

# UNITED STATES PATENT OFFICE

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## AQUEOUS RUST PREVENTIVE COMPOSITION

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This invention relates to aqueous rust preventive and cleansing compositions. More particularly it relates to aqueous compositions adapted to inhibit or prevent salt-type corrosion, and particularly fingerprint corrosion, of metals.

Salt-type corrosion of metals is so named because corrosion of the metal is apparently due to adherent inorganic salt particles rather than to external fluid agencies. A particularly ubiquitous 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 the salt deposited on the metal from perspiration transferred from the hands.

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 the face of extensive developments in the field of slushing compounds. Slushing compounds are petroleum rust preventives and are usually classified as oils or greases from the standpoints of appearance, handling and service properties. Slushing compounds appear to exert a protective effect on metal surfaces, in part, by forming an adherent coating which excludes the atmosphere and, in part, by the effects which may be attributed to antirust agents dissolved or dispersed in the petroleum vehicle. For reasons not clearly understood in the art, it has been found that salt-type corrosion can continue under a protective coating of slushing compound in numerous instances where the metal has been handled manually before the application of the slushing compound. Frequently, as in metal working, it is well-nigh impossible to avoid manual handling of metal stocks prior to the application of a slushing compound.

It is an object of this invention to provide novel aqueous compositions especially adapted to prevent or inhibit the corrosion of metals. Another object of this invention is to provide aqueous emulsions particularly adapted to combat salt-type corrosion. Still another object of this invention is to provide bright, stable aqueous dispersions containing antirust agents and capable of inhibiting metal corrosion, particularly salt-type corrosion, and of removing corrosion products from metal surfaces. Further objects of this invention will become apparent as the description of the invention proceeds.

Briefly, and in generalized terms, we have found that aqueous dispersions or solutions comprising certain detergents, antirust agents and homogenizing organic solvents are surprisingly effective in preventing or inhibiting salt-type corrosion of metals. The discovery that aqueous compositions would inhibit salt-type corrosion was unexpected since it is known that water, be-

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cause of its low viscosity, has poor covering power for metals, and further because aqueous solutions or dispersions frequently aggravate rather than decrease the corrosion of metals.

A wide variety of detergents may be used for the purposes of our invention, including various organic sulfonates, sulfates, quaternary ammonium salts, phosphorated higher alcohols, fatty acid soaps of alkylolamines, substituted amides of alkyl phosphates and the like. A particularly desirable class of detergents comprises organic sulfonates including alkyl sulfonates, petroleum sulfonates, alkyl aromatic sulfonates, alkyl phenol sulfonates, sulfonates of aromatic acids, sulfonated ethers. Another particularly desirable class of detergents comprises organic sulfates, including sulfates of higher alcohols, sulfated esters of fatty acids, sulfated fatty acids, sulfated glycerylamides, sulfated amides of fatty acids and the like.

Generally we prefer to use sulfonates or sulfates of metals in group I of the periodic system, particularly sodium and potassium salts, although we may use sulfonates or sulfates of metals in other groups of the periodic system or of ammonia or ammonia derivatives such as amines and the like.

We prefer to use preferentially oil-soluble detergents, especially soaps of preferentially oil-soluble sulfonic acids, e. g. soaps of oil-soluble petroleum sulfonic acids, commonly known as mahogany acids. Specifically, we have obtained very excellent results with sulfonates of the type obtainable by treating petroleum distillates of from about 50 to about 1000 seconds or even higher, and preferably from about 200 to about 600 seconds Saybolt Universal viscosity at 100° F. with from about 6 to about 9 pounds of strong sulfuric acid, preferably fuming sulfuric acid, per gallon of oil. The method of obtaining desirable soaps of preferentially oil-soluble sulfonic acids derived from petroleum oils is illustrated by the following example, which describes the preparation of a sodium soap.

