

# UNITED STATES PATENT OFFICE

2,242,837

## ANTICORROSION AGENT

James E. Shields, Niagara Falls, N. Y., assignor  
to Alex Corporation, New York, N. Y., a cor-  
poration of New York

No Drawing. Application January 24, 1938,  
Serial No. 186,753

4 Claims. (Cl. 260—29)

This invention relates to the provision of specific organic salts of lead, and of specific compositions, containing such lead salts, adapted for use in providing corrosion-preventing coatings on metal surfaces.

An anti-corrosion material, to be completely successful, should answer the following criteria:

1. A film thereof should adhere to the metal surface well, making intimate contact with the surface.

2. It should provide a continuous film.

3. The film should not be porous but should effectually impede moisture or other corrosive gases or liquids.

4. It should be stable not only under conditions of storage but also under service conditions.

5. It should not volatilize readily.

6. It should be chemically inert to the metal.

7. In certain specific applications, it should not readily become brittle.

8. It should be capable of ready application to the metal surface by ordinary workshop methods (e. g., by brushing, spraying, dipping, roller-levelling, or the like). In addition, it should not constitute a fire hazard; should not melt and run off the metal at summer temperatures; should not crack, craze, peel, or otherwise permit access of moisture, corrosive gases or liquids to the metal surface to be protected; and, in particular cases, should be resistant to abrasion (e. g., resistant to removal by wind, water, handling and rubbing).

For reasons of economy such films should be as thin (i. e., require a minimum amount of material) as possible comparable with proper protection.

It has been found that while oxidized higher molecular weight hydrocarbons, e. g., oxidized paraffin (and other mineral waxes, and oxidized petroleum oil fractions, possess many of the above-mentioned qualifications they are deficient in others. Thus, they tend to be removed too easily (as by chance rubbing) from the metal surfaces being protected, and in some cases have less than desirable adherence to said surfaces. However, oxidized petroleum fractions, alone, or oxidized higher molecular weight hydrocarbons from paraffin and other mineral waxes, alone, prevent corrosion of corrodible metal over relatively long periods of time.

In certain cases metals, such as aluminum, copper, or alloys of copper, tin, etc., such as brass, bronze, etc., should show no effect on the films and such films should show no, or very low,

chemical activity toward metallic oxides. In other cases it is important that such films be not active to ferrous or ferric hydroxides, zinc oxide, zinc carbonate or lead oxide and lead basic carbonate.

Actinic rays (sunlight) with the presence of water vapor accelerate the rate of corrosion of corrodible metal while oxidized petroleum fractions and oxidized waxes of mineral origin retard this action. Greater retardation of actinic rays is accomplished by the addition of certain organic salts of lead and compositions containing such lead salts as described in the following.

It is an object of the present invention to improve the over-all utility of the oxidized hydrocarbon masses above described in the named relations. A further object of the invention is the provision of anti-corrosion compositions containing said oxidized hydrocarbons, which compositions have improved properties.

I have found that the above, and other, desired results are attained by preparation of a composition consisting essentially of the aforesaid oxidized hydrocarbons in intimate admixture with lead salts of relatively high molecular weight, saturated aliphatic hydroxycarboxylic acids of mineral origin, of the class hereinafter more particularly described, and produced by the controlled, liquid-phase, partial oxidation, with an oxidizing gas, of hydrocarbons of mineral origin (particularly, paraffinic hydrocarbons) at an elevated reaction temperature and at a pressure greater than atmospheric pressure in the presence of an agent expediting the oxidation of said hydrocarbons.

It has been found that lead salts of relatively high molecular weight, saturated, aliphatic carboxylic acids of mineral origin, and compositions containing such lead salts, applied in relatively the same thickness on the surface of metal, prevent corrosion of corrodible metal over greater periods of time, by virtue of being less volatile and more impervious to moisture, water vapor, liquids and corrosive gases. Also, they form tougher films which are less readily abraded by handling (e. g., in transportation, handling machinery and assembling machinery parts): in addition, by virtue of the higher melting points or deformation points of said lead salts and compositions containing said lead salts as contrasted with those of oxidized petroleum or oxidized waxes of mineral origin, the use of the former is extended in preventing corrosion of corrodible metal exposed to high temperatures prevailing in tropical climates.

