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RUST INHIBITING COMPOSITION

Knapel F. Schiermeier, Alton, and Paul W. Jones, East Alton, Ill., assignors to Shell Development Company, San Francisco, Calif., a corporation of Delaware

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This invention relates to an all-purpose corrosion inhibiting composition. More particularly, this invention pertains to corrosion inhibiting compositions having the ability of forming on metal surfaces a tenacious protective film, which is impervious to moisture and other contaminants.

It is well known that moisture, corrosive fluids and gases, e. g. H_2S, SO_2, etc. readily attack not only metallic surfaces but non-metallic surfaces and cause corrosion, rusting, pitting and other damage to such surfaces. Also aqueous solutions when in contact with a metallic surface readily attack it and cause corrosion and rusting. Under certain conditions the problem of corrosion becomes exceedingly serious because once started it becomes progressively accelerated. Thus, oils containing small amounts of water become very corrosive to contacting metals. This is due to the fact that oils and particularly liquid petroleum hydrocarbons are relatively good solubilizers of oxygen and any moisture present therein becomes surrounded by an almost inexhaustible store of oxygen. Moisture under such conditions is inhibited from evaporating and since the rate of transfer of oxygen from hydrocarbons, such as mineral oil or gasoline, to water is limited, ideal conditions for rusting and corrosion are set up. The presence of electrolytes and formation of corrosive decomposition products in oils and the like also greatly increase the rate of corrosivity.

Countless materials and compositions have been tried for protecting surfaces by forming on said surfaces a non-reactive corrosion protective film. Metal surfaces have been coated or treated with greases, fatty compositions, waxes, organic compounds, e. g. organic acids, amines, inorganic compounds and the like in order to protect them against corrosion. In almost all cases where no chemical reaction occurs between the surface treated and the corrosion or rust inhibitor very little benefit was derived. This is due to the fact that non-chemical reactive inhibitors are incapable of penetrating the surface being protected and are incapable of displacing the contaminant therefrom. In cases where such inhibitors are able to form protective coatings on surfaces they are easily displaced by moisture or rupture readily. They are relatively ineffective against corrosive acidic materials and gases such as are formed during operation of combustion and turbine engines and are easily destroyed when applied to surfaces which are subjected to high temperatures.

It has now been discovered that various metallic surfaces can be protected against corrosion by coating said surfaces with a composition comprising a major amount of a mixture, in substantially equal portions, of a light hydrocarbon liquid having a boiling point below about 650° F., e. g. an aromatic solvent and an oxidized waxy hydrocarbon, said mixture having incorporated therein a minor amount, generally not exceeding 5% and preferably less than 1%, of an organic acid.

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The preferred liquid hydrocarbon suitable for use in compositions of this invention are aromatic solvents which may be obtained by any suitable means such as the treatment of petroleum products with various selective solvents or mixtures of solvents which are adapted to segregate the relatively more aromatic constituents from the non-aromatic constituents. Suitable solvents may be represented by sulfur dioxide, phenol, furfural, nitro-benzene, cresol, aniline, beta,beta dichloro-diethyl ether and the like. Hydrocarbons which are particularly suitable for treatment with the above type of solvents are petroleum hydrocarbons having a boiling range of from about 300° F. to about 600° F. and may be specifically represented by kerosene, gas oil, light hydrocarbon oil fractions and the like. Particularly preferred are aromatic solvents obtained by the sulfur dioxide treatment of a 300° F. to 370° F. petroleum hydrocarbon cut according to the well-known Edeleanu process. Characteristics of aromatic solvents obtained by subjecting light petroleum distillate to the Edeleanu process are given below:

Gravity °API at 60° F	35.3–35.2
Spec. gravity 60/60° F	0.8438–0.8483
Flash tag cc. °F	119–112
Aniline pt., °F. ASTM	9.0–31
Aromatics, ASTM percent v.	58–68
Alkyl phenols (SMS .246)	11–15
Aromatic free residue, tool	32–42
Naphthenes, mol percent, Maltiello	61–63
Paraffins	37–39

Aromatic solvents suitable for use as a component of compositions of this invention may be obtained by other means than solvent extraction of petroleum distillates. Thus aromatic solvents may be obtained from catalytic conversion of petroleum hydrocarbons such as obtained from recycle stocks from catalytic cracking. Also aromatics such as napththalene, fluorene, phenanthrene anthracene, coal tar residues and the like may be admixed in small amounts with aromatic solvents of the type described above.

The aromatic solvents should comprise at least

about 40% of the composition. If desired, part of the aromatic solvent may be replaced with a light liquid hydrocarbon fraction and/or fractions provided the aromatic solvent constitutes a major proportion of the blend and the light liquid hydrocarbon constitutes a minor proportion of the blend. Generally, the aromatic solvent comprises at least two-thirds of the mixture when blended with a light hydrocarbon. Preferably, the aromatic solvent is used as the sole carrier, or diluent for additives of this invention.

The light liquid hydrocarbon fractions which may be blended with aromatic solvents may be obtained from any type of petroleum base such as paraffinic, naphthenic, asphaltic and/or their fractions. The fractions desired are those normally liquid fractions which have a boiling point range below that of lubricating oil. Specific liquid hydrocarbons which may be obtained from petroleum distillate by any suitable means include kerosene, mineral seal oil, mineral spirits, light spindle oil, light spray oils, petroleum solvent naphtha as well as various other petroleum naphtha cuts, petroleum ethers, octane, isooctane, dodecane; cycloparaffins, e. g., cyclohexane, methylcyclohexane, etc.

The oxidized substantially non-aromatic waxy hydrocarbons may be obtained from hydrocarbon in the manner fully described hereinbelow. Waxy hydrocarbons also may be obtained by polymerization of olefinic materials by the Fischer-Tropsch process or by dehydration of long-chain aliphatic alcohols and oxidizing said materials.

Waxy hydrocarbons may be recovered from suitable petroleum fractions such as Pennsylvania crude, East Texas crudes, Mid-Continent crudes, and the like, by de-asphaltizing the hydrocarbon and thereafter removing the wax from the asphalt-free hydrocarbon fraction by any known suitable means. The asphalt may be separated from the oil either by distillation or solvent extraction and used as a component of composition of this invention. In the solvent process a solvent is selected in which the oil is relatively soluble but in which the asphaltic materials are relatively insoluble. Among such solvents are the light liquid hydrocarbons such as ethane, propane, butane, as well as naphtha and gasoline. Oils treated with such solvents extract the oil and wax leaving behind the asphaltic materials as residue which can be utilized as a component of composition of this invention. The wax-oil mixture may be removed from the asphalt-free solution by chilling the solution, and then separating the precipitated wax by settling, filtering or centrifuging. Waxy materials thus produced are known in the art as slop waxes, petrolatum stock, slack waxes, scale waxes, paraffin waxes, malcrystalline and needle waxes, micro-crystalline waxes and the like. These waxes are differentiated from each other by the degree of de-oiling to which they are subjected and all of them may be used provided they are substantially free from aromatics.

De-waxing or separation of the above waxy constituents from the oil may be accomplished by selective solvent treatment using as the diluents liquefied normally gaseous hydrocarbons such as propane, butane, and other corresponding olefins and/or their mixtures as well as oxygen-containing liquid organic substances such as alcohols, ethers, esters, ketones, aldehydes, acids and/or their mixtures. These may include methyl, ethyl, propyl, butyl, amyl alcohols, methyl or methylethyl ether, acetones, diethyl, dimethyl and methylisobutyl ketones and the like. Chlorinated hydrocarbons such as carbon tetrachloride or trichloroethylene and mixtures of chlorinated hydrocarbons as mentioned above also may be used.

The first step in obtaining waxy constituents from petroleum crudes, for example, such as Mid-Continent crude, is to treat said crude with about six volumes of liquid propane so as to remove the asphalt. The propane from the propane-oil solution is vaporized so that the ratio of propane to oil is reduced approximately 2 to 1. The solution is then chilled to about —40° F. and lower, causing separation of the wax from the oil. The wax can be removed by filtration and the propane separated from the de-asphalted and dewaxed oil and waxy material by distillation.

Waxy materials can also be recovered from the distillate or residuum lube oil fractions and these wax fractions can be split still further into special wax cuts having desired characteristics by use of selective solvents. This is based on a difference in solubility of different waxy fractions in a given solvent. Thus, when using a methylethyl ketone type solvent the aromatic constituents can be removed by successively cooling the mixture down to between about —40° F. and 76° F. so as to remove the aromatics which become substantially soluble in the solvent as the temperature is lowered, while the straight-chain waxes and isoparaffins become substantially insoluble in the solvent. The straight-chain waxes can be separated from the isoparaffins by extraction and fractional crystallization. Depending upon the distillate cut used waxes of from 12 to above 36 carbon atoms and higher can be obtained.

The above type of waxy hydrocarbons may be admixed with synthetic waxes produced by polymerization of olefins under pressure or by dehydrating long-chain fatty alcohols such as octadecyl alcohol and the like. Admixed with non-aromatic waxy hydrocarbon may be minor amounts of waxy materials obtained from non-hydrocarbon services such as marine or animal waxes, vegetable waxes and the like, and specifically may be illustrated by spermaceti, Japan wax, carnauba wax, montan wax, sugar cane wax, cotton wax, etc. and the mixture oxidized.

Instead of subjecting the above liquid hydrocarbons to a dewaxing and solvent extraction process in order to obtain the above disclosed waxy hydrocarbons, residual oils containing the desired waxy constituents after removal of the distillates can also be used. These residual fractions need not be subjected to solvent extraction or dewaxing but must be oxidized in the manner proposed in the succeeding paragraph.

The waxy material and its mixtures may be oxidized by any suitable means such as blowing with an oxidizing gas such as air, air enriched with oxygen, pure oxygen, oxygen diluted with inert gas and the like. Substantially the waxy material may be oxidized by such means as are disclosed in the following U. S. patents: 1,863,004, 2,043,923, 2,156,226, 2,186,910, and 2,216,222. If desired minor amounts not exceeding about one-third, and preferably less, of non-oxidized waxy materials may be admixed with the oxidized products.

The amount of oxidized material used in compositions of this invention is substantially the same as the aromatic solvent used and may vary from 40% to 60%.

The organic acids which are blended into the above mixture can be selected from the group consisting of higher molecular weight fatty acids, polycarboxylic acids, fatty acids containing a functional group, e. g. hydroxy, keto and amino fatty acids and aromatic acids containing at least one functional group other than the carboxylic acid radical. Mixtures of such acids can also be used. The above organic acids may be exemplified by:

A. FATTY ACIDS

Capric, undecylic, lauric, myristic palmitic, stearic, arachidic, lignoceric, montanic, melistic, oleic, linolic, erucic, linolenic, brassidic, stearolic acids, etc.

B. FATTY ACIDS DERIVED FROM

Castor oil, cashew nut oil, coconut oil, palm oil, corn oil, cottonseed oil, rapeseed oil, soya bean oil, codfish oil, herring oil, menhaden oil, sardine oil, seal oil, whale oil, etc.

C. SUBSTITUTED FATTY ACIDS

I. *Hydroxy aliphatic carboxylic acids*

Dimethyl hydroxy caprylic, dimethyl hydroxy capric ricinoleic, ricinelaidic, 12-hydroxy stearic 1,10 dihydroxy stearic acid, 4-hydroxy palmitic acid, linusic, sativic, lanoceric, dihydroxy behenic acids, etc. The preferred hydroxy fatty acids are those in which the hydroxy group is at least 12 carbon atoms removed from the carboxyl group.

II. *Keto acids*

Licanic, 12-keto stearic, 13-keto behenic, jojoba oil fatty acids, etc.

III. *Miscellaneous acids*

Acids produced by oxidation of hydrocarbons, e. g., paraffin wax, mercapto, oleic acid, mercapto stearic acid, amino fatty acids, etc.

D. ALKYLATED POLYCARBOXYLIC ACIDS

Succinic, glutaric, adipic, pimelic, suberic, azelaic, tricarballytic, etc. acids. The alkyl radical should contain 12 or more carbon atoms.

E. AROMATIC ACIDS

Alkylated phthalic, alkylated salicylic, hydroxy naphthoic, anthranilic, hydroxy substituted aromatic fatty acids, etc. The alkyl radical should contain 12 or more carbon atoms.