A petroleum oil distillate having a Saybolt Universal viscosity at 100° F. of from about 200 seconds to about 850 seconds is treated with from about 6 to about 9 pounds of fuming sulfuric acid per gallon of oil in one-half pound increments or "dumps." After the acid sludge from each one-half pound acid "dump" is settled and withdrawn, the next one-half pound of fuming sulfuric acid is added to the oil. The temperature of the oil before the fuming acid is added thereto is maintained below about 60° F. but due to the heat of reaction upon the addition of the sulfuric acid, the temperature of the oil may rise to from about 90° F. to about 100° F. After the required total amount of fuming sulfuric acid has been added to the oil and the oil freed of acid sludge, the

acid treated oil containing oil-soluble sulfonic acids dissolved therein is neutralized with a solution of sodium hydroxide. The aqueous alkali solution is then separated from the oil solution containing dissolved therein sodium soaps of sulfonic acids and the latter then separated from the oil by extraction with alcohol of about 60% strength. The alcohol layer containing dissolved sodium sulfonates is then separated from the oil and subsequently distilled to recover the alcohol and remove water. The crude sulfonic soap obtained in this manner contains from about 30% to about 60% sodium sulfonate, from about 30% to about 60% oil, from about 1% to about 10% water, and up to 10% inorganic salts which may be removed by the procedure hereinafter described.

The above procedure may be modified after the acid sludge is removed from the acid-treated oil. The oil containing dissolved sulfonic acids is extracted with about 60% alcohol to remove the sulfonic acids which may then be neutralized with sodium hydroxide and subsequently freed of the alcohol by distillation.

The crude soaps of these preferentially oil-soluble sulfonic acids obtained by the procedure described above may be freed of inorganic salts by purification. This purification is preferably accomplished by dilution of the crude soap with from about 1/2 to about 10 parts, preferably 1 to 2 parts of 50% or higher strength alcohol, preferably alcohol of 60 to 70% strength, and allowing the salts to settle while maintaining the mixture within the temperature range of 130 to 175° F., preferably 155 to 165° F. When the salts have settled the supernatant alcohol-soap layer is separated and the alcohol is recovered by conventional distillation procedure. By this method of purification the salt content of the crude sulfonic soap can be readily reduced to 5% or less, e. g., to about 3.5%.

Although we have described a specific method for the preparation of petroleum sulfonic acids suitable for the purposes of our invention, it should be understood that our invention is not restricted thereto, but that suitable organic sulfonates having similar properties can be used, however made.

We have found sodium nitrite to be an excellent antirust agent in compounding the aqueous salt-type rust preventive and cleansing compositions of our invention. We have found that sodium nitrite appears to function not only as an antirust agent but also exerts a solubilizing effect on the other ingredients of our aqueous compositions, rendering possible the production of "bright" products, i. e. clear, highly stable aqueous dispersions wherein the dispersed phase is present in a state of subdivision apparently approaching "true" solution. These "bright" products are highly desirable because of their stability in storage and because of their sales appeal. Accordingly, sodium nitrite constitutes a preferred antirust agent for the purposes of our invention.

Although we prefer to use sodium nitrite as an antirust agent, we may also use other antirust agents of the same type including, for example, ammonium nitrite, potassium nitrite or other water-soluble nitrites, sodamide or an equivalent solution of caustic and ammonia, sodium or potassium dichromates, sodium chrom-glucosate and the like. It is not to be inferred that these antirust agents are precisely equivalent to sodium nitrite in their effects in our compositions, but

in specific instances their use may be found desirable.

Other antirust agents which we have found to be highly desirable in compounding our novel compositions comprise alkylolamine soaps. Thus, we may use alkylolamine soaps of carboxylic acids such as fatty acids or naphthenic acids, or of sulfonic acids and the like. We have obtained particularly stable, bright and effective aqueous rust preventives and metal cleansers by using alkylolamine soaps of naphthenic acids. We may use soaps of mono-, di-, or tri-ethanolamine, choline, propanolamines, butanolamines and the like. We have obtained excellent protection of metals against salt-type corrosion by the use of butanolamine soaps, and accordingly these constitute a preferred class for the purposes of our invention. Suitable butanolamines include 2-amino-1-butanol and 2-amino-2-methyl-1-propanol. We may use both an alkylolamine soap and an antirust agent of the type of sodium nitrite for compounding our novel compositions.

In order to prepare stable aqueous compositions we have found it necessary to use a homogenizing organic solvent therein. Many of the volatile organic solvents, i. e. organic solvents boiling below about 350° F. at atmospheric pressure, can be used to prepare suitable aqueous dispersions of detergents and antirust agents for the purposes of our invention. However, after prolonged and diligent study we have succeeded in finding a group of volatile, oxygenated organic solvents which when used in our compositions will render possible the production of the preferred "bright" aqueous metal cleansers and rust preventives. We have been unable thus far to discover what particular quality of a volatile, oxygenated organic solvent is essential for the production of "bright" products for our purposes. The solvents which we have found suitable for the preparation of "bright" products are isobutyl alcohol, diacetone alcohol, the methyl ether of ethylene glycol monoacetate and ethylene glycol diethyl ether. Diacetone alcohol may be used in combination with either isobutyl alcohol or ethylene glycol diethyl ether.

