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PROCESS OF STABILIZING HYDRAZINE AND HYDRAZINE HYDRATE AND MIXTURES OF EITHER OF THEM WITH ALCOHOLS OR WATER

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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 the stabilization of hydrazine and its mixtures with water or alcohols against the decomposition caused by contact with iron.

It is well known that anhydrous hydrazine, hydrazine hydrate and mixtures of either of them with water or alcohols are decomposed by contact with metals like iron. On the other hand, these substances are quite valuable as propellant fuels, particularly for rockets. Accordingly, a primary object of our invention is to provide means for stabilizing the above mentioned rocket propellants in the presence of iron.

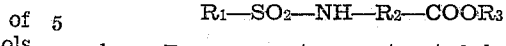
It is equally well known that hydrazine and fuels containing it are very corrosive towards metals, including the iron frequently found in fuel systems. A second object of our invention is therefore provisions of means to prevent the corrosion of iron in the presence of hydrazine and mixtures thereof with water or alcohols.

Obviously means which will simultaneously prevent the decomposition of a fuel by iron and protect iron against the corrosive action of the fuel has advantages over separate means for accomplishing the same purposes. A third object of our invention is consequently provision of a method whereby corrosion of iron by hydrazine and decomposition of hydrazine by iron are prevented at the same time.

Several methods of accomplishing the previously enumerated objects of our invention could possibly be devised, such as, for example, coating the surface of any iron exposed by hydrazine with an inert material. We have chosen, however, to prevent the decomposition and corrosion by means of a chemical to be added directly to the fuel. This chemical should not detract greatly from the calorific value of the fuel and should therefore probably be at least partly organic in nature. Consequently another object of our invention is provision of an organic chemical to prevent simultaneously the corrosion of iron and the decomposition of the above mentioned hydrazine containing fuels. Other objects of the invention will be evident hereinafter.

We have found that certain known compounds will both prevent the decomposition of anhydrous hydrazine, hydrazine hydrate and mixtures thereof with water or alcohol in contact with iron and inhibit the corrosion of iron surfaces exposed to these liquids even at the boundary between the gaseous, liquid and metal phases where corrosion is particularly heavy. These compounds have the following composition:

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where R_1 represents a saturated hydrocarbon radical having a chain length of from 12 to 18 carbon atoms; R_2 represents an aliphatic radical of the formula $-C_nH_{2n}-$ or an aryl radical; and R_3 represents sodium, potassium and ammonium ions or substituted ammonium radicals such as aniline, cyclohexylamine or methylamine.

These compounds will not appreciably diminish the propellant properties of hydrazine because they can be used in very small amounts and, in addition, consist themselves mainly of combustible components.

The preparation of the stabilizing and anticorrosion agents of this application are described in U. S. Patent 2,225,960, granted December 24, 1940.

Our invention will be more fully understood by reference to the following examples, given as illustrative only:

EXAMPLE 1

To test the amount of decomposition in contact with iron, the liquid to be tested was placed in a glass flask, herein referred to as the reaction flask, tightly connected through a reflux condenser with a two neck receiver containing water. The second neck of the receiver carried a glass pipe leading close to the bottom of the receiver. The outlet of this glass pipe extended into a graduated cylinder. By this means the generated gas was measured by the amount of water forced over from the receiver into the graduated cylinder. The reaction flask was put into a heating bath, for example, an oil bath regulated by a thermostat at about 130° C., so that the contents of the flask would boil smoothly. By this means the necessary test time was shortened by the increase of the velocity of reaction at elevated temperature. This apparatus was used for all the comparison tests of this and the following examples.

Thirty-five cubic centimeters of anhydrous hydrazine, 94.7% N_2H_4, was placed into the reaction flask and an iron specimen of about 20 square centimeters surface was put into the liquid. The progressing decomposition was shown by the water which was forced out of the receiver into the graduated cylinder during constant boiling of the contents. As may be seen in Table I

below, the gas generation started immediately at the boiling point and increased constantly during the test time.

The same size of iron specimens was put into 35 ccm. of anhydrous hydrazine, 94.7% N_2H_4, after an addition of 1% mepasin-sulfamido-acetic-acid-sodium salt has been made. The term "mepasin" in this description refers to a mixture of saturated hydrocarbons with a chain length between 12 and 18 carbon atoms which was originated by the Fischer-Tropsch synthesis. In this case, as shown in Table I below, the influence of the inhibitor delayed the start of the gas generation for about 1 hour, and during the succeeding intervals of time the gas generation stood only as a small fraction of the gas generated during the test without the inhibitor.

Table I

Decomposition of anhydrous hydrazine by contact with iron. Gas generation of 35 ccm. liquid and an iron specimen of about 20 cm.^{2} surface without and with inhibitor at the boiling point of anhydrous hydrazine.

Time of boiling (minutes)	No inhibitor ccm. gas	1% inhibitor ccm. gas
10	9	
20	11	
40	17	
60	18	1
80	20	1
100	32	2
125	63	2
170	79	3
180	88	4

EXAMPLE 2

The test method of Example 1 was applied to hydrazine hydrate. Table II, given below, shows the result that an addition of 1% of octadecyl-sulfamido-butyric-acid-ammonium-salt to the liquid decreased the velocity of decomposition remarkably.

Table II

Decomposition of hydrazine hydrate in contact with iron: Test conditions, same as Table I.

Time of boiling (minutes)	No inhibitor ccm. gas	1% inhibitor ccm. gas
10	7	3
20	11	9
50	17	16
80	24	24
110	32	28
125	34	29
140	38	32
170	105	72
200	116	77
240	118	80

EXAMPLE 3

An equal mixture of anhydrous hydrazine (94.7% N_2H_4) and methanol was tested under the conditions of Example 1. The liquid containing 1% of the inhibitor octadecyl-sulfamido-acetic-acid did not show any decomposition for the first two hours, although the comparison test without the inhibitor started to generate gas immediately upon reaching the boiling temperature. The results of this test are given in Table III below.

Table III

Decomposition of a mixture of anhydrous hydrazine and methanol 50:50 in contact with iron. Conditions: same as Table I.

Time of boiling (minutes)	No inhibitor ccm. gas	1% inhibitor ccm. gas
20	5	
40	12	
80	19	
120	23	
140	26	
160	28	2
215	32	4

EXAMPLE 4

This example corresponds to Example 1, but the iron sample dipped into the liquid was so large that only the lower half of it was covered with the liquid. The upper half came only in contact with the vapor. Table IV below shows that even in this case the inhibitor, which was added in an amount of 1% to the liquid, hydrocarbon-) C_{12}–C_{18} mixture) sulfamido-acetic-acid-sodium-salt caused a delay of the decomposition and decreased the gas generation as well.

Table IV

Decomposition of anhydrous hydrazine, 94.7% N_2H_4, by contact with iron half-covered with liquid. Conditions. same as Table I.

Time of boiling (minutes)	No inhibitor ccm. gas	1% inhibitor ccm. gas
10	3	
40	9	1
50	12	3
60	14	5
80	19	7
100	23	9
110	25	10
140	29	13
160	31	15
180	32	16
200	35	16

EXAMPLE 5

Two test tubes each carrying 15 ccm. anhydrous hydrazine and an iron specimen, half dipped in the liquid, but with one containing an addition of 3% mepasin-sulfamido-acetic-acid-sodium salt, were kept at ambient temperature. After two days, the iron sample in the pure anhydrous hydrazine showed heavy rust above the liquid, but the sample of the test tube containing the inhibitor was only slightly affected by the hydrazine.

We claim:

1. The process of stabilizing against contact with iron a material selected from the group consisting of hydrazine, hydrazine hydrate and mixtures thereof with a liquid medium selected from the group consisting of water and alcohol which comprises accomplishing said contact in the presence of a small but effective amount of a stabilizing agent of the formula

$$R_1—SO_2—NH—R_2COOR_3$$

in which R_1 is a saturated hydrocarbon radical with a chain length of from 12 to 18 carbon atoms, R_2 is an aliphatic radical of the formula $—C_nH_{2n}—$, and R_3 is a member of the group consisting of hydrogen sodium, potassium and ammonium ions, and aniline, cyclohexylamine and methylamine radicals.

2. A rocket propellant comprising a member of the group consisting of hydrazine, hydrazine hydrate and mixtures thereof with a liquid medium selected from the group consisting of water and alcohol, said propellant carrying therein a small but effective amount of an inhibitor

against the corrosion of iron and decomposition of the propellant in contact with iron, said inhibitor have the formula

$$R_1—SO_2—NH—R_2COOR_3$$

in which R_1 is a saturated hydrocarbon radical with a chain length of from 12 to 18 carbon atoms, R_2 is an aliphatic radical of the formula $—C_nH_{2n}—$, and R_3 is a member of the group consisting of hydrogen sodium, potassium and ammonium ions, and aniline, cyclohexylamine and methylamine radicals.

3. A rocket propellant consisting essentially of hydrazine hydrate carrying therein about 1% by weight of the ammonium salt of octadecyl-sulfamido-butyric acid.

4. A rocket propellant consisting essentially of a 50:50 mixture of hydrazine and methanol carrying therein about 1% of octadecyl-sulfamido-acetic acid.

5. A rocket propellant consisting essentially of hydrazine to which has been added about 1% of the sodium salt of mepasin-sulfamido-acetic acid.

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