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3,086,871

**COATING COMPOSITION**

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This application is a continuation-in-part of application Serial No. 759,849, filed September 9, 1958, now abandoned.

The invention concerns a coating composition which gives long-lasting protection against corrosion to coated metal surfaces, especially chromium plated, or stainless steel surfaces. The composition contains about 5 to 80% water, about 1 to 80% low-boiling hydrocarbon, about 0 to 9% high-boiling petroleum hydrocarbon, about 0.5 to 10% boiled linseed oil, about 1 to 10% petroleum paraffin wax having a melting point of about 125 to 145° F., and about 0.1 to 2% sorbitan mono fatty acid ester, about 0.05 to 1% of a sulfonate selected from the group consisting of oil-soluble ammonium aromatic sulfonate, and an oil-soluble sodium aromatic sulfonate, about 0 to about 1.0% of an antioxidant, 0 to about 1.0% of a germicide and 0 to about 15% of an antifreeze agent.

The coating composition of this invention is designed to plug the naturally-occurring cracks and pores in chrome plate, leaving behind a surface film which detracts to a minimum degree from the bright chromium surface, although it has protective and lasting properties comparable to thick coatings. This surface film can be polished after evaporation of the solvent. It has been shown that the composition is more effective when water is present. The linseed oil content gives a tougher film, curing to a hard finish. The wax component acts as an emulsifier and also gives barrier protection as well as overcoming stickiness due to the linseed oil. