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RUST PREVENTIVE COMPOSITIONS

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This invention relates to cleansing and rust preventive compositions, and more particularly relates to compositions adapted to remove corrosive saline products from metal surfaces and to inhibit corrosion and/or rusting. More specifically, the invention is directed to coating agents having fingerprint removing and rust preventive properties.

Anti-rust or slushing compositions are used for the protection of metals either in the form of stock or fabricated articles against corrosion and/or rusting. Metals prior to storage should be coated with an anti-rust material to prevent corrosion and/or rusting while in storage, and finished articles and finished or semi-finished metal stocks destined for shipment by rail or by water must be protected against attack by moisture by coating such materials with anti-rust or slushing compounds. Materials for shipment overseas, particularly, must be protected against attack by salt spray. Since the necessity of protecting materials for overseas shipment is of the utmost importance, slushing compositions for this purpose must meet rigid specifications.

A specific type of metal corrosion is the so-called salt-type which is apparently due to adherent inorganic salt particles rather than to external fluid agencies. A particular form of salt-type corrosion is the so-called fingerprint corrosion which generally follows manual handling of metal stocks and is in some way related to salt deposited on the metal surfaces from perspiration transferred from the hands of the workers handling such materials.

Salt-type, and particularly fingerprint corrosion, is particularly difficult to avoid or inhibit in spite of the fact that its general nature has been recognized by metal workers for many years. This type of corrosion problem has persisted in spite of the fact that there have been extensive developments in the field of slushing compounds. Slushing compounds appear to exert a protective effect on metal surfaces in part by forming an adherent coating which excludes the corrosion inducing media. In some cases the protective properties of slushing compounds may be attributed to anti-rust agents dissolved or dispersed in the slushing composition vehicle. For reasons not clearly understood in the art it has been found that salt-type corrosion can continue under the protective coating of slushing compounds in numerous instances where the metal article has been handled manually before the application of the slushing compound. Frequently, as in metal working, it is almost impossible to avoid manual handling of metal stocks prior to the application of a slushing compound.

It is an object of the invention to provide novel compositions especially adapted to prevent or inhibit the corrosion and/or rusting of metals. An-

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other object of the invention is to provide compositions adapted to combat salt-type corrosion. Still another object of the invention is to provide a dual function composition possessing the properties of removing saline products which cause corrosion and/or rusting from metal surfaces and to prevent the corrosion and/or rusting of such surfaces. Further objects and advantages of the invention will become apparent from the following description thereof.

Briefly, in general terms, we have found that effective rust preventive compositions can be obtained by employing in combination about 5% to 40% of a preferentially oil-soluble alkali metal and/or alkaline earth sulfonate, about 1% to 10% of a morpholine soap of an aliphatic mono-basic acid having at least about 12 carbon atoms, 0% to about 15% of a water-soluble aliphatic ketone or alcohol, about 5% to about 80% of a normally liquid hydrocarbon, and from about 0% to about 80% water.

The alkali metal and/or the alkaline earth metal soaps of preferentially oil-soluble sulfonic acids, including alkyl sulfonic acids, petroleum sulfonic acids, alkyl aryl sulfonic acids and aralkyl sulfonic acids can be employed in our composition. While we prefer to use the calcium sulfonates, other sulfonates, such as the sodium, potassium, lithium, barium, and strontium sulfonates, or mixtures thereof, can be suitably used. We prefer to use the above soaps of preferentially oil-soluble petroleum sulfonic acids commonly known in the petroleum refining art as mahogany acids.

The preferentially oil-soluble petroleum sulfonic acids commonly referred to as mahogany acids are produced by treating petroleum distillates between about 50 to about 1000 seconds or higher Saybolt Universal viscosity at 100° F., with between about 3 to 9 pounds, and preferably about 3 to 6 pounds of concentrated or fuming sulfuric acid per gallon of oil. After removal of the sulfuric acid sludge the acid-treated oil is treated with a suitable alcohol of about 60% strength to remove the oil-soluble petroleum sulfonic acid. The alcoholic fraction containing the sulfonic acids is then neutralized with the desired neutralizing agent, such as for example, CaO or slack lime, the mixture allowed to settle and the alcohol layer containing the mahogany acid soap drawn off and distilled to remove the alcohol. To facilitate handling, the soaps are preferably dissolved in a petroleum oil to give a blend containing 35% to about 50% soap. The molecular weights of the preferentially oil-soluble sulfonic acids obtained in the acid treatment of petroleum oils vary from about 420 to about 500, depending upon the petroleum oil treated and the amount of sulfuric acid employed. While any one of the preferentially oil-soluble petroleum sul-

fonic acids can be used, we prefer to use those acids having molecular weights within the range of 410 to about 450, although soaps of mixtures of the lower molecular weight sulfonic acids and the higher molecular weight sulfonic acids can be used.

The morpholine soap used in the present composition is preferably a morpholine soap of an aliphatic mono-basic acid having at least about 10 carbon atoms. Examples of suitable morpholine soaps are morpholine laurate, morpholine oleate, morpholine palmitate, morpholine stearate, morpholine naphthenate, morpholine myristate, morpholine arachidate, morpholine behenate, morpholine montenate, morpholine ricinoleate and morpholine linoleate.

The normally liquid hydrocarbon used is suitably any hydrocarbon boiling above about 150° F., for example, gasoline, naphtha, gas oil, etc. The hydrocarbon found particularly well suited for this purpose is a heavy naphtha boiling within the range of from about 300° F. to about 400° F., such as for example, Stoddard solvent. For some uses it will be found advantageous to mix heavier liquid hydrocarbons with the lower boiling hydrocarbons such as a mixture of Stoddard solvent with heavier hydrocarbon oils, such as kerosene and/or gas oil, or more viscous petroleum oils having a Saybolt Universal viscosity at 100° F. of from about 60 seconds to about 500 seconds.

In preparing the fingerprint removal and rust preventive composition the sulfonate and the morpholine soap are combined and heated with stirring to a temperature sufficient to melt the morpholine soap but not in excess of about 212° F. To the heated mixture is then added the desired amount of hot water and the mixture rapidly stirred. After the emulsification has taken place, the mixture is cooled to a temperature below the boiling point of the alcohol or ketone to be used and the alcohol and/or ketone added, and the hydrocarbon solvent subsequently introduced into the mixture. For example, to 30 parts of a mixture of approximately 42% calcium mahogany soap in a petroleum oil are added 2 parts of morpholine stearate and the mixture heated to 190° F., with stirring until the morpholine stearate is melted and thoroughly integrated in the mass. To this mixture is added 53 parts of water at a temperature of 180° F., while stirring at a very fast rate until emulsification takes place. The mixture is then cooled to a temperature of about 155° F., or lower, and 5 parts of isopropyl alcohol added while stirring. After the alcohol has been incorporated into the mixture, 10 parts of the hydrocarbon solvent is slowly added and mixed into the product.

Effective rust preventive or slushing compositions are obtained with blends of the morpholine soap, sulfonate and liquid hydrocarbon. Illustrative of compositions suitable for use as rust preventives in accordance with the teachings of the present invention are the following examples, which are given merely by way of illustration and are not intended to limit the scope thereof.

Example I

	Per cent
Morpholine stearate	4.8
Calcium soap of mahogany acid ¹	29.8
Petroleum oil	41.6
Stoddard solvent	23.8

¹ Molecular weight, 430-450.

This product is an effective slushing compound

for preventing the rusting and/or corrosion of metal surfaces.

Example II

	Per cent
Morpholine stearate	3.0
Calcium soap of mahogany acid ¹	13.8
Petroleum oil	25.9
Stoddard solvent	14.9
Kerosene (B. P. 320-515° F.)	37.4

¹ Molecular weight of acid, 430-450.

This product will afford protection against rusting and/or corrosion of metal surfaces similar to that of Example I. The liquid hydrocarbon mixture being somewhat more viscous than the hydrocarbon solvent of Example I will afford better lubrication to moving metal parts, under circumstances where a relative low viscosity lubricant is required. When necessary, the relatively low viscosity hydrocarbon liquids in the above formulae can be replaced by more viscous oils, such as light pale oils having a Saybolt Universal viscosity of at least about 60 seconds at 100° F.

Compositions of the type of Examples I and II are effective and suitable rust preventive or slushing compositions to prevent the corrosion and/or rusting of metal surfaces. However, when it is desired to remove corrosive saline deposits, such as fingerprints, from the metal surfaces and at the same time provide a rust preventive coating, the above-described composition is modified by using in combination therewith an aliphatic alcohol or ketone and water. Examples of suitable water-soluble aliphatic alcohols and ketones include isopropyl alcohol, propyl alcohol, ethyl alcohol, methyl alcohol, butyl alcohol, dimethyl ketone, methyl ethyl ketone, butyl ketone, acetone, etc. It is preferred to use the water-soluble aliphatic alcohols of less than about five carbon atoms, such as for example, isopropyl alcohol.