In our compositions, we may best use about 5 to about 40% by weight of detergent, about 0.01 to about 10% by weight of antirust agent, about 2 to about 25% by weight of the homogenizing organic solvent and about 50 to about 80% by weight of water. We prefer to use an antirust agent of the type of sodium nitrite in the range of about 0.02 to about 2%. We prefer to use an antirust agent of the alkylolamine amine soap type in the range of about 0.25 to about 10%. It is to be understood that the use of certain specific detergents, antirust agents or organic solvents within the scope of our invention may necessitate some departure from the ranges set forth above, but generally we have found that formulations within the above ranges yield satisfactory products.

The compositions of our invention may contain not more than about 20% of a hydrocarbon oil and preferably less than about 10%, e. g. 5% of a hydrocarbon oil. Entirely suitable compositions may be made containing either traces or no detectable amounts of hydrocarbon oil. We have found that the residue left by our aqueous cleansing and rust preventive compositions is less tacky when a small proportion of a hydrocarbon oil is included therein, e. g. 5% of a hydrocarbon oil having a Saybolt Universal viscosity at 100° F. of 55.

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The following examples are adduced for the purpose of illustrating, but not limiting, our invention.

#### Example 1

The following composition was prepared:

	Percent by weight
Sodium soaps of preferentially oil-soluble petroleum sulfonic acids.....	15
Aqueous solution of NaNO <sub>2</sub> (0.5 g. NaNO <sub>2</sub> /100 ml. water).....	63
Methyl ether of ethylene glycol mono acetate.....	22
Triethanolamine.....	0.5

The purpose of adding triethanolamine was to make the composition slightly basic. This composition was subjected to a fingerprint removal test. In this test a sandblasted S. A. E. 1020 steel strip was spotted with a drop of synthetic fingerprint solution and dried in an oven at 250° F.

The synthetic fingerprint solution, i. e. a solution approximating human perspiration in its corrosive effect on metals, was prepared by dissolving

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

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

At the end of five minutes the steel strip was removed from the drying oven, allowed to cool to room temperature and then slushed for 1½ minutes in the above fingerprint removal composition. The strip was immediately thereafter rinsed in naphtha and then in hexane. Upon evaporation of the latter the strip was immersed in molten ivory petrolatum, which is known to have no fingerprint-rust-preventive capacity. After draining and cooling for one hour the strip was suspended in a humidity cabinet to determine if rusting would occur. If the compound fails to remove the fingerprint salts the first rusting occurs in the area covered by the fingerprint salts and general rusting of the strip is not observed.

In the humidity cabinet the steel strip is suspended in an atmosphere of 100% humidity at 100° F. The humidity cabinet is provided with heating units and thermal regulators for automatic temperature control. A water level of two to three inches is maintained in the cabinet to give approximately 100% humidity at all times. The steel strip is suspended by a glass hook from a glass rod running across the top of the humidity cabinet. From 1 to 1.5 complete changes of saturated air per hour are provided in the cabinet. The fingerprint removal and rusting preventive composition described above when subjected to the fingerprint removal test removed the salts so well that only general corrosion of the strip was evident at the end of 16 hours.

The above fingerprint removal and rust preventive composition was also subjected to a 100-hour humidity cabinet test, which is a very severe accelerated test for rust preventives. In this test a sand-blasted S. A. E. 1020 steel strip is slushed in the product to be tested, allowed to drain over night and then suspended in the humidity cabinet, as described above, for 100 hours at 100° F. utilizing 1 to 1.5 changes of saturated

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air per hour. The above fingerprint removal and rust preventive composition prevented rusting of the steel strip in this severe test.

#### Example 2

The following bright, aqueous salt-removal and corrosion-preventive composition was prepared:

	Percent by weight
Sodium soaps of preferentially oil-soluble petroleum sulfonic acids.....	13.5
2-methyl-2-amino-1-propanol naphthenate	3
Aqueous solution of NaNO <sub>2</sub> (0.5 g. NaNO <sub>2</sub> /100 ml. water).....	72
Isobutyl alcohol.....	4
Diacetone alcohol.....	3.5
Hydrocarbon oil (viscosity 55 seconds Saybolt Universal at 100° F.).....	4

This composition like that in Example 1 showed only general rusting in the fingerprint removal test, as described in Example 1, after 16 hours and passed the 100-hour humidity-cabinet test.

#### Example 3

A composition capable of removing salts from metal surfaces and of preventing salt-type corrosion was prepared, containing:

	Percent by weight
Sodium soaps of preferentially oil-soluble petroleum sulfonic acids.....	12
2-amino-1-butanol naphthenate.....	3
Isobutyl alcohol.....	4
Diacetone alcohol.....	3.5
Hydrocarbon oil (viscosity 55 seconds Saybolt Universal at 100° F.).....	4
Water.....	73.5

This composition had a Pinsky Martens closed flash point of 105° F. and a viscosity of 11.9 centistokes at 100° F. The composition performed satisfactorily when subjected to the following stability tests.

A sample of the composition was placed in a test tube and cooled to -20° F. for one hour. On being allowed to thaw without agitation the composition showed no separation which could not be dispersed by gentle agitation. Upon repetition of the test five times, the sample showed no separation after standing at room temperature for twenty-four hours. Another example of the composition in a loosely stoppered test tube was heated for forty minutes at 150° F. and allowed to cool to 70° F. without agitation or stirring; no separation took place.

#### Example 4

A bright, aqueous salt-type corrosion preventive was prepared according to the following formulation:

	Per cent by weight
Sodium soaps of preferentially oil-soluble petroleum sulfonic acids <sup>1</sup> .....	26
2-methyl-2-amino-1-propanol naphthenate.....	6
Isobutyl alcohol.....	8
Diacetone alcohol.....	7.4
Hydrocarbon oil (viscosity 55 seconds Saybolt Universal at 100° F.).....	8
Water.....	44.6

<sup>1</sup>Of the type produced by treating a petroleum distillate having a viscosity in the range of about 50 to about 1000 seconds Saybolt Universal at 100° F. with from about 6 to about 9 pounds of strong sulfuric acid per gallon of oil.

This corrosion preventive is preferably diluted up to double its volume with water for use as a salt remover and salt-type corrosion preventive.

## Example 5

The following formula gave perfect performance in the finger-print removal and 100-hour humidity cabinet tests described in Example 1:

	Per cent by volume
Sodium soap of a preferentially oil-soluble petroleum sulfonic acid <sup>1</sup> .....	13
2-amino-2-methyl-1-propanol naphthenate.....	3
Isobutyl alcohol.....	5
Diacetone alcohol.....	3.9
Water.....	70.1
Hydrocarbon oil (viscosity 55 seconds Saybolt Universal at 100° F.).....	5

<sup>1</sup>Of the type produced by treating a petroleum distillate having a viscosity in the range of about 50 to about 1000 seconds Saybolt Universal at 100° F. with from about 6 to about 9 pounds of strong sulfuric acid per gallon of oil.

Although we have described various components of our novel compositions in general terms, such as detergent, antirust agent and solvent, it is to be understood that these terms do not necessarily describe all of the functions performed by the specific agents thus designated in the compositions of our invention.

We claim:

1. An aqueous, substantially oil-free composition adapted to inhibit fingerprint corrosion of metals comprising a dispersion of about 5 to about 40% of a preferentially oil-soluble detergent, about 0.01 to about 10% of a water soluble antirust agent, about 2 to about 25% of a volatile organic solvent boiling below 350° F. at atmospheric pressure, and about 50 to about 80% of water.

2. The composition of claim 1 wherein the volatile organic solvent is selected from the group consisting of isobutyl alcohol, diacetone alcohol, the methyl ether of ethylene glycol monoacetate and ethylene glycol diethyl ether.

3. A bright, stable, aqueous, rust preventive and cleansing composition comprising a dispersion of a soap of a preferentially oil-soluble petroleum sulfonic acid, an antirust agent of the type of sodium nitrite and a volatile oxygenated organic solvent selected from the group consisting of isobutyl alcohol, diacetone alcohol, the methyl ether of ethylene glycol monoacetate and ethylene glycol diethyl ether in a major proportion of water.

