

UNITED STATES PATENT OFFICE

2,366,074

CORROSION RESISTANT COMPOSITION

Jones I. Wasson, Union, and Carroll J. Wilson,
Westfield, N. J., assignors to Standard Oil De-
velopment Company, a corporation of Dela-
ware

No Drawing. Application May 26, 1942,
Serial No. 444,546

11 Claims. (Cl. 252—53)

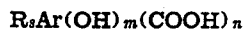
This invention relates to a new additive which imparts corrosion resistant or rust preventing properties to organic materials, especially to mineral lubricating oils which are used in contact with cupric alloy or iron or steel surfaces, particularly when small amounts of water are present.

The materials to which corrosion resistant or rust preventing properties are given by the additives of the present invention are particularly the light mineral lubricating oils of about 50 to 1,500 seconds viscosity Saybolt at 100° F. which are suitable for use especially as turbine oils, as hydraulic fluid or as lubricants for the bearings of machinery which is much in contact with water, such as paper mills, and as insulating oils in refrigerators, and in general in all cases where a lubricating oil is used under conditions in which it may pick up or absorb small amounts of water from atmospheric condensation or other sources of contamination. The additives may likewise be used in other lubricating oil, and other petroleum fractions, such as fuels, and in mineral oil base greases as well as in fatty oils. In general, they may be used to impart corrosion resistant properties to organic materials of a wide variety where water may become admixed therewith and tend to cause corrosion of metal surfaces; and by preventing such corrosion they also greatly reduce wear between rubbing surfaces of metals where the additives are present in lubricants.

It is generally known that many, if not most, of the additives which are incorporated in mineral oil compositions to prevent rusting have a deleterious effect on the oxidation stability or life of the oil. Oils containing these compositions become peculiarly susceptible to deterioration by the action of oxygen. Also, many well known antioxidants are effective in increasing the normal service life of the oil, but they do not impart corrosion resistant properties. It has now been found, in accordance with the present invention, that remarkable improvement in corrosion resistance and very excellent antioxidant characteristics may be imparted at the same time by the use of a combination of an aromatic amine and an alkylated aromatic acid containing at least one hydroxyl group and at least one carboxyl group. The alkylated salicylic acids are particularly effective and are readily obtainable. It has been found that the alkylated hydroxy aromatic acids will cause increased resistance to corrosion when used alone or with non-basic antioxidants, but in this case the normal life of the oil will be considerably reduced. The fur-

ther addition of the aromatic amine not only has the remarkable effect of increasing the service life of the oil, as measured, for example, by the Staeger Oxidation Test, to an extent far beyond that which is obtained when the amine is used alone as an antioxidant, but at the same time the corrosion resisting effect of the acid is retained.

The alkylated hydroxy aromatic acids used in accordance with the present invention are those which have the composition



where Ar represents an aromatic nucleus, which may, for illustration, be a single benzene ring, a diphenyl nucleus or a condensed nucleus, e. g., naphthalene, anthracene, phenanthrene, acenaphthene, etc., R represents an aliphatic, preferably an alkyl group, straight chain or branched, and m , n , and s are integers, one or greater, representing the number of various groups which are attached to the aromatic nucleus. In general, the length and number of the groups R will be such as to impart the necessary solubility of the material in the oil or other organic material in which it is to be incorporated. The more preferred compounds of this class, especially suited for use in turbine oils and other mineral lubricating oils, are the alkylated salicylic acids, where the alkyl group or groups contain a total of at least six carbon atoms. Included within the scope of the above formula are compounds which have additional substituent atoms or groups which do not offset the essentially acid character of the compound. These may include, for example, aryl groups, ether groups, halogen atoms, sulfur-containing groups, nitrogen-containing groups, phosphorus-containing groups, and the like. As suitable examples of this class of compounds may be mentioned isooctyl salicylic acid, diisobutyl salicylic acid, diamyl salicylic acid, isooctyl meta hydroxy benzoic acid, diamyl para hydroxy benzoic acid, isooctyl alpha hydroxy beta naphthoic acid, diisobutyl beta beta hydroxy naphthoic acid, and the like.

