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CORROSION PREVENTIVE

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This invention deals with substances capable of preventing or retarding corrosion of ferrous and other metals, and more particularly relates to alkyl maleic acids whose olefinic double bonds have been substantially saturated with sulfur or halogen or both. The acids of this invention are soluble in mineral oils, fatty oils, resins and the like, and are particularly useful when dissolved therein in small quantities.

Accordingly, it is a purpose of this invention to produce a new type of anti-rusting compounds which can be applied to metal surfaces by any conventional means, either by themselves or preferably in dilution of a suitable vehicle, such as a hydrocarbon oil. It is another purpose to produce mineral oils, such as lubricating oils, Diesel fuels, etc., having positive corrosion protective properties. Still another purpose is to produce lubricating oils which are capable of retaining their anti-corrosive action over long periods of time when in regular service.

It is already known that oil-soluble alkylated maleic acids in which the alkyl radicals contain a total of at least 12, and preferably between 18 and 30, carbon atoms are capable of materially preventing corrosion of various metals, particularly ferrous metals. In this property, the alkylated maleic acids are far more effective than monocarboxylic acids of the same numbers of carbon atoms or other dicarboxylic acids, the carboxyl radicals of which are separated by more than 2 carbon atoms. Suitable alkylated maleic acids can be produced by reacting maleic acid anhydride at moderately elevated temperatures with olefines, preferably boiling above 250° C., and then hydrolyzing the resulting alkylated anhydrides.

The resulting free acids are either alkyl maleic acids or alkylene succinic acids, or mixtures of the two, having bromine numbers normally ranging from about 30 to 50. For simplicity, I shall hereinafter call these products alkyl maleic acids.

It has been found that while the unsaturated alkyl maleic acids are quite effective in preventing corrosion, they have the disadvantage of being unstable and susceptible to rapid deterioration by oxidation. Hydrogenation of the unsaturated acids to eliminate the olefinic double bond largely overcomes this difficulty, but hydrogenation is relatively expensive and quite difficult to carry out, as it tends to attack and reduce simultaneously the carboxyl radicals, thereby materially lowering the yield of the anti-corrosion active material.

Now I have discovered that the unsaturated alkyl maleic acids can be rendered relatively stable in a much simpler and easier manner than by hydrogenation. I have found that by treating the alkyl maleic acids or their anhydrides with halogen or sulfur or both under conditions to effect an addition of these elements, the olefinic unsaturation can be reduced sufficiently to render the products as stable as the corresponding succinic acids obtained by hydrogenation. In this process of sulfurization or halogenation, no losses of valuable acids occur, the yields of sulfurized or halogenated alkyl succinic acids being substantially 100%. This is a very great advantage over hydrogenation, in the course of which losses may be caused through destruction of carboxyl radicals which are often quite considerable.

Toward ferrous metals, the protective powers of the sulfurized halogenated and hydrogenated products are approximately the same. Toward certain alloyed hard bearing metals, such as copper-lead, cadmium-nickel, cadmium-silver, etc., the sulfurized acid in particular appears to exert a considerably greater protection. In addition, the sulfur- or halogen-containing acids possess mild extreme pressure properties which may be very useful in lubricating oils. The combination of corrosion protection and extreme pressure properties makes the acids or their soaps very valuable as addition agents to cutting oils.

Sulfurization may be achieved by simply heating the free unsaturated alkyl maleic acids to a temperature of about 160°–200° C. for one to two hours. Depending upon the original degree of unsaturation, up to about 20% sulfur may be absorbed.

Halogenation takes place readily at room temperature. The unsaturated alkyl maleic acid is advantageously dissolved in a suitable solvent which is not attacked by halogens under the conditions of the treatment, such as carbon tetrachloride, chloroform, etc., and the halogen is then merely added to the solution in the approximate amount calculated from the bromine number of the acid. When chlorinating, some substitution of hydrogen by chlorine may take place simultaneously with simple addition.