When a petroleum hydrocarbon mixture (be it normally solid wax, or a normally liquid fraction of the crude petroleum, or mixtures of the same, or crude petroleum itself) or similar mineral hydrocarbon mixture is contacted, in liquid phase, with an oxidizing gas (e. g., air) at an elevated reaction temperature (i. e., above room temperature and not exceeding, say, 135° C. or 150° C.) and at a pressure greater than atmospheric pressure (e. g., at a pressure of from about 200 pounds to about 300 pounds per square inch), as has been disclosed in, for instance, U. S. Patents Nos. 1,690,768 and 1,690,769 to Arthur W. Burwell, there is produced a crude oxidation reaction product which, after the same is freed from moisture and a small content of volatile acids (usually formic, acetic and propionic acids) by simple heating, is a mixture of a great number of different compounds which may, for clarity, be grouped thus:

1. Unoxidized (i. e., "original") hydrocarbons;
2. Aliphatic alcohols, largely secondary and tertiary;
3. Aliphatic ketones;
4. Keto-alcohols;
5. High molecular weight (C<sub>10</sub>—C<sub>35</sub>) saturated aliphatic carboxylic and hydroxycarboxylic acids having end methyl groups, etc.; and
6. Neutral esters and lactones derived from the aforesaid acids and the aforesaid alcohols, or from the aforesaid acids, respectively.

Differently grouped, the mixtures are separable broadly into (a) saponifiables and (b) unsaponifiables: into the latter group fall the alcoholic and ketonic compounds aforesaid (and, of course, the unoxidized hydrocarbons), whereas the acids, esters and lactones are grouped as saponifiables. Said high molecular weight saturated aliphatic carboxylic, and hydroxy carboxylic, acids having end methyl groups, which are, per se, described in "Industrial and Engineering Chemistry," vol. 26 (1934), pages 204-7, are the starting materials from which the lead salts of the compositions of the present invention are derived.

According to one embodiment of the present invention, I may mix finely divided litharge (or basic lead carbonate or acetate, or other suitable lead compound) with the oxidation mixture described in the preceding paragraph and heat the resulting admixture at above 100° C., e. g., at from about 110° to about 150° C. for a few hours or for a period of sufficient duration to effect dissolution of the lead compound. Thereby the lead compound is caused to react with the acids, and the resulting product contains lead soaps of the free acids content of the reaction mixture: the lactone and ester contents of the reaction mixture may be reacted with the lead compound also, whereby to increase the proportion of lead soaps. In general, I aim to avoid leaving any unreacted lead compound in the oxidized hydrocarbons mixture, and hence make certain that the amount of lead compound added is in any case not more than that amount which is actually combinable with the above named compounds and usually is considerably less than that.

The melting point of the composition may be controlled in part by the amount of lead compound added and reacted, and in part by the time of heating.

The so-reacted mixture containing lead soaps produced in situ constitutes the basis of an operable composition for preventing the corrosion of corrodible metal surfaces. It may be applied, as such, to the metal surfaces to be protected, the

normally solid products being for this purpose heated to above their melting points and applied as a film, in such molten form, by dipping or brushing or in other desirable manner. In lieu thereof I may, and prefer to, employ a solution of the aforesaid basis material in an appropriate organic solvent which desirably is fairly volatile, e. g., a light petroleum distillate such as gasoline, Stoddard solvent, or the like: such solution may, for example, contain 60—40% by volume, more or less, of the aforesaid basis composition and 40—60%, more or less, of the selected organic solvent. The solution may be spread as a film over the metal surface to be protected in any suitable manner and the solvent allowed to evaporate. A composition consisting essentially of 60% of the lead soap-containing oxidized hydrocarbons mixture derived from paraffin wax or sharples wax (i. e., an amorphous wax separable from petroleum: see U. S. Patent No. 2,043,923) or a mixture thereof and 40% Stoddard solvent is of a heavy "brushing consistency." This basis composition leaves a relatively hard, tough, non-porous coating having considerable ability to resist the solvent action of lubricating oils casually contacted therewith.

