United States Patent Office

3,068,081

Patented Dec. 11, 1962

3,068,081

ABIETIC ACID AND SALTS AS INHIBITORS

Karl F. Hager, Huntsville, Ala., and Morris Rosenthal, Alexandria, Va., assignors to the United States of America as represented by the Secretary of the Army

No Drawing. Filed June 29, 1954, Ser. No. 440,304

15 Claims. (Cl. 44—53)

(Granted under Title 35, U.S. Code (1952), sec. 266)

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

This invention relates to the protection of metals against corrosion.

Water-soluble organic fuels represent an important development in the aircraft and automobile industry. Though these fuels, represented for example by alcohol-water and acetone-water solutions, have proven successful in numerous applications, they are all corrosive towards the commonly used metals such as iron, steel, magnesium, aluminum and the like. The main object of the present invention is therefore to protect metals against the corrosive effects of aqueous liquids and more particularly against the corrosive effects of fuels containing water. Other objects will be evident hereinafter.

Various means have been utilized in the past to avoid corrosion. Probably the oldest method used is the selection of noncorrodible materials for contact with corrosive liquids. Such materials frequently suffer from the disadvantages of excessive cost or of excessive weight.

Another method that has been utilized is to treat the surface of exposed metals so that the surface alone becomes corrosive resistant. Methods of surface treatment include the mechanical, such as painting, the purely chemical, such as deposition from a solution, or electrochemical, such as electrodeposition or anodization. In each case where the surface alone is treated a thin film is formed covering the metal. If this film is ruptured corrosion may take place under the remaining film which is thus rendered useless.

A third method of protection against corrosion is the use of small amounts of sacrificial metals. Less noble metals such as magnesium are placed in contact with the more noble metal to be protected, iron for example, and the corrosive solution. As long as any of the magnesium is present it, as the less noble metal, will be corroded preferentially to the iron. Such a method reveals obvious limitations when an active metal like aluminum or magnesium is itself to be protected.

A fourth method of corrosion prevention, and that adopted by the present inventors, is the rendering of the corrosive medium innocuous, by the addition of a small amount of soluble material functioning as an inhibiting agent. Some metals, notably aluminum, are corroded by contact with an alkaline medium. Consequently any inhibitor for a liquid coming in contact with aluminum should be neutral or slightly acidic in nature.

The inventors have found abietic acid, its partially neutralized and its neutralized salts inhibit the corrosive attack of water containing fuels against aluminum, magnesium and ferrous metals. Abietic acid that is 50% or more neutralized inhibits the corrosiveness of such fuels against iron and steel. Unneutralized abietic acid can be used only to inhibit corrosion against aluminum and magnesium metals and alloys of the materials tested. The partially or totally neutralized acid can be used to inhibit the water-soluble organic fuels from attacking any metal container.

Abietic or abietinic acid is a yellow resinous powder with a melting point of 182° C. prepared by alcoholic

extraction from colophony or common rosin. The formula of the compound is variously reported as $C_{44}H_{64}O_5$, $C_{19}H_{29}COOH$ and $C_{20}H_{30}O_2$. It is soluble in such organic solvents as alcohol, ether, chloroform and benzene but insoluble in water. An organic compound, it will not detract greatly from the heating value of any fuel to which it is added and may even enhance this value. If neutralized with ammonia or an amine it will burn without leaving any solid residue.

As illustrative of the invention, the following examples are given:

Example 1

A magnesium container was half filled with a 50:50 acetone-water solution. After two weeks, there were many deep pits in the magnesium in contact with the liquid phase. This corrosion increased with time.

Example 2

Three magnesium containers were half filled with 50:50 acetone-water solutions containing 0.25% of abietic acid, its neutral sodium salts and a 50:50 mixture of the acid and its sodium salts respectively. In each case corrosion was very slight after six weeks. Retardation was over 95% by comparison with uninhibited solutions.

Example 3

Tests in Examples 1 and 2 were repeated using a 75% ethanol-25% water solution as the corrosive fuel. The uninhibited piece began to develop pits within three days with corrosive action such as pits and salt deposits increasing with time. The magnesium pieces in the inhibited solutions were discolored but revealed little evidence of pits or other corrosive action.

Example 4

The tests of Examples 1, 2 and 3 were repeated using mild steel containers to provide test metal. The uninhibited fuels caused rust formation within two hours. This corrosion rapidly increased so that the entire immersed portion of each container was totally rusted in two days. The container with the unneutralized abietic acid in ethanol-water solution was uncorroded after two days but showed traces of rust after one month in that part in contact with the liquid phase. The fuel consisting of acetone-water-unneutralized abietic acid caused rust spots in two days and complete corrosion within one month. The fuels containing the totally and partially neutralized abietic acid caused no damage within two months and afforded 99% protection over the period of a year.

Example 5

A mild steel container was filled with a fuel mixture of 75% ethanol and 25% water. After 24 hrs. storage time, corrosion was visible. After one month storage time, the interior of the mild steel container was severely corroded.

Example 6

A similar set of mild steel containers to that used in Example No. 5 were filled with the same alcohol-water mixture as Example No. 5. However, container A held a saturated solution of the ammonium salt of abietic acid dissolved in the fuel mixture; in container B 0.25% by wt. of the ammonium salt of abietic acid was added to the fuel; the fuel in container C was saturated with the triethanolamine salt of abietic acid; in container D 0.25% by wt. of the triethanolamine salt of abietic acid was added to and dissolved in the fuel mixture; in container E the fuel mixture was saturated with the morpholine salt of abietic acid; and 0.1% by wt. of the abietic acid morpholine salt was added to the fuel in

container F. None of the containers was rusted after twelve months storage at ambient temperature.

Example 7

The tests of Example #6 were performed, except that instead of totally neutralized abietic acid salts being employed as the inhibitors, the abietic acid was neutralized to pH values of 5.2 to 7.0. In all cases corrosion of the steel container was inhibited after one month storage.

Example 8

Example 5 was repeated, using a magnesium alloy container. Corrosion was visible the next day and in one month, the container was badly corroded.

Example 9

The tests of Examples Nos. 6 and 7 were repeated with the magnesium alloy containers and in all cases, corrosion was inhibited for six months.

Example 10

The tests of Examples No. 1 and 7 were repeated using 24STH Aluminum containers. Corrosion was evident after one month inside the container containing uninhibited alcohol-water mixture, but was absent in the containers with the abietic acid salts neutralized to a pH range 5.2 to 7.0. Abietic acid salts with pH values over 7.0 tend to attack aluminum and its alloys depending on the alloy and the degree of alkalinity of the solution being stored. The pH of the solution of the fuel and inhibitor should be regulated so that, although the pH should be greater than 7.0 (a condition which eliminates corrosion due to the alcohol-water mixture), determination of the degree of alkalinity and the rate of attack of the alkaline solution on the aluminum discloses that the aluminum container is not corroded through for the number of years that it is to remain in service. With these calculations known, even a saturated solution of the inhibitors in Example 6 in the ethanol-water mixture, can be used satisfactorily as corrosion inhibitors.

Example 11

The tests of Examples 5 through 10 were repeated using a 50% solution of acetone in water as the fuel. The results showed that the acetone-water mixture was corrosive to the metal containers, but that this corrosion was inhibited as indicated by Examples Nos. 6, 7, 9 and 10.

In carrying out our invention the corrosion inhibiting materials employed were (1) abietic acid, (2) fully neutralized salts of abietic acid which are soluble to at least 0.1% in organic water-soluble compounds such as alcohols, ketones and aldehydes, and which can be burned in rocket or internal combustion engines, (3) salts of abietic acid neutralized to a pH range of 5.0 to 7.0 which are soluble to a minimum of 0.1% in water-soluble organic compounds usable as fuels, and (4) mixtures of (1), (2) and (3) above. It is evident from the results obtained in the above examples that the water-soluble salts, when partially neutralized to a pH range between 5.0 and 7.0 are effective as corrosion inhibitors when used to protect aluminum or aluminum alloy containers exposed to the water-soluble organic fuels. For protection of ferrous metal and magnesium alloy containers from corrosion by water-soluble organic fuels such as ethanol, methanol and acetone-water solutions, the totally neutralized salts of abietic acid along with abietic acid itself are equally effective. The final pH of the mixture of the fuel and the inhibitors may be any value obtained from the pH determination of the mixture and a saturated, totally neutralized alkali or organic base salt of abietic acid.

This case is a continuation-in-part of our application Serial No. 228,773, filed on May 28, 1951, now abandoned.

It will be apparent to those skilled in the art that many variations may be made in the foregoing detailed description of the invention without departing from the spirit and scope thereof. We therefore intend to be limited only in accordance with the following patent claims.

We claim:

1. The method of protecting metallic surfaces of iron, aluminum and magnesium and their alloys from the corrosive action of fuels, said fuels consisting essentially of, and selected from the group consisting of, aqueous solutions of ethyl alcohol and aqueous solutions of acetone, which consists of adding to said solutions from about 0.1% to about .25% by weight of an inhibiting agent consisting of water soluble nitrogen-containing salts of abietic acid, treating said surfaces with said inhibiting agent contained in said solutions to produce an inhibiting action by said agent upon said surfaces, whereby said surfaces are rendered substantially inactive with respect to the normal corrosive action of said aqueous solutions.

2. The method of claim 1 wherein the inhibiting agent is a water-soluble, neutralized nitrogen-containing salt of abietic acid.

3. The method of claim 1 wherein the inhibiting agent is a water-soluble nitrogen-containing salt of abietic acid, partially neutralized to a pH range of 5.0 to 7.0.

4. The method of claim 1 wherein the inhibiting agent is an ammonium salt of abietic acid.

5. The method of claim 1 wherein the inhibiting agent is the triethanolamine salt of abietic acid.

6. The method of claim 1 wherein the inhibiting agent is the morpholine salt of abietic acid.

7. A fuel consisting essentially of and selected from the group consisting of aqueous solutions of ethyl alcohol and aqueous solutions of acetone normally corrosive to metal surfaces, and from about 0.1% to about 0.25% by weight of a corrosion inhibiting agent consisting of water-soluble nitrogen-containing salts of abietic acid.

8. The fuel of claim 7 wherein the aqueous solution contains ethyl alcohol.

9. The fuel of claim 7 wherein water is present in an amount of 25–50%.

10. The fuel of claim 1 wherein the inhibiting agent is a neutralized water-soluble nitrogen-containing salt of abietic acid.

11. The fuel of claim 7 wherein the inhibiting agent is a water-soluble nitrogen-containing salt of abietic acid neutralized to a pH range of 5.0 to 7.0.

12. The fuel of claim 7 wherein the inhibiting agent is an ammonium salt of abietic acid.

13. The fuel of claim 7 wherein the inhibiting agent is the triethanolamine salt of abietic acid.

14. The fuel of claim 7 wherein the inhibiting agent is the morpholine salt of abietic acid.

15. A fuel, consisting essentially of and selected from the group consisting of solutions of ethyl alcohol and aqueous solutions of acetone, normally corrosive to metal surfaces, and as a corrosion inhibiting agent therefor .1% by weight of the morpholine salt of abietic acid.

References Cited in the file of this patent

UNITED STATES PATENTS

1,613,808	Schreiber	Jan. 11, 1927
1,752,145	Calcott et al.	Mar. 25, 1930

FOREIGN PATENTS

586,651	France	Apr. 1, 1925

OTHER REFERENCES

The Condensed Chemical Dictionary, 4th edition, 1950, Reinhold Publishing Corp., N.Y., p. 572.

Baker et al.: Ind. & Eng. Chem., vol. 41, No. 1, January 1949, pp. 137–144 inclusive.