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FINGERPRINT CORROSION INHIBITING COMPOSITIONS

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This invention relates to compositions, and more particularly pertains to rust-preventive compositions adaptable as water displacers, cleansing agents and rust inhibitors or preventives in finger print type of corrosion.

It is an object of our invention to provide improved compositions for combating and/or preventing corrosion of metals. Another object of our invention is to provide clear and stable compositions especially adapted to displace water in combating corrosion of metals. Still another object of our invention is to provide compositions for protecting metal surfaces against fingerprint-type of corrosion. A further object of our invention is to provide clear and stable compositions especially suited for displacing water, and possessing excellent properties for combating and/or inhibiting corrosion of metals, particularly fingerprint-type of corrosion. Other objects and advantages of our invention will be apparent during the following description and explanation thereof.

Fingerprint corrosion is apparently caused by acids and salts present in human perspiration, and these corrosive substances adhere to the surfaces of metals when transferred thereon during handling or manual operations. Heretofore extensive developments have been undertaken to combat and/or prevent this type of corrosion, but for reasons not too clearly understood in the art, the problem does persist. In analyzing the problem, generally, we have observed that corrosion inhibiting compositions should be able to: (1) readily displace water; (2) remove substantially all adherent corrosive substances; and (3) suppress or inhibit further corrosive influences. An especially important function of corrosion inhibiting compositions is to be able to displace water when present on the surface of metals, otherwise the efficacy of the composition is seriously hindered.

In accomplishing the objects of our invention, compositions having approximately the following component proportions are found particularly effective:

	Parts by volume	
Hydrocarbon solvent	per cent.	75
Water-soluble oxygenated organic solvent		
	per cent.	11
Preferentially oil-soluble detergent	do.	9
Water	do.	4.5
Coupling agent	do.	0.5

The hydrocarbon solvent should boil chiefly in the range of between about 100° and 650° F. at

atmospheric pressure, and may be employed in amounts in the range of 5 and 85%, preferably 30 and 80%. The water soluble oxygenated organic solvent should boil below about 180° F. and may be an aliphatic alcohol or an aliphatic ketone, the amount employed being in the range of between about 1 and 20%, preferably 5 and 15%. The oil-soluble detergent may be a high molecular weight petroleum sulphonate or synthetic alkylaryl sulphonate preferably prepared with an alkaline earth metal and may be used in amounts in the range of between about 1 and 30%, preferably 3 and 15%. The amount of water may be in the range of between about 1 and 10%, preferably 2 and 6%. The coupling agent is preferably a water solubilized sulphonated vegetable or animal oil and may be used in amounts in the range of between about 0.1 and 5.0%, preferably 0.1 and 2%.

For the purposes of our invention, preferentially oil-soluble detergents serve as anti-rust agents, and also have desirable properties suited for obtaining clear and stable compositions when in admixture with other components of our compositions. Of these preferentially oil-soluble detergents various soaps may be used including synthetic alkyl-aryl sulphonates having at least about eighteen carbon atoms to the molecule and the preferentially oil-soluble soaps of petroleum sulfonic acids. These synthetic alkylaryl sulphonates and petroleum sulfonates may be prepared from metals in groups I and II of the periodic system, or of ammonia and ammonia derivatives, such as amines. While we may use soaps of the aforementioned types, particularly good results are obtained by employing preferentially oil-soluble soaps of petroleum sulfonic acids, commonly referred to as mahogany soaps, of the alkaline earth metals.

The preferentially oil-soluble mahogany soaps of the alkaline earth metals are produced by treating petroleum distillates of between about 50 and 1000 seconds or higher Saybolt Universal viscosity at 100° F. and preferably between about 80 and 300 seconds SSU at 100° F. with between about 3 and 9 pounds, and preferably between about 3 and 6 pounds of concentrated sulfuric acid, preferably fuming sulfuric acid, per gallon of oil. The calcium soaps of preferentially oil-soluble mahogany acids are preferred, and the preparation thereof is illustrated by the following example.

A Mid-Continent petroleum distillate having a Saybolt Universal viscosity at 100° F. of between about 220-230 seconds is treated with 6 pounds

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of fuming sulphuric acid per gallon of oil in one-half pound dumps. After the separation of the acid sludge, the acid-treated oil is treated with a suitable alcohol, for example, ethanol, of about 60% strength, to remove crude petroleum sulphonic acid. The alcoholic layer containing the crude sulphonic acid is then treated with lime slurry to neutralize the petroleum sulphonic acid. The mixture is allowed to settle, the alcoholic layer containing the calcium mahogany soap is drawn off, and then passed to a distillation column wherein the alcohol is recovered. The resultant calcium mahogany soap is usually a 70-80% concentration in unreacted oil. To facilitate handling of the soap, it is preferred to further dilute the soap with a paraffinic oil having a viscosity of between about 80 and 85 seconds, SSU at 100° F., to a concentration of about 37%. The molecular weight of the sulfonate soap may lie in the range of 410 to 450 or about 430.

The coupling or wetting agent of the present invention is selected from a variety of compounds, including various sulfonated fish or animal oils, vegetable oils, fats and waxes, and preferably selected from sulfonated castor compounds rendered water-soluble by being partially or wholly neutralized with a caustic solution, for example sodium and potassium, or ammonium hydroxide. In practicing our invention, excellent results are obtained by employing a water-soluble sulfonated castor oil material. Generally this material is prepared by adding to a sulfonated castor oil, sufficient caustic solution to neutralize any residual or unreacted sulfuric acid and wholly or partially neutralizing the sulfonated fatty acid content until the material thus formed dissolves in water to the extent desired.

The hydrocarbon solvent found applicable for the purposes herein is preferably a petroleum fraction. For example, in our invention we may use hydrocarbon solvents such as petroleum ether, gasoline, naphthas and kerosenes. Of these petroleum fractions, it is preferred to employ a solvent boiling in the gasoline-kerosene boiling range. Particularly good results are obtained when employing a so-called heavy naphtha boiling in the range of between about 300° and 400° F. at atmospheric pressure, such as for example Stoddard's solvent.

In order to prepare, bright and stable compositions, and yet produce compositions especially adapted to penetrate and displace water on the surfaces of metals for removal of corrosive substances, we have found it necessary to employ as a mutual solvent for the water and oil as well as an aid in fingerprint removal a water-soluble oxygenated organic solvent selected from the class consisting of alcohols and ketones boiling below about 180° F. at atmospheric pressure. We have observed that the use of a water-soluble oxygenated organic solvent boiling above about 180° F. decreases the volatility of our compositions, however the resultant composition is not stable and readily loses its clear quality at low temperatures. Compounds which may be used for the purposes of our invention include water-soluble aliphatic alcohols and ketones, such as isopropyl alcohol, propanol, ethanol, methanol, dimethyl ketone and methyl ethyl ketone. Of these compounds we prefer to use the water-soluble aliphatic alcohols, and of these particularly isopropyl alcohol since the use of this mutual solvent permits the use of larger proportions of water in the finished composition.

In formulating our compositions, a preferred

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procedure is followed to avoid obtaining compositions lacking clarity, although other procedures may be used with varying degrees of success. Preferably, it is desirable to mix together the water, alcohol or ketone solvent, and coupling or wetting agent in the desired amounts, and agitate same at a temperature in the range of between about 40° and 125° F., preferably between about 65 and 90° F., until a substantially homogeneous mixture is obtained. The oil-soluble detergent, in the desired amount, is added to the hydrocarbon solvent of predetermined amount, and thoroughly agitated at a temperature within the range of between about 40° and 125° F., preferably between about 65° and 90° F., to insure good mixing. The two mixtures are then combined and agitated mildly at a temperature between about 40° and 125° F., preferably between about 65° and 90° F., to obtain a clear and bright mixture.

Unless otherwise specified, for the purposes of this specification and the subjoining claims, all parts of compositions are by volume.

Having thus described our invention, the following examples are illustrative thereof:

Example I

	Parts by Weight	Parts by Volume	
Calcium Mahogany Soap Blend ¹	30	} 83.0	
Stoddard's Solvent.....	70		
Water.....			5.8
Isopropyl Alcohol.....			10.7
Water-Soluble Sulfonated Castor Oil.....		0.5	

¹ 37% soap of about 430 molecular weight.

The composition given in Example I was subjected to a copper corrosion test at 210° F., and after three hours at this elevated temperature no evidence of corrosion was apparent. The stability of this composition was determined by maintaining a sample thereof at 32° F. for a period of twenty-five hours, and the tested sample retained the same clearness or stability as possessed before the test. This composition was also subjected to fingerprint removal tests. In these tests sandblasted and polished panels of SAE 1020 steel were respectively spotted with drops of synthetic fingerprint solution and dried in an oven at 210° F.

The synthetic fingerprint solution, having approximately the same corrosive effect on metals as human perspiration, was prepared by dissolving

	Grams
NaCl	7
Urea	1
Lactic acid.....	4

in 50 per cent methanol and diluting to 250 ml. with 50 percent methanol. This solution was diluted by addition of 4.33 ml. of methanol per 1 ml. of solution before use.

At the end of five minutes the steel strips were removed from the drying oven, permitted to cool, and then slushed into composition of Example I. Following the slushing the steel strips were rinsed with naphtha, and then with hexane. After the strips are substantially dry, they are immersed in molten petrolatum, which is known to have appreciably no fingerprint rust preventive quality. After cooling, the strips were suspended in humidity cabinets (a description thereof given hereinafter) to determine if rusting would occur. In the event that the synthetic fingerprint solution was not removed, rust-

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ing would occur where the synthetic fingerprint solution was applied; otherwise, if the synthetic fingerprint solution was removed general rusting of the panels occurred. In both panels it was observed that general rusting occurred after having been subjected to the humidity cabinet treatment for about 72 hours. This shows that our composition effectively removed the synthetic fingerprint solution.

Example II

	Parts by Weight	Parts by Volume
Calcium Mahogany Soap ¹	30	85.7
Stoddard's Solvent.....	70	
Water.....		2.8
Dimethyl Ketone.....		11.00
Water-Soluble Sulfonated Castor Oil.....		0.50

¹ The same as the calcium mahogany soap in Example I.

Example III

	Parts by Weight	Parts by Volume
Calcium Mahogany Soap ¹	30	84.3
Stoddard's Solvent.....	70	
Water.....		4.5
Methyl Ethyl Ketone.....		10.7
Water-Soluble Sulfonated Castor Oil.....		0.5

¹ The same as the calcium mahogany soap in Example I.

In determining the rust preventive performance of the above compositions, illustrated in Examples I, II and III, widely accepted humidity tests were made. In these tests, panels of cooled rolled SAE 1020 steel measuring 2'' x 4'' x 1/8'', either polished or sandblasted, are coated by submerging into the compositions and then suspended by glass hooks from a glass rod running across a special humidity cabinet. In this cabinet the temperature is maintained at 100° F. by heating units and thermal regulators for automatic temperature control. The humidity is 100%, and is maintained at this value by keeping a water level of 2 to 3 inches in the bottom of the cabinet at all times. From about 1 to 1.5 complete changes of saturated air per hour are provided in the cabinet. It is generally recognized that a satisfactory rust preventive should give about a minimum of 200 hours protection to steel panels in the humidity test.

In the case of the above compositions, the polished and sandblasted panels did not show evidence of corrosion until a time substantially over 200 hours.

To determine the water displacing property of the above composition, a special test was devised which indicates the relative ability of a particular composition to displace water. In this instance, the relative water displacing property of our composition was determined by comparison with other commercial compositions known to be good water displacers.

In Table I below, compositions A and B are commercial products, and C, D and E are embodiments of the present invention corresponding to Examples I, II and III, respectively. Composition A contains about 30 weight percent calcium mahogany soap in about 70 weight percent hydrocarbon solvent boiling between about 310° and 395° F. at atmospheric pressure. The 30 percent soap is composed of a blend of 37 percent soap and 63 percent oil. This soap solution is made up in the same manner as set forth in Example I, that is, the unreacted oil remaining after the

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extraction step with ethanol is supplemented with a paraffin oil having a viscosity of about 80 seconds, SSU at 100° F., to give a calcium mahogany soap concentration of about 37 percent. Composition B contains about 3.05 weight percent sodium sulfonate, 0.27 weight percent calcium sulfonate, about 18.48 weight percent inert hydrocarbon boiling in the lubricating oil range, and about 78.2 weight percent hydrocarbon solvent boiling between about 326° and 393° F. at atmospheric pressure.

Table I

Composition.....	A	B	C	D	E
Water Displacement in Seconds...	200	300	60	110	100

In these tests, a polished steel plate was marked off into centimeter squares by means of a sharp instrument, and when not in use, it was stored in methyl alcohol to prevent corrosion. Before each test, the steel plate is removed from the methyl alcohol by means of tongs or a glass hook wiped dry with a paper towel, and rubbed lightly with fine emery cloth to remove any deposited matter or corrosion products. Following, the panel is washed with water, and thoroughly dried with a paper towel. During the preparation of the marked steel plate, the surfaces are never in contact with fingers of the operator. Following next, a drop of water is deposited in the center of one of the centimeter squares, by means of a burette located about 0.4 cm. above the surface of the metal plate. Similarly, a drop of the composition to be tested is placed next to the drop of water on the plate. The water displacement property of the composition is the time required for the drop of water to spread over an area of one square centimeter, from the time that the drop of composition is applied.

During the development of this test, in order to observe the phenomenon of water displacement, an oil-soluble Calco Fluorescent yellow dye was dissolved in the composition and observations were made with ultra violet light. It was noticed that after the drop of composition is placed next to the drop of water, the composition surrounds the droplet of water and penetrates the water until the surface of the metal under the droplet of water is completely coated with the composition. At this time the droplet of water is completely displaced, or what is termed as cleavage, so that the water spreads over the surface of the metal plate. It was found that when the water spreads to an area of one square centimeter, the composition was substantially cleaved all of the water from the area where it was originally deposited.

While we have described various components in our compositions, it should be clearly understood that the descriptive and explanatory notes accompanied therewith do not necessarily describe all functions performed by the said components, and hence the limit or scope of our invention is defined by the following claims.

We claim:

1. A composition of matter comprising eventually between about 1 and 30% of a preferentially oil-soluble sulfonate between about 5 and 85% of a hydrocarbon solvent boiling in the range between about 100° F. and about 650° F., between about 1 and 20% of a water soluble oxygenated organic solvent boiling below about 180° F. at atmospheric pressure and selected from the class

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consisting of an aliphatic alcohol and an aliphatic ketone, between about .1 and 5% of a water soluble sulphonated vegetable oil and between about 1 and 10% water.

2. A composition of claim 1 wherein the preferentially oil-soluble sulfonate is a preferentially oil-soluble mahogany soap of an alkaline earth metal.

3. The composition of claim 1 wherein the water soluble sulphonated vegetable oil is a water soluble sulphonated castor oil.

4. A composition of matter comprising essentially between about 1 and 30% of a preferentially oil-soluble sulfonate, between about 5 and 85% of a hydrocarbon solvent boiling in the range between about 100° F. and about 650° F., between about 1 and 20% of a water soluble aliphatic alcohol boiling below about 180° F. at atmospheric pressure, between about .1 and 5% of a water soluble sulphonated vegetable oil, and between about 1 and 10% water.

5. A composition of matter comprising essentially between about 1 and 30% of a preferentially oil-soluble sulfonate, between about 5 and 80% of a hydrocarbon solvent boiling in the range between about 100° F. and about 650° F., between about 1 and 20% of a water soluble aliphatic ketone boiling below about 180° F. at atmospheric pressure, between about .1 and 5% of a water soluble sulphonated vegetable oil, and between about 1 and 10% water.

6. A composition of matter consisting essentially of between about 3 and 15% of a preferentially oil-soluble sulfonate, between about 30 and 80% of a hydrocarbon solvent boiling in the range between about 100° F. and about 650° F., between about 5 and 15% of a water soluble oxygenated organic solvent boiling below about 180° F. at atmospheric pressure and selected from the class consisting of an aliphatic alcohol and an aliphatic ketone, between about .1 and 2% of a water soluble sulphonated vegetable oil, and between about 1 and 10% water.

7. The composition of claim 6 wherein the preferentially oil-soluble sulfonate is a preferentially oil-soluble mahogany soap of an alkaline earth metal.

8. The composition of claim 6 wherein the water soluble sulphonated vegetable oil is a water soluble sulphonated castor oil.

9. The composition of claim 6 wherein the hydrocarbon solvent is a naphtha boiling essentially between about 300 to 400° F. at atmospheric pressure.

10. A composition of matter consisting essentially of between about 3 and 15% of a preferentially oil-soluble sulfonate, between about 30 and 80% of a hydrocarbon solvent boiling in the range between about 100° F. and about 650° F., between about 5 and 15% of a water soluble aliphatic alcohol boiling below about 180° F. at atmospheric

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pressure, between about .1 and 2% of a water soluble sulphonated vegetable oil, and between about 1 and 10% water.

11. A composition of matter consisting essentially of between about 3 and 15% of a preferentially oil-soluble sulfonate, between about 30 and 80% of a hydrocarbon solvent boiling in the range between about 100° F. and about 650° F., between about 5 and 15% of a water-soluble aliphatic ketone boiling below about 180° F. at atmospheric pressure, between about .1 and 2% of a water soluble sulphonated vegetable oil, and between about 1 and 10% water.

12. A composition of matter consisting essentially of between about 3 and 15% of a preferentially oil-soluble mahogany soap of an alkaline earth metal, between about 30 and 80% of a naphtha fraction boiling in the range of about 300 to 400° F. at atmospheric pressure, between about 5 and 15% of a water soluble oxygenated organic solvent boiling below about 180° F. at atmospheric pressure and selected from the class consisting of aliphatic alcohol and aliphatic ketone, between about .1 and 2% of a water-soluble sulphonated castor oil, and between about 1 and 10% water.

13. The composition of claim 12 wherein the preferentially oil-soluble mahogany soap of an alkaline earth metal is the preferentially oil-soluble calcium mahogany soap.

14. A composition for protecting metal against fingerprint corrosion which composition is approximately as follows:

	Per cent
Hydrocarbon solvent	75
Water soluble oxygenated organic solvent...	11
Preferentially oil-soluble sulfonate	9
Water	4.5
Coupling agent	0.5

the hydrocarbon solvent boiling essentially in the gasoline-kerosene range, the water soluble oxygenated organic solvent boiling below about 180° F. at atmospheric pressure and selected from the class consisting of an aliphatic alcohol and an aliphatic ketone and the coupling agent being a water soluble sulphonated vegetable oil.

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