Sulfur-chlorination may be carried out by reacting the alkyl maleic acid with a sulfur chloride, e. g., SCl_2 or $\text{S} \cdot \text{Cl}_2$, at room temperature, if desired in the presence of a solvent inert to halogenation.

In order that the treated acid be sufficiently

stable for ordinary use, such as may occur, for instance, during conventional lubrication, it is necessary that the unsaturation of the acid be reduced to a bromine number below 15, and preferably below 10. In the case of the halogenated product, the bromine number can be determined directly. However, in sulfurized products, actual determination of the bromine number may be misleading, and therefore should be calculated by difference from the bromine number of the untreated acid and the amount of sulfur or halogen plus sulfur introduced.

From the above, it will be realized that the amount of halogen and sulfur which should be introduced depends on the unsaturation, i. e., the bromine number of the unsaturated alkyl succinic acid. As indicated before, the bromine number is normally somewhere between 35 and 50, and the approximate amount of addition element to be introduced therefore is approximately equal to or slightly lower than the amount A in pounds per 100 pounds of unsaturated acid, where

A=

$$\frac{\text{bromine number} \times \text{atomic weight of element}}{80}$$

Taking into consideration that the bromine number of the reaction product should preferably not be greater than 10, it will be seen that, in general, about 8 to 22 pounds of chlorine or sulfur or both are to be reacted with 100 pounds of the alkyl maleic acid, which normally results in products containing from about 7% to 18% by weight of these elements.

The amounts of my sulfurized or halogenated acids required for effective corrosion protection will vary between wide limits, depending on the type of protection required and on the method of application. In general, I prefer to prepare dilute solutions or colloidal dispersions of the acid in a suitable carrier material which may be sprayed or painted, or which may flow over the surface to be protected, as in the case of lubrication or metal cutting. Suitable carrier materials comprise various types of mineral oils, as naphthas, kerosene, Diesel fuels, lubricating oils, petroleum plastics, e. g., black asphalts or albedo asphalts; synthetic resins, such as are used as paints, enamels, varnishes, e. g., drying fatty oils, Bakelite type varnishes, cellulose ester lacquers, etc.; common solvents, as alcohols, ketones, ethers, chlorinated hydrocarbons, water, etc. Again, depending on the particular use, the concentration in the carrier material may vary between wide limits, e. g., from about .005% to 10%. In general, low concentration from .005% to .5% are preferred unless it is desired to make use of the extreme pressure properties of my products, in which case it may be desirable to dissolve amounts between .5% to 10% in the vehicle.

In general, suitable vehicles should be resistant to deterioration by oxidation over long periods of time. If desired, their resistance to oxidation may be improved by the addition of anti-oxidants, such as alkyl phenols, amino phenols, aromatic secondary amines, etc.

Alkali metal or ammonia soaps of my acids are strong emulsifying agents and are therefore highly useful for producing so-called soluble cutting oils. The amounts of these soaps required to produce rapid emulsification of mineral or fatty oils with water are usually between about .2% to 2%. To take full advantage of the rust-preventing properties of my acids, I prefer in

general that such emulsible oils contain an excess of the free acid over the cation.

The following examples further illustrate my invention:

5 An unsaturated alkyl succinic acid was prepared by reacting olefines obtained in the cracking of wax and boiling from 280° to 340° C. with maleic acid anhydride, and hydrolyzing the reaction product. The acid had a bromine number 10 of 44.

To a sample of this acid was added 18.5% by weight of flowers of sulfur, and the mixture was heated with stirring at 150° C. for one hour and thereafter at 180° C. for another hour. An oil 15 resulted, which was clear when hot, but turbid when cold. It was dissolved in benzene and filtered to remove small amounts of unreacted sulfur. The benzene was then removed by distillation and the residual product had a sulfur content of 15.4%. This indicated that between 98% 20 and 99% of the sulfur had reacted. The unsaturation of the sulfurized acid as estimated from the amount of sulfur absorbed corresponded to a bromine number of zero.