The aromatic amines which are preferred to be used in combination with the alkylated hydroxy aromatic acids, in accordance with the present invention, include all types of compounds having the general formula



where Ar' is any aromatic nucleus, such, for ex-

ample, as a single benzene ring, a diphenyl nucleus or a condensed nucleus, e. g., naphthalene, anthracene, phenanthrene, acenaphthene, etc., and R' represents hydrogen or an organic group, for example, an aliphatic or another aromatic group. There may be attached to the nucleus various substituent atoms or groups, such as halogens or hydroxyl or mercapto groups, which do not prevent the compound from exhibiting a basic character, also additional amino groups.

As examples of the above-described class of aromatic amines may be mentioned the amino phenols (a particularly preferred group), aniline, diphenylamine, alpha or beta naphthylamine, beta beta dinaphthylamine, benzyl para amino-phenol, the phenylene diamines, and the like.

In general, the quantity of each ingredient to be used will vary between 0.01 and 0.5%, and approximately molecular ratios between the two ingredients are in general preferred. The quantity to be used in a particular case will naturally depend on the nature of the material treated and on the properties of the particular acid and amino compounds employed.

In addition to the compounds to be added to lubricating oils, according to the present invention, other agents may also be used, such as dyes, pour depressors, sulfurized fatty oils, organo metallic compounds, metallic or other soaps, other basic compounds, such as heterocyclic bases or onium compounds, which may be used to absorb excess of acid or as buffer agents for the acids of the present invention, also other antioxidants, thickeners, oiliness agents, and other ingredients normally employed as oil additives.

As indicated above, the new anticorrosion additive may be used to advantage with many types of organic substances in addition to the lubricating oils described above. They may be used generally in lubricating oils of all types, particularly those suitable for use in internal combustion engines, compressors, steam engines or Diesel engines; also they may be used in industrial oils, e. g., spindle oils and machinery lubricants, also in hydraulic and insulating oils. They may be added to "white products" obtained from petroleum, such as kerosene, white oils, and waxes. They may also be used in gasolines and other petroleum products of the motor fuel type. They may be used in drying oils and in paints and other coating compositions and in fatty oils of animal or vegetable origin. They are particularly effective in greases, extreme pressure lubricants, etc., where they serve to prevent metal catalyzed oxidation.

In the following example are shown the results of tests of a base oil alone, and in combination with an aromatic amino compound, with and without an alkylated salicylic acid, also, for comparison, in combination with the alkylated salicylic acid and another type of antioxidant compound, and in combination with other types of agents having varying degrees of corrosion preventing characteristics.

EXAMPLE 1

A light turbine oil of 150-160 seconds viscosity Saybolt at 100° F., obtained by the solvent refining of a paraffin stock, was submitted to the corrosion and oxidation tests described below, with and without additives. The antioxidant employed was phenyl alpha-naphthylamine, and the alkylated salicylic acid was isooctyl salicylic acid, prepared by the Kolbe synthesis, in which 58 parts of the sodium salt of isooctyl phenol in

200 parts of pyridine were heated to 190-240° C. for 3 to 5 hours in a bomb in the presence of carbon dioxide. The product was acidified and washed with water and further treated with sodium carbonate to separate it from the phenol present. The salt formed was separated, acidified and extracted with a solvent to obtain the purified acid.

The test of the effect of the oil blend on the corrosion of steel when 10% of distilled water was present in the oil was conducted as follows:

A flat polished, cold-rolled steel strip, approximately 121 mm. long, 12.7 mm. wide, and 3 mm. thick, was suspended in a small vessel containing 300 mls. of the oil. The oil was agitated by means of a glass stirrer, 30 mls. of water were added, and the mixture was maintained at a temperature of 140° F., with continued stirring, for a period of 48 hours. The steel specimen was then removed, washed with naphtha, and its condition with regard to rusting observed.

The rate of deterioration of the oil was determined by the Staeger oxidation test which was conducted as follows:

200 cc. of the oil were poured into a glass beaker. To accelerate aging, a cleaned and polished copper strip 40 x 70 x 1 mm. was put into the beaker as a catalyst. The beaker containing the oil and catalyst were placed on a rotating shelf in an oven, the oven temperature being maintained at 110° C. and the shelf rotated at 5-6 R. P. M. Purified air was blown through the oven at the rate of 1.5 to 2 cu. ft. per hour. The life of the oil was determined by observing the time required for the oil to show deterioration as evidenced by a neutralization number of 0.2.

