

UNITED STATES PATENT OFFICE

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COMPOSITION FOR USE IN PREVENTION OF
CORROSION OF METAL SURFACES

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This invention relates to methods for the protection of corrodible metal surfaces against corrosion, and is concerned more particularly with film-forming coating compositions, adapted for use as protectives of metal surfaces, consisting essentially of partially oxidized hydrocarbons derived from petroleum, shale oil, or like "mineral" hydrocarbonaceous starting materials such as tar oils from the low temperature coking of coal, lignite, etc.

I have found that the rusting of exposed surfaces of iron and steel articles may for a longer period be prevented by application thereto, by spraying, painting, pouring, immersing, or the like, of films of certain partially oxidized petroleum hydrocarbon products (hereinafter more specifically described), either used alone or combined with other ingredients into protective film-forming compositions. The said partially oxidized petroleum hydrocarbon products may be applied in molten form to the metal surfaces (in case the compounds or compositions selected are, at normal room temperature, semi-solid to solid in consistency), or they may be applied in the form of a solution in an appropriate solvent, preferably a substantially anhydrous organic solvent, therefor.

Films of the partially oxidized petroleum hydrocarbon products are, in general, very thin, particularly when applied in solution form and the solvent thereafter evaporated, but they are continuous and uniquely tenaciously adherent to metal (e. g., bright metal) surfaces, and penetration of corrosive agents (e. g., water, water vapor, acid vapors, vapors of caustic alkalis, dusts, etc.) is long delayed thereby. However, where heavier, more solid, or mechanically stronger protective films are desired, I may and frequently do associate with the partially oxidized petroleum hydrocarbon products one or more thickening, solidifying or strengthening agents, such, for instance, as rosin, rosin oil, drying oils, waxes, etc., and pigments or inorganic materials or other organic film-forming substances which are both (1) miscible in or with the aforesaid petroleum products and the solvents, if any, employed therewith and (2) substantially chemically inert to the metal. Thereby I enhance the protective qualities of my anti-corrosion agents against the hazards of rough handling of the articles protected therewith.

The aforesaid films have been exhaustively tested by me and by a governmental agency, and have been found to be efficacious in the protection of iron and steel surfaces against moisture,

moist air containing halogen acids, salt spray solutions, nitric acid, aqueous nitric acid, mixtures of nitric and hydrochloric acids, chlorine, caustic soda in flake or powder form, rain, snow, sleet, cold and sunshine. Exposures of metal, e. g., iron and steel, surfaces, so protected, for periods of over two weeks, to aqueous nitric acid have had no effect on the films and no corrosive effect on the metal surfaces. Likewise, the films have been found to be impenetrable by alternate sprays of caustic and carbonate dust with intermediate washing with water. Salts dried on such films have been found to have no effect in penetrating the same to cause corrosion of the underlying metal. Sheet iron drums exposed in the neighborhood of escaping gaseous chlorine, salts sprays containing high percentages of caustic soda, caustic soda dust from caustic melting pots, sleet, snow, sunshine—all combined—have had no effect upon the films, the drums remaining exactly of the same appearance as when exposed. Nine months of such exposure produced no change in the surface.

The base of my anti-corrosion compositions is a mixture of partial oxidation products produced by the liquid-phase, controlled, partial oxidation of a mixture of petroleum hydrocarbons, e. g., ceresin wax, paraffin wax, rod wax, scale wax, amorphous (i. e., "Sharples") wax and higher boiling petroleum distillates (e. g., 36-40 fuel oil) all of which are, per se, mixtures, or mixtures of two or more thereof, the oxidation being effected by blowing air or other oxygen-containing gas (e. g., oxygen-enriched air) through a liquid body of the petroleum hydrocarbon mixture maintained at a temperature above at least 100° C. and not greater than about 185° C. and at a superatmospheric pressure of from 150 pounds to 350 pounds per square inch, the oxidation being continued for a period of, say, nine hours, and preferably until incipient formation of bodies insoluble in petroleum hydrocarbons and in the reaction mixture sets in. The process above described is that disclosed in Patent Nos. 1,690,768 and 1,690,769, granted to Arthur W. Burwell. The resulting reaction product 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 saturated aliphatic carboxylic and hydroxycarboxylic acids; 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.

Any and all of the aforesaid oxidized petroleum hydrocarbon products, I have found, have to some extent the property of arresting the corrosion of iron and steel surfaces. However, I prefer to select as the base of the anti-corrosion composition one or more of the neutral types of oxidized products, i. e., the neutral, unsaponifiable, alcoholic, ketonic and/or keto alcoholic compounds, because they do not offer the possibility of soap decomposition and, moreover, because they in general yield tougher, harder anti-corrosion films than do the acids or salts and esters of those acids. In this connection I note that I prefer to employ in the present relation the unsaponifiable partial oxidation products obtained from ceresin or from higher melting point petrolatums, since these yield tougher films, which films apparently undergo a progressive toughening apparently akin to the toughening of films of drying oils. Thus, I have found to be particularly advantageous the unsaponifiable neutral bodies separated from the reaction product obtained by oxidizing (in the manner above described) a mixture of amorphous wax and paraffin wax.

As stated above, these neutral mixtures 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. In lieu thereof I may employ a solution of the neutral mixture in an appropriate organic solvent, e. g., a light petroleum distillate such as gasoline or the special petroleum distillate known as Stoddard solvent. Thus, I may use a composition comprising 40%, more or less, of the aforesaid neutral bodies and 60%, less or more, of Stoddard solvent or equivalent.

For greater protection against acids (e. g., acid mists), I may and preferably do incorporate with the unsaponifiable compounds, or in their solutions or compositions, an amine such as an ethanol amine (e. g., triethanol amine) or other more or less volatile amine. Where amines are added, I prefer to use them in the ratio of the equivalent of 1 part by weight of triethanol amine to from 20 to 1,000 parts by weight of the aforesaid neutral bodies. This latter mixture may, advantageously, be used in the upper cylinder parts of automotive engines, particularly airplane engines which have been run with gasoline containing tetraethyl lead mixtures, which mixtures almost always contain halogen organic compounds. These compounds burn in the explosion chamber forming halogen acids which penetrate the metal parts and cause serious corrosion upon access of moisture or after the lapse of considerable time, especially under conditions of higher temperature together with moisture. These halogen acids being in the metal must be neutralized by means of some soluble alkali or soaps of alkali metals soluble in the materials forming the film. In this connection, it is possible to dissolve either sodium or potassium soaps of the aforesaid acids in the alcoholic ketonic bodies described, the whole being then melted and painted upon the surfaces or dissolved in

suitable solvents and sprayed upon the surfaces or otherwise applied.

The invention will be described with greater particularity with reference to the following further illustrative examples of compositions coming within the concept of this invention:

Example I

	Parts by weight
The aforesaid neutral unsaponifiable bodies from paraffin wax	20-35
Rosin	20-5
Stoddard solvent	60

Example II

	Parts by weight
The aforesaid neutral unsaponifiable bodies from paraffin wax	5-20
Tung oil	95-80

The above may be used warm, or diluted with a suitable quantity of thinner or solvent.

Example III

	Parts by weight
The aforesaid neutral unsaponifiable bodies from a mixture of paraffin and amorphous waxes	5-25
Rosin (or rosin hardened with lime)	15-5
Linseed oil, to make	100

This may be applied in undiluted state, or may have thinner added.

Example IV

	Parts by weight
The aforesaid neutral unsaponifiable bodies from a mixture of paraffin and amorphous waxes	5-35
Triethanolamine	0.5-5.0
Rosin oil	20-10
Stoddard solvent, to make	100

Example V

	Parts by weight
The aforesaid neutral unsaponifiable bodies from road wax	5-20
Tung oil	95-80

This composition, which gives an especially tough film, may be applied, as such, in warm state, or admixed with a suitable volatile solvent.

Example VI

	Parts by weight
The aforesaid neutral unsaponifiable bodies from "Sharples" wax	5-40
Finely divided iron oxide	10-5
Linseed oil, to make	100

Instead of the iron oxide of the above example I may use a substantial amount of another pigment such, for instance, as lead carbonate, zinc oxide, lithopone, or the like. Instead of the linseed oil, I may employ another drying oil, e. g., tung oil.

Example VII

	Parts by weight
The aforesaid neutral unsaponifiable bodies from ceresin wax	3-30
Triethanolamine	0.5-5.0
Dichlor diethyl ether, to make	100

It is to be understood that in place of the dichlor diethyl ether another suitable volatile solvent may be used.

I claim:

1. Film-forming protective composition adapted for use on metal surfaces, consisting essentially

of an oily solution of a mixture of neutral unsaponifiable oxidized petroleum hydrocarbons obtained by the liquid-phase partial oxidation of a mixture of petroleum hydrocarbons, said mixture of neutral unsaponifiable compounds consisting essentially of aliphatic alcohols, aliphatic ketones, aliphatic keto-alcohols and neutral esters and lactones of high molecular weight saturated aliphatic carboxylic acids, said composition being substantially anhydrous and inert to metal.

2. Film-forming protective composition as defined in claim 1, characterized in that the mixture of neutral unsaponifiable oxidized petroleum hydrocarbons is dissolved in a relatively volatile organic solvent therefor.

3. Film-forming protective composition as defined in claim 1, characterized in that a film-forming thickening agent is admixed therein.

4. Film-forming protective composition as defined in claim 1, characterized in that an amine is admixed therein.

5. Film-forming protective composition adapted for use on metal surfaces, being an oily solution of a mixture of neutral unsaponifiable saturated oxidized hydrocarbons obtained by the liquid-phase partial oxidation of a hydrocarbon mixture of the group consisting of petroleum wax, petroleum distillate, shale oil, shale wax, and tar oils from the low-temperature distillation of coals, said mixture of neutral unsaponifiable compounds consisting essentially of aliphatic alcohols, aliphatic ketones, aliphatic keto-alcohols and neutral esters and lactones of high molecular weight saturated aliphatic carboxylic acids.

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