According to a second embodiment of the invention, I may produce lead salts of the aforesaid saturated aliphatic hydrocarboxylic acids of high molecular weight, as a separate entity, and homogeneously disperse such lead salts either in and through a body of the aforesaid free acid-containing oxidation reaction mixture or, preferably, in and through the neutral or relatively neutral residue obtained by removing all or the larger part of the free acids from the oxidation reaction mixture. The removal of the free acids content from oxidation reaction mixtures, as a process forms no part of the present invention; U. S. Patent No. 2,012,252 to Arthur W. Burwell discloses one operable method therefor.

In carrying out this latter embodiment of the invention I may admix about 10 parts by weight of litharge (or other operable lead compound) with from about 70 to about 90 parts by weight of the aforesaid isolated but mixed free acids of mineral origin and heat the mixture for some hours at a temperature of from about 100° to about 150° C. (preferably, at about 150° C.), through which measure all of the litharge is reacted with the acids yielding a reaction mixture containing lead salts (soaps) of the various acids. A unit amount by weight of this lead salts-containing mixture is then homogeneously dispersed (dissolved) in from about 19 to about 9 parts by weight of the product produced by contacting air under superatmospheric pressure with molten scale wax (crude paraffin) maintained at an operative elevated temperature in the presence of a suitable oxidation catalyst (or, in the presence of a suitable amount of unsaponifiable, "ketonic" partial oxidation products from a previous charge) and thereafter separating out and removing the free acids content of the oxidation reaction mixture. The resulting composition, like the composition described hereinbefore under the first embodiment, can be spread as a film over the metal surface to be protected either as such (in molten state) or as a solution in an appropriate solvent.

It is within the scope of my invention to substitute for all or part of one of the more readily volatile organic solvents above specifically mentioned a less volatile or non-volatile organic liquid such, for instance, as tung oil, linseed

oil, paraffine oil, rosin oil or the like. Also, it is within the scope of the invention to incorporate into the compositions other film-modifying agents; e. g., a finely divided metal oxide.

Any one of the aforesaid lead salts-containing compositions may, for particular applications, be altered by the introduction therinto of a synthetic resin compatible with the other constituents of the compositions. According to this further embodiment, I may incorporate 1 part by weight of resinous phenol-formaldehyde condensation products, cumaron resins, phthalic acid resins, phenolic resins modified by ester gums and other modifying agents (or equivalent compatible synthetic resin) in from about 1 to about 2 parts by weight of any one of the compositions described above. The resulting resin-containing compositions yield films which are somewhat harder and more resistant to abrasion, less tacky, etc., also present greater impedance to moisture, corrosive gases and liquids, than the films yielded by the compositions not containing the synthetic resin.

I claim:

1. A film-forming protective composition adapted for use as an anti-corrosion material on surfaces of corrodible metals, consisting essentially of a mixture of neutral unsaponifiable oxidized mineral hydrocarbons including saturated aliphatic alcohols, saturated aliphatic

ketones, saturated aliphatic keto-alcohols, and neutral esters and lactones of high molecular weight saturated aliphatic carboxylic acids, said oxidized mineral hydrocarbons being produced by controlled, liquid-phase, partial oxidation of a mixture of saturated mineral hydrocarbons, said mixture containing dispersed therein a lead salt of a relatively high molecular weight saturated aliphatic carboxylic acid of mineral origin, said acid having an end methyl group.

2. A film-forming protective composition, as defined in claim 1, characterized in that it contains a compatible oily solvent for the mixed oxidized mineral hydrocarbons in an amount sufficient to render the composition fluid.

3. A film-forming protective composition, as defined in claim 1, characterized therein that the composition contains, dispersed therein, a synthetic resin compatible with the other ingredients of the composition.

4. A film-forming protective composition, as defined in claim 1, characterized in that the composition contains, dispersed therein, a synthetic resin compatible with the other ingredients of the composition, and in that it contains a compatible oily solvent for the mixed oxidized mineral hydrocarbons and for the synthetic resins in an amount sufficient to render the composition fluid.

JAMES E. SHIELDS.