The results of the tests are recorded in the following table:

Table I

Oil composition	Corrosion of steel in oil+10% water	Hours life of oil (Staeger test)
Base oil	Heavy	72
Base oil+0.02% isooctyl salicylic acid	Nil	48
Base oil+0.05% phenyl alpha-naphthylamine	Heavy	550
Base oil+0.05% phenyl alpha-naphthylamine +0.02% isooctyl salicylic acid	Nil	1,300
Base oil+0.01% naphtheneic acid	Light	48
Base oil+0.05% phenyl alpha-naphthylamine +0.01% naphtheneic acid	do	150
Base oil+0.05% phenyl alpha-naphthylamine +0.01% oleic acid	Medium	250
Base oil+0.05% phenyl alpha-naphthylamine +0.01% stearic acid	do	140
Base oil+0.05% phenyl alpha-naphthylamine +0.027% benzoic acid	Light	60
Base oil+0.05% phenyl alpha-naphthylamine +0.0093% benzoic acid	Medium	125
Base oil+0.05% phenyl alpha-naphthylamine +0.02% hydroxy stearic acid	Light	130
Base oil+0.25% tert. butyl ether of ortho tert. butyl para-cresol	Heavy	790
Base oil+0.25% tert. butyl ether of ortho tert. butyl para-cresol +0.02% isooctyl salicylic acid	Nil	720

It can be seen from the above results that the isooctyl salicylic acid alone, while giving the desired protection against corrosion, markedly reduced the normal life of the oil. The phenyl alpha-naphthylamine alone improved the life of the oil, but was of no value in preventing corrosion. The combination of the two additives not only prevented corrosion but increased the life of the oil to a far greater extent than did the antioxidant alone. By comparison, various other compounds having some inhibiting effect on the corrosion were not as efficient for this purpose as isooctyl salicylic acid and were detrimental in their effects on the stability of the oil. It can

be seen, also, that the isooctyl salicylic acid in combination with the non-basic ether antioxidant exhibited no unexpected advantage and even lowered the life of the oil somewhat.

EXAMPLE 2

A medium turbine oil of 375-385 seconds viscosity Saybolt at 100° F. was submitted to the corrosion and oxidation tests described in Example 1, with and without additives. As additives were used phenyl alpha-naphthylamine alone and in combination with a molecular equivalent of isooctyl salicylic acid.

The results of the tests are shown in the following table:

Table II

Oil composition	Corrosion of steel in oil+10% water	Hours life of oil (Staeger test)
Base oil	Heavy	72
Base oil+0.2% phenyl alpha-naphthylamine	do	635
Base oil+0.2% phenyl alpha-naphthylamine +0.23% isooctyl salicylic acid	Nil	1,120

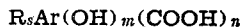
Again it can be seen that the combination of the alkylated salicylic acid with the phenyl alpha-naphthylamine gives a remarkable improvement in the life of the oil while effectively inhibiting corrosion.

The advantageous effects of adding the above described acids and amines to lubricating oils and other organic materials can be obtained equally well by first preparing a salt of the amine and the acid by the simple addition of the amine and the acid, or by any other method, and then adding the product to the material to be treated, and the invention is to be understood as embracing compositions prepared in this manner as well as by adding the acid and amines separately.

This invention is not to be considered as limited by any of the examples mentioned or described herein, nor by any theory of the operation of the invention, but solely by the terms of the appended claims.

We claim:

1. A method of preventing the corrosion of ferrous metal surfaces when in contact with a mineral oil in the presence of substantial amounts of water which comprises incorporating in the said oil before contacting the same with the metal surface a small quantity of a compound of the formula



where Ar is an aromatic nucleus, R is an aliphatic radical, and m , n , and s are integers, one or greater, the sum of such integers being not greater than the number of replaceable hydrogen atoms in the aromatic nucleus, and a small quantity of a compound of the formula



where Ar' is an aromatic nucleus and R' is a member of the class consisting of hydrogen, aliphatic groups, aromatic groups and aliphatic-aromatic groups.