The acids may be used in amounts not exceeding 5% and preferably are used in amounts ranging from 0.25 to 1% by weight.

A general formula of compositions of this invention may be represented as follows:

Essential additives:	Per cent by weight
Organic acid and mixtures thereof	0.25–5
Oxidized waxy hydrocarbon	40–60
Optional additives, e. g., amines, inorganic nitrates, sulfonates, etc.	0–1
Base aromatic solvent and/or mixture of aromatic solvent and a light liquid hydrocarbon	Balance

Specific examples of preferred compositions of this invention are:

Composition A:	Per cent by weight
Oxidized W. Texas Ellenberger short residue (208° FSP)	47.4
Mineral spirits	52.1
Oleic acid	0.5

Composition B:	
Oxidized W. Texas Ellenberger short residue (260–270° FSP)	45.5
Aromatic solvent	54.0
Oleic acid	0.5

Other composition of this invention can be exemplified by the following formulations in which each component must be within the critical range set forth above:

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Essential Additives:																		
Oxidized short residue petrolatum	x			x			x		x		x		x		x			
Oxidized slop wax		x														x		x
Oxidized paraffin wax					x									x				
Oxidized microcrystalline wax			x							x								
Oxidized slack wax						x												
Mixture of oxidized short residue petrolatum and short residue petrolatum								x				x					x	
Aromatic solvent	x			x		x	x		x		x				x	x		
Mineral spirit		x											x					
Blend of aromatic solvent and kerosene					x							x					x	
Blend of aromatic solvent and petroleum naphtha			x					x		x				x				x
Oleic acid					x	x					x		x		x			
Castor oil fatty acids				x					x							x		
Hydrogenated fish oil fatty acids										x								x
Stearic acid	x													x				
Alkyl succinic acid							x										x	
Alkyl salicylic acid								x				x						
Optional Additives:																		
Petroleum sulfonates											x							
Octadecyl amine														x				
Lithium nitrite																x		
Dicyclohexylamine nitrite													x		x		x	

Compositions of this invention may be prepared in a simple manner by heating the components comprising said composition for from 5 to 10 hours at a temperature varying from 250° F. to 350° F. under agitation and preferably in an enclosed vessel. The product is then allowed to cool and may be reheated to about 150–200° F. for a short period of time if desired in order to obtain a more homogeneous and stable product.

In order to determine the protective properties which compositions of this invention possess, metal strips were coated with compositions of this invention and subjected to the following tests.

SALT SPRAY TEST

In this test polished steel panels which have been coated with a desired product to be evalu-

ated are exposed continuously at a constant temperature (95° or 100° F.) to a salt mist or fog which is produced by the atomization of a 20% sodium chloride solution. The average time until rusting occurs on the faces of the panels is taken as the life of the coating.

ULTRAVIOLET WEATHERING UNIT TEST

In this test polished or sandblasted steel panels which have been coated with a desired product to be evaluated are continuously exposed to intense light from a carbon arc and are intermittently wetted by a fine water spray. The average time until rusting occurs on the faces of the panels is taken as the life of the coating.

TEST RESULTS

Composition	Test	Results
Composition B	Salt Spray 20%, 10 days	No rust.
Composition X [1]		Rust.
Composition B	Ultraviolet Weathering Unit Test, 25 days.	No Rust.
Composition X		Rust.

[1] Composition X consists of equal parts of oxidized wax and aromatic solvent.

Compositions of this invention may be modified by addition thereto of organic salts, e. g. sulfonates, salicylates, oleates, stearates, sulfated oils, salts of inorganic acids, e. g. metal phosphates, nitrites, chromates, organic esters, e. g. dilauryl phosphate, phosphites, etc.

Compositions of this invention may, if desired, be very easily removed by flushing, wiping or any other suitable means. Compositions of this invention may also be applied to non-metallic surfaces which require protection against corrosion, moisture, the elements and the like.

Many modifications and variations of this invention as hereinbefore set forth may be made without departing from the spirit and scope thereof and, therefore, only such limitation should be imposed as indicated in the appended claims.

We claim as our invention:

1. A rust-inhibiting composition of matter consisting essentially of the following constituents in the following proportions:

	Per cent by weight
Oxidized short residue petroleum wax	45.5
Aromatic solvent	54.0
Oleic acid	0.5

2. A rust-inhibiting composition of matter consisting essentially of the following constituents in the following proportions:

	Per cent by weight
Oxidized short residue petroleum wax	47.4
Mineral spirit	52.1
Oleic acid	0.5

3. A rust-inhibiting composition of matter consisting essentially of the following constituents in the following proportions:

	Per cent by weight
Oxidized wax hydrocarbon	40–60
Higher aliphatic carboxylic acid containing at least 10 carbon atoms per molecule	0.25–5
Light liquid petroleum stock boiling below 650° F	Balance

4. A composition of matter adapted for use as a rust inhibitor consisting essentially of a blend of equal parts by weight of an oxidized short residue petroleum wax and an aromatic solvent, said blend having incorporated therein from about 0.25% to about 5% by weight of oleic acid.

5. A composition of matter adapted for use as a rust inhibitor consisting essentially of a blend of equal parts by weight of an oxidized short residue petroleum wax and mineral spirits, said blend having incorporated therein from about 0.25% to about 5% by weight of oleic acid.

6. A composition of matter adapted for use as a rust inhibitor consisting essentially of a blend of about equal parts by weight of an oxidized short residue petroleum wax and a light liquid petroleum stock boiling below 650° F., said blend having incorporated therein from about 0.25% to about 5% by weight of a higher aliphatic carboxylic acid having at least 10 carbon atoms.

7. A composition of matter adapted for use as a rust inhibitor consisting essentially of a blend of about equal parts by weight of an oxidized wax hydrocarbon and a light liquid petroleum stock boiling below 650° F., said blend having incorporated therein from about 0.25% to about 5% by weight of an alkyl succinic acid, said alkyl radical having at least 12 carbon atoms.

8. A composition of matter adapted for use as a rust inhibitor consisting essentially of a blend of equal parts by weight of an oxidized wax hydrocarbon and a light liquid petroleum stock boiling below 650° F., said blend having incorporated therein from about 0.25% to about 5% by weight of an alkyl substituted polycarboxylic acid said alkyl substituent containing at least 12 carbon atoms.

9. A composition of matter adapted for use as a rust inhibitor consisting essentially of a blend of equal parts by weight of an oxidized petroleum slop wax and a light liquid petroleum stock boiling below 650° F., said blend having incorporated therein from about 0.25% to about 5% by weight of a soluble higher aliphatic carboxylic acid containing at least 10 carbon atoms per molecule.

10. A composition of matter adapted for use as a rust inhibitor consisting essentially of a blend of equal parts by weight of an oxidized paraffin wax and a light liquid petroleum stock boiling below 650° F., said blend having incorporated therein from about 0.25% to about 5% by weight of a soluble higher aliphatic carboxylic acid containing at least 10 carbon atoms per molecule.

11. A composition of matter adapted for use as a rust inhibitor consisting essentially of a blend of about equal parts by weight of an oxidized short residue petroleum wax and aromatic solvent, said blend having incorporated therein from about 0.25% to about 5% by weight of an alkyl succinic acid, said alkyl radical having at least 12 carbon atoms.

12. A rust-inhibiting composition of matter consisting essentially of the following constituents in the following proportions:

	Percent by weight
Oxidized wax hydrocarbon	40–60
Higher fatty acid, having at least 10 carbon atoms per molecule	0.25–5
Light liquid petroleum stock boiling below 650° F.	Balance

13. A rust-inhibiting composition of matter

consisting essentially of the following constituents in the following proportions:

	Percent by weight
Oxidized wax hydrocarbon	40–60
Higher unsaturated fatty acid, having 18 carbon atoms per molecule	0.25–5
Light liquid petroleum stock boiling below 650° F.	Balance

14. A rust-inhibiting composition of matter consisting essentially of the following constituents in the following proportions:

	Percent by weight
Oxidized short residue petrolatum	40–60
Higher aliphatic carboxylic acid, having at least 10 carbon atoms per molecule	0.25–5
Light liquid petroleum stock boiling below 650° F.	Balance

KNAPEL F. SCHIERMEIER.
PAUL W. JONES.

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