Suitable fingerprint removal and rust preventive compositions are obtained by providing a product falling within the following formula:

	Per cent
Alkali metal or alkaline earth soap of preferentially oil-soluble sulfonic acid	5 to 40
Morpholine fatty acid ¹ soap	1 to 10
Hydrocarbon diluent	5 to 80
Water-soluble alcohol or ketone	1 to 15
Water	5 to 80

¹ Containing at least 12 carbon atoms.

The following examples are illustrative of effective compositions having the desired fingerprint removal and rust preventive properties:

Example III

	Per cent
Calcium mahogany soap	5 to 20
Morpholine stearate	1 to 5
Hydrocarbon diluent	5 to 40
Isopropyl alcohol	2 to 8
Water	40 to 60

Example IV

	Per cent
Morpholine stearate	2.0
Calcium soap of mahogany acid ¹	12.5
Hydrocarbon solvent ²	10.0
Petroleum oil	17.5
Isopropyl alcohol	5.0
Water	53.0

¹ Molecular weight of acid, 430-450.

² Distillation range, 300-400° F.

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Example V

	Per cent
Morpholine oleate.....	4.0
Barium soap of mahogany acid ¹	14.5
Hydrocarbon diluent.....	30.5
Butyl alcohol.....	4.0
Water	47.0

¹ Molecular weight of acid, 430-450.

Example VI

	Per cent
Morpholine laurate.....	8.0
Calcium polybutene ¹ alkylated benzene sulfonate	25.0
Hydrocarbon diluent.....	15.0
Methyl ethyl ketone.....	3.0
Water	49.0

¹ Molecular weight, 1000.

Example VII

	Per cent
Morpholine stearate.....	2.0
Sodium soap of mahogany acid ¹	12.5
Hydrocarbon diluent.....	27.5
Isopropyl alcohol.....	5.0
Water	53.0

¹ Molecular weight of acid, 470-500.

Example VIII

	Per cent
Morpholine stearate.....	2.0
Sodium soap of mahogany acid ¹	8.5
Calcium soap of mahogany acid ²	4.5
Hydrocarbon diluent.....	27.0
Isopropyl alcohol.....	5.0
Water	53.0

¹ Molecular weight of acid, 470-500.² Molecular weight of acid, 430-450.

In the above examples, a ketone, such as for example, methyl ethyl ketone, dimethyl ketone, etc., can be used in place of the alcohol.

The ability of compositions of the type of Examples III to VIII, inclusive, to remove fingerprint stains from metal surfaces is demonstrated by the following test:

Sand-blasted and polished steel panels were spotted with drops of a synthetic fingerprint solution and dried in an oven at 210° F. At the end of five minutes the steel specimen were removed from the drying oven, permitted to cool, and then dipped into the composition of Example IV. Following the slushing, the steel strips were rinsed with naphtha, dried, and then coated with molten petrolatum which is known to have substantially no rust preventive qualities. After cooling, the steel specimen, coated with the petrolatum, were suspended in a humidity cabinet, maintained at 100° C. and 100% humidity, to determine the occurrence of rusting. In the event that the synthetic fingerprint solution was not removed, rusting would first occur where the synthetic fingerprint solution was applied; otherwise, if the synthetic fingerprint solution was removed, general rusting of the steel specimen would occur at a much later time. It was observed that general rusting of the steel specimen occurred after being in the humidity cabinet for about seventy-two hours, demonstrating the removal of the synthetic fingerprint stain.

The synthetic fingerprint solution used in this test, and which has substantially the same corrosive effect on metals as human perspiration, was prepared by dissolving 7 grams of sodium chloride, 1 gram of urea and 4 grams of lactic acid in 250 cc. of 50% methyl alcohol. The solu-

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tion used for testing was prepared by mixing 1 cc. of this solution with 4.33 cc. of methylalcohol.

To determine the rust preventive properties of the herein-described composition, sand blasted and polished steel specimens were coated by submerging in compositions such as Example IV and suspending by glass hooks from glass rods in a special humidity cabinet. In the humidity cabinet, a temperature of 100° F. and a humidity of 100% was maintained, and during the test period from 1 to 1½ complete changes of saturated air per hour provided. In this test the sand blasted steel specimen remained unrusted for 1600 hours (67 days) and the polished steel specimen remained unrusted for 1000 hours (45 days). In outdoor protection tests the sand blasted and polished steel specimen showed only a slight darkening without rusting at 35 days at which time only widely scattered very minute specks of rusting appeared. In the shed test, the sand blasted and polished steel specimen showed no rusting at the end of 2400 hours or 100 days.