4. A bright, stable aqueous rust preventive and cleansing composition comprising a dispersion of a soap of a preferentially oil-soluble sulfonic acid, an antirust agent of the type of alkylamine soaps and a volatile, oxygenated organic solvent selected from the group consisting of isobutyl alcohol, diacetone alcohol, the methyl ether of ethylene glycol monoacetate and ethylene glycol diethyl ether in a major proportion of water.

5. An aqueous composition adapted to inhibit fingerprint corrosion of metals comprising about 5 to about 40% of a preferentially oil soluble organic sulfonate, about 0.02 to about 2% of an antirust agent of the type of sodium nitrite, not more than about 20% of a hydrocarbon oil, about 2 to about 25% of a homogenizing organic solvent boiling below about 350° F. at atmospheric temperature and about 50 to about 80% of water.

6. An aqueous composition adapted to inhibit fingerprint corrosion of metals comprising about 5 to about 40% of a preferentially oil soluble

organic sulfonate, about 0.02 to about 2% of an antirust agent of the type of sodium nitrite, about 2 to about 25% of a homogenizing organic solvent boiling below about 350° F. at atmospheric temperature, and about 50 to about 80% of water.

7. An aqueous substantially oil-free rust preventive and cleansing composition comprising about 5 to about 40% of a preferentially oil soluble organic sulfonate, about 0.25 to about 10% of an antirust agent of the type of alkylamine soaps, about 2 to about 25% of a homogenizing organic solvent boiling below about 350° F. at atmospheric temperature and about 50 to about 80% of water.

8. An aqueous rust preventive and cleansing composition comprising about 5 to about 40% of a soap of a preferentially oil-soluble petroleum sulfonic acid, about 0.02 to about 2% of an antirust agent of the type of sodium nitrite, about 2 to about 25% of a homogenizing organic solvent boiling below about 350° F. at atmospheric temperature, and about 50 to about 80% of water.

9. An aqueous rust preventive and cleansing composition comprising about 5 to about 40% of a soap of a preferentially oil-soluble petroleum sulfonic acid, about 0.25 to about 10% of an antirust agent of the type of alkylamine soaps, about 2 to about 25% of a volatile, oxygenated organic solvent boiling below about 350° F. at atmospheric pressure selected from the group consisting of isobutyl alcohol, diacetone alcohol, the methyl ether of ethylene glycol monoacetate and ethylene glycol diethyl ether, and about 50 to about 80% of water.

10. The composition of claim 9 wherein the petroleum sulfonic acid is of the type produced by treating a petroleum distillate having a viscosity in the range of about 50 to about 1000 seconds Saybolt Universal at 100° F. with from about 6 to about 9 pounds of strong sulfuric acid per gallon of oil.

11. An aqueous composition adapted to inhibit fingerprint corrosion of metals having the following formula:

	Per cent by volume
Sodium soap of a preferentially oil-soluble petroleum sulfonic acid <sup>1</sup> .....	13
2-amino-2-methyl-1-propanol naphthenate.....	3
Isobutyl alcohol.....	5
Diacetone alcohol.....	3.9
Water.....	70.1
Hydrocarbon oil (viscosity 55 seconds Saybolt Universal at 100° F.).....	5

<sup>1</sup>Of the type produced by treating a petroleum distillate having a viscosity in the range of about 50 to about 1000 seconds Saybolt Universal at 100° F. with from about 6 to about 9 pounds of strong sulfuric acid per gallon of oil.

12. An aqueous rust preventive and cleansing composition comprising about 5 to about 40% of a preferentially oil-soluble organic sulfonate, about 0.02 to about 2% of an antirust agent of the type of sodium nitrite, about 0.25 to about 10% of an antirust agent of the type of alkylamine soaps, about 2 to about 25% of a homogenizing organic solvent boiling below about 350° F. at atmospheric pressure, and about 50 to about 80% of water.

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**Certificate of Correction**

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It is hereby certified that errors appear in the printed specification of the above numbered patent requiring correction as follows: Column 7, lines 68-69, claim 5; column 8, lines 4-5, claim 6; line 13, claim 7; lines 21-22, claim 8; for the word "temperature" read *pressure*; and that the said Letters Patent should be read with these corrections therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 3rd day of September, A. D. 1946.

**[SEAL]**

**LESLIE FRAZER,**  
*First Assistant Commissioner of Patents.*