2. A method of preventing the corrosion of ferrous metal surfaces when in contact with a mineral oil in the presence of substantial amounts of water which comprises incorporating in the said oil before contacting the same with the metal surface a small quantity of a compound of the formula

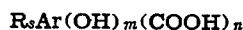


where Ar is an aromatic nucleus, R is an aliphatic radical, and m , n , and s are integers, one or greater, the sum of such integers being not greater than the number of replaceable hydrogen atoms in the aromatic nucleus, and a small quantity of a compound of the formula



where Ar' is an aromatic nucleus and R' is a member of the class consisting of hydrogen, aliphatic groups, aromatic groups and aliphatic-aromatic groups, the said two compounds being in chemical combination as a salt.

3. A method of preventing the corrosion of ferrous metal surfaces when in contact with a mineral oil of the lubricating oil range in the presence of substantial amounts of water which comprises incorporating in the said oil before contacting the same with the metal surface a small quantity of a compound of the formula

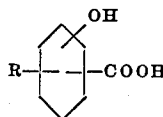


where Ar is an aromatic nucleus, R is an aliphatic radical, and m , n , and s are integers, one or greater, the sum of such integers being not greater than the number of replaceable hydrogen atoms in the aromatic nucleus, and a small quantity of a compound of the formula



where Ar' is an aromatic nucleus and R' is a member of the class consisting of hydrogen, aliphatic groups, aromatic groups and aliphatic-aromatic groups.

4. A method of preventing the corrosion of ferrous metal surfaces when in contact with a mineral oil of the lubricating oil range in the presence of substantial amounts of water which comprises incorporating in the said oil before contacting the same with the metal surface a small quantity of a compound of the formula



where R is an alkyl radical, and a small quantity of a compound of the formula



where Ar is an aromatic nucleus.

5. A method of preventing the corrosion of ferrous metal surfaces when in contact with a mineral oil of the lubricating oil range in the presence of substantial amounts of water which comprises incorporating in the said oil before contacting the same with the metal surface a small quantity of an alkylated salicylic acid and a small quantity of a naphthylamine.

6. A method of preventing the corrosion of ferrous metal surfaces when in contact with a mineral oil of the lubricating oil range in the presence of substantial amounts of water which comprises incorporating in the said oil before contacting the same with the metal surface a small quantity of an alkylated salicylic acid and a small quantity of phenyl alpha-naphthylamine.

7. A method of preventing the corrosion of ferrous metal surfaces when in contact with a mineral oil of the lubricating oil range in the presence of substantial amounts of water which comprises incorporating in the said oil before

contacting the same with the metal surface a small quantity of isooctyl salicylic acid and a small quantity of a naphthylamine.

8. A method of preventing the corrosion of ferrous metal surfaces when in contact with a mineral oil of the lubricating oil range in the presence of substantial amounts of water which comprises incorporating in the said oil before contacting the same with the metal surface a small quantity of isooctyl salicylic acid and a small quantity of phenyl alpha-naphthylamine.

9. A method of preventing the corrosion of ferrous metal surfaces when in contact with a refined mineral lubricating oil having a viscosity of about 50 to about 1500 seconds Saybolt at 100° F. in the presence of substantial amounts of water which comprises incorporating in the said oil before contacting the same with the metal surface about 0.01% to about 0.5% of an alkylated salicylic acid and about 0.01% to about 0.5% of a compound of the formula



where Ar is an aromatic nucleus.

10. A method of preventing the corrosion of ferrous metal surfaces when in contact with a refined mineral lubricating oil having a viscosity of about 50 to about 1500 seconds Saybolt at 100° F. in the presence of substantial amounts of water which comprises incorporating in the said oil before contacting the same with the metal surface about 0.01% to about 0.5% of an alkylated salicylic acid and about 0.01% to about 0.5% of a naphthylamine.

11. A method of preventing the corrosion of ferrous metal surfaces when in contact with a mineral turbine oil of about 150 to about 150 seconds viscosity Saybolt at 100° F. in the presence of substantial amounts of water which comprises incorporating in the said oil before contacting the same with the metal surface about 0.02% of isooctyl salicylic acid and about 0.05% of phenyl alpha-naphthylamine.

JONES I. WASSON.

CARROLL J. WILSON.