25 Another sample of the above unsaturated alkyl succinic acid was dissolved in carbon tetrachloride, and chlorine was passed slowly through it until 19 grams of chlorine per 100 grams of the acid had been absorbed. The solvent was removed by distillation, leaving an oily residue behind. The bromine number of the latter was 7, 30 and its chlorine content, as determined by analysis, was 11.1%.

The effectiveness of the products so obtained 35 as anti-corrosive was determined by the so-called Kuebler turbine oil rusting test, which consists of suspending a clean bright strip of cold rolled steel in a beaker containing 350 cc. of a light mineral oil and 35 cc. water. The mixture is 40 agitated violently for 48 hours at 75° C. At the end of this time, the strip is removed and inspected.

In some of the tests, results of which are given below, a solution of 2% NaCl in water was substituted for the water.

45 For comparison, the effect of unsaturated alkyl succinic acid prior to sulfurization or chlorination is also shown:

Oil sample containing—	In presence of—	Area of steel strip covered by rust
		Percent
No anti-corrosive.....	Water.....	100
.01% unsaturated acid.....	do.....	None
.01% sulfurized acid.....	do.....	None
.01% chlorinated acid.....	do.....	None
.01% unsaturated acid.....	2% salt solution.....	90
.01% sulfurized acid.....	do.....	50
.01% chlorinated acid.....	do.....	50

60 I claim as my invention:

1. A new composition of matter comprising an alkyl maleic acid, the alkyl radicals of which contain at least 12 carbon atoms, and the olefinic double bonds of which are at least partially saturated with an element selected from the group consisting of halogen and sulfur, said acid having a bromine number below 15.

2. A new composition of matter comprising an alkyl maleic acid, the alkyl radicals of which contain at least 12 carbon atoms, and the olefinic double bonds of which are at least partially saturated with an element selected from the group consisting of halogen and sulfur, said acid having a bromine number below 10.

3. A new composition of matter comprising an

alkyl maleic acid having a bromine number below 15 and containing between 7% and 18% by weight of an element selected from the group consisting of chlorine and sulfur, the alkyl radicals of said acid containing at least 12 carbon atoms.

4. A new composition of matter comprising an alkyl maleic acid, the alkyl radicals of which contain 18 to 30 carbon atoms and the olefinic double bonds of which are at least partially saturated with an element selected from the group consisting of halogen and sulfur, said acid having a bromine number below 15.

5. The alkali metal soap of a new composition of matter comprising an alkyl maleic acid, the alkyl radicals of which contain at least 12 carbon atoms, and the olefinic double bonds of which are at least partially saturated with an element selected from the group consisting of halogen and sulfur, said acid having a bromine number below 15.

6. A corrosion protective composition of matter comprising a vehicle capable of being distributed over a metallic surface, which vehicle is substantially resistant to deterioration by oxidation and contains finely distributed a small amount of an alkyl maleic acid whose alkyl radicals contain at least 12 carbon atoms and whose olefinic double bonds are at least partially saturated with an element selected from the group

consisting of halogen and sulfur, said acid having a bromine number below 15.

7. The composition of claim 6 wherein said vehicle is a hydrocarbon compound.

8. The composition of claim 6 wherein said vehicle is a lubricating oil.

9. A lubricating oil of anti-corrosive properties comprising a mineral lubricating oil and from .05% to .5% of an alkyl maleic acid having a bromine number below 15 and containing from 7% to 18% of an element selected from the group consisting of sulfur and chlorine, the alkyl radicals of said acid containing from 12 to 30 carbon atoms.

10. An emulsible cutting oil comprising a mineral oil and a small amount of a salt of an alkyl maleic acid having a bromine number below 15 and containing from 7% to 18% of an element selected from the group consisting of sulfur and chlorine, the alkyl radicals of said acid containing from 12 to 30 carbon atoms, and the cation of said salt being selected from the group consisting of alkali metal and ammonium ions.

11. The cutting oil of claim 10 wherein said amount is between .2% to 2.0%.

12. The cutting oil of claim 10, which is acid-reacting by virtue of an excess of said alkyl maleic acid over the equivalent amount of cation.

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