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OXIDIZING AGENT

Manuel A. Pino, Berkeley, Calif., assignor to California Research Corporation, San Francisco, Calif., a corporation of Delaware

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This invention relates to an oxidizing agent containing nitric acid as the essential oxidizing component and characterized by a low freezing point and high stability.

Hypergolic fuels for use in thrust engines ordinarily contain two components: a reducing component which is an organic compound, and nitric acid which is the oxidizing component. Upon mixing of the two components, spontaneous ignition occurs and the ejection of the gaseous products of combustion from the engine provide the desired thrust. White fuming nitric acid is commonly employed as the oxidizing component of such fuels.

Nitric acid has two disadvantages in this area of use. First, nitric acid tends to decompose on storage according to the reaction:

$$4HNO_3 \rightarrow 4NO_2 + 2H_2O + O_2$$

Over a period of time gas pressures build up in the storage vessels to a point which may constitute a serious hazard. Secondly, white fuming nitric acid has a relatively high freezing point, about —40° F. In jet powered aircraft, operated at high altitudes, this relatively high freezing point constitutes a serious operating disadvantage. The nitric acid may freeze either in the storage tanks or in the lines connecting the storage tank to the combustion chambers of the thrust engines.

Nitric acid would be much better adapted to use in thrust engines of aircraft if its storage stability could be increased and its freezing point lowered. The problem of accomplishing these ends is further complicated by the fact that the ignition delay of the mixture of nitric acid with the organic component of the hypergolic fuel must not be materially increased as one seeks to improve the stability and reduce the freezing point of the nitric acid.

It is an object of this invention to provide a nitric acid oxidizing composition which is stable on storage, which has a very low freezing point, and which has a short ignition delay when mixed with suitable organic compounds to constitute a hypergolic fuel.

It has been found that fuming nitric acid is materially improved in respect to its storage stability and freezing point by the addition to the nitric acid of a small amount of sodium nitrite and a small amount of water. The quantities of sodium nitrite and water employed are each in the range from 1 to 5 parts by weight per 100 parts of fuming nitric acid.

The effect of sodium nitrite and water on the freezing point of pure nitric acid is shown in the following Table I:

TABLE I

Composition of WFNA (Wt. Percent)		Sodium Nitrite in WFNA (Wt. Percent)	Freezing Point (° F.)
Nitric Acid	Water		
100	0	0	—40
100	0	2	—48
100	0	3	—54
100	0	4	—59
99	1	0	—44
99	1	4	—65
98	2	0	—48
98	2	2	—63
98	2	4	—72
97	3	0	—52
97	3	4	—86
96	4	0	—57
96	4	4	—97

It will be noted that when water and sodium nitrite are both added to nitric acid, the freezing point lowering obtained is greater than the sum of the freezing point lowerings obtained by adding these materials separately to nitric acid; for example, 2% by weight of water lowers the freezing point 8 Fahrenheit degrees; 2% by weight of sodium nitrite lowers the freezing point of the nitric acid by 8 Fahrenheit degrees; but 2% by weight of water and 2% by weight of sodium nitrite lower the freezing point by 23 Fahrenheit degrees. Similarly, 4% by weight of water lowers the freezing point of nitric acid 17 Fahrenheit degrees; 4% by weight of sodium nitrite lowers the freezing point by 19 Fahrenheit degrees; but 4% by weight of water and 4% by weight of sodium nitrite lower the freezing point by nearly 60 Fahrenheit degrees. From the basis of freezing point, a very desirable composition is one that contains 3 to 5 parts by weight of sodium nitrite and 2 to 4 parts by weight of water to each 100 parts by weight of HNO_3.

The storage stability of nitric acid, of nitric acid containing sodium nitrite, and of nitric acid containing sodum nitrite and water has been studied. Nitric acid decomposes on storage, forming nitrogen dioxide, oxygen, and water. Stability is determined by collecting the oxygen released from nitric acid held at a temperature of 122° F. in a given period of time. Prior to initiating the gas collection, a 50 cc. sample of nitric acid is frozen by immersion in a bath of solid carbon dioxide and acetone. The gas collection system is then evacuated and held under a vacuum for about one-half hour to de-gas the acid. At the end of about one-half hour, helium is introduced into the system to restore atmospheric pressure. The acid sample is then melted and placed in a constant temperature bath maintained at 122° F. The gas formed by decomposition of the acid is passed through a U tube packed with granular strongly basic material which absorbs nitrogen dioxide liberated so that only the oxygen formed in the composition is collected and measured. For each mole of oxygen collected, 4 moles of nitric acid have decomposed. The following Table II shows the volume of oxygen collected at various time intervals from the decomposition of white fuming nitric acid, white fuming

nitric acid containing sodium nitrite, and from white fuming nitric acid containing sodium nitrite and water.

TABLE II

Gas volume in cc.

Time, Hours	2	4	6	8	10	12	14	16	18	20	22	24
Anhydrous WFNA (100% HNO_3)	5	11	18	23	29	34	39	42	47	54	59	64
99% WFNA+1% $NaNO_2$	2	4	6	7.5	11	13	15	17.5	19.9	22	24	26
97% WFNA+3% $NaNO_2$	1	1.5	2.5	3	4	4.7	5.5	6.5	7	8	9	9.5
94 parts WFNA, 4 parts H_2O and 4 parts $NaNO_2$	0	0	0	0	0	0	0	0	0	0	0	[1]0

[1] No gas was evolved during 48 hours at 122° F.

It will be noted that the rate of decomposition is considerably reduced by the presence of sodium nitrite and that when both sodium nitrite and water were present in the acid, no decomposition occurred during a 48 hour test period.

The data presented above indicates the effectiveness of sodium nitrite and water to lower the freezing point of fuming nitric acid and to stabilize it. These results are obtained without seriously increasing the ignition delay period of most hypergolic fuels which use nitric acid as the oxidizing component. An ignition delay period of about 50 milliseconds may be arbitrarily set as a practical working maximum. If the ignition delay period is appreciably longer, the amount of the hypergolic fuel mixture which is injected into the combustion chamber of a thrust engine before ignition occurs may be so large that when the body of hypergolic fuel finally does ignite, an explosive force may be exerted which may damage the combustion chamber.

Ignition delays were measured using a mixture of diallyl sulfide and diallyl aniline as the reducing component of the hypergolic fuel and using white fuming nitric acid containing varying amounts of water and/or sodium nitrite as the oxidizing component. Ignition delays for these hypergolic mixtures at −40° F. are set out in the following Table III in milliseconds:

TABLE III

Composition of WFNA (Wt. Percent)		Sodium Nitrite in WFNA (Wt. Percent)	Corrected Average Ignition Delay (Ms.)
Nitric Acid	Water		
100	0	0	7
100	0	4	22.5
99	1	0	8.5
99	1	4	34.5
98	2	0	20
98	2	4	39
97	3	0	38.5
97	3	4	52
96	4	0	80
96	4	4	52

From the table it will be noted that nitric acid compositions containing 96 parts by weight of 96% HNO_3 and 4 parts by weight of sodium nitrite have an ignition delay period of 52 milliseconds, which is a safe value. It will be noted that a mixture of 96 parts by weight of HNO_3 and 4 parts by weight of water containing no sodium nitrite has an ignition delay period of 80 milliseconds, which is high.

While only sodium nitrite has been exemplified above, the other alkali metal nitrites may be substituted for sodium nitrite; they are, however, generally more expensive and less effective than sodium nitrite.

I claim:

1. A stable oxidizing agent having a low freezing point consisting essentially of nitric acid, sodium nitrite and water, the amounts of sodium nitrite and water being each at least 1 part by weight and not more than 5 parts by weight to 100 parts by weight of nitric acid.

2. A stable oxidizing agent having a low freezing point consisting essentially of nitric acid, sodium nitrite and water, the parts by weight of sodium nitrite and water per 100 parts by weight of nitric acid being in the ranges 2 to 5 and 2 to 4, respectively.

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