Since it is generally recognized that the satisfactory rust preventive should give about a minimum of 200 hours protection in the humidity cabinet test, the marked effectiveness of the herein-described rust preventive compositions is strikingly demonstrated.

The herein described rust preventive compositions can contain, in addition to the aforementioned components, other materials to give desired properties, such as for example, petrolatums, paraffin waxes, oiliness agents, resins, glycerine, vegetable and mineral waxes, halogenated hydrocarbons, etc.

Percentages given herein and in the appended claims are weight percentages, unless otherwise specified.

While the present invention has been described by reference to specific embodiments thereof, these are given by way of illustration only, and the invention is not to be limited thereto, but includes within its scope such modifications and variations as come within the spirit of the appended claims.

We claim:

1. A composition consisting essentially of from about 5% to about 40% of a preferentially oil-soluble sulfonic acid soap selected from the group consisting of a preferentially oil-soluble alkali metal sulfonate, a preferentially oil-soluble alkaline earth sulfonate and mixtures thereof, from about 1% to about 10% of a morpholine soap of an aliphatic mono-basic acid of at least about 12 carbon atoms, and from about 5% to about 80% of a normally liquid hydrocarbon.

2. A composition as described in claim 1, in which the sulfonate is an alkyl aryl sulfonate.

3. A composition consisting essentially of from about 5% to about 40% of an alkaline earth soap of a preferentially oil-soluble petroleum sulfonic acid, from about 1% to about 10% of a morpholine soap of an aliphatic mono-basic acid having at least about 12 carbon atoms, and from about 5% to about 80% of a normally liquid hydrocarbon.

4. A composition as described in claim 3 in which the alkaline earth soap of a preferentially oil-soluble petroleum sulfonic acid is calcium soap.

5. A composition as described in claim 3 in which the alkaline earth soap of a preferentially oil-soluble petroleum sulfonic acid is barium soap.

6. A composition as described in claim 3 in which the alkali metal soap of the preferential-

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ly oil-soluble petroleum sulfonic acid is sodium soap.

7. A composition as described in claim 3 in which the normally liquid hydrocarbon is a naphtha boiling within the range of from about 300° F. to about 400° F.

8. A composition as described in claim 3 in which the morpholine soap is morpholine stearate.

9. A composition as described in claim 3 in which the morpholine soap is morpholine oleate.

10. A composition as described in claim 3 in which the morpholine soap is morpholine laurate.

11. A rust preventive composition comprising essentially

	Per cent
Morpholine stearate.....	4.8
Calcium mahogany soap.....	29.8
Stoddard solvent.....	23.3
Petroleum oil.....	41.6

12. A rust preventive composition comprising essentially

	Per cent
Morpholine stearate.....	3.0
Calcium mahogany soap.....	18.8
Stoddard solvent.....	14.9
Kerosene (B. P. 320-515).....	37.4
Petroleum oil.....	25.9

13. A composition consisting essentially of from about 5% to about 40% of a preferentially oil-soluble sulfonate selected from the group consisting of an alkali metal soap of a preferentially oil-soluble sulfonic acid, an alkaline earth soap

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of a preferentially oil-soluble sulfonic acid and mixtures thereof, from about 1% to about 10% of a morpholine soap of a high molecular weight fatty acid of at least 12 carbon atoms, from about 5% to about 80% of a normally liquid hydrocarbon diluent, from about 1% to about 15% of a water-soluble oxygenated organic compound selected from the group consisting of an aliphatic water-soluble ketone and an aliphatic water-soluble alcohol, and from about 5% to about 80% water.

14. A composition consisting essentially of from about 5% to about 20% calcium mahogany soap, from about 1% to about 5% morpholine stearate, from about 5% to about 40% of a normally liquid hydrocarbon diluent, from about 2% to about 80% isopropyl alcohol, and from about 40% to about 60% water.

15. A composition consisting essentially of about 12.5% calcium mahogany soap, 2% morpholine stearate, 10% hydrocarbon solvent, distilling between about 300° F. to 400° F., 17.5% petroleum oil, 5% isopropyl alcohol, and 53% water.

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