.]

Anhydrous HNO_3, Vol. Percent	Methane Sulfonic Acid, Vol. Percent	Ignition Delay (milliseconds)
100	0	400
95	5	26
90	10	16
85	15	15
80	20	16
75	25	19
60	40	33

It will be noted that the presence of 5% by volume of methane sulfonic acid in the anhydrous fuming nitric acid reduced the ignition delay period from 400 milliseconds to only 26 milliseconds.

Parallel tests using mixtures of fuming nitric acid and ethane sulfonic acid and using mixtures of anhydrous fuming nitric acid and mixed alkane sulfonic acids containing 1 to 5 carbon atoms gave comparable reductions in the ignition delay period.

The mercaptal formed by the reaction by acetaldehyde and methyl mercaptan was mixed with white fuming nitric acid and with white fuming nitric acid containing 20% by volume of ethane sulfonic acid, and the ignition delay periods were measured. The mixture of white fuming nitric acid and the mercaptal showed an ignition delay of 100 milliseconds, while the ignition delay observed when a mixture of fuming nitric acid and ethane sulfonic acid containing 20% by volume of the latter was substituted for the fuming nitric acid alone was 10 milliseconds.

Similar reductions in ignition delay periods are observed when the oxidizing agent of the invention is mixed with other hypergolically active reducing agents such as diethylaminomethyl ethyl sulfide, diallyl sulfide, diallyl aniline, and the like.

The value of the oxidizing composition of this invention will be readily apparent to those skilled in the hypergolic fuel art. Ignition delay periods in excess of 50 milliseconds create a severe operating hazard during the start-up of a thrust engine. The greater the ignition delay, the greater is the accumulation of hypergolic fuel in the combustion chamber before ignition occurs and the greater is the strain imposed on the combustion chamber at the instant of ignition.

The composition of the invention is not only useful as the oxidizing component of hypergolic fuels, but is a valuable reagent for general oxidation of organic compounds. For example, para-xylene was rapidly oxidized to toluic acid and terephthalic acid at 200 F. with a 30% aqueous solution of a mixture of fuming nitric acid and methane sulfonic acid containing 85 mole per cent HNO_3 and 15 mole per cent methane sulfonic acid.

I claim:

1. An oxidizing agent consisting essentially of a blend of (*a*) a major proportion of nitric acid containing at least 95% by weight of HNO_3 and (*b*) a minor proportion not exceeding about 30% by volume of an alkane sulfonic acid containing 1 to 5 carbon atoms.

2. An oxidizing agent consisting essentially of fuming nitric acid and 2 to 30% by volume of an alkane sulfonic acid containing 1 to 5 carbon atoms per molecule.

3. The composition of claim 2, wherein the alkane sulfonic acid is methane sulfonic acid.

4. The composition of claim 2, wherein the alkane sulfonic acid is ethane sulfonic acid.

5. The composition of claim 2, wherein the alkane sulfonic acid is a mixture of at least two alkane sulfonic acids containing 1 to 5 carbon atoms per molecule.

References Cited in the file of this patent

UNITED STATES PATENTS

2,489,051	Sayward et al.	Nov. 22, 1949
2,489,318	Proell	Nov. 29, 1949
2,573,471	Malina et al.	Oct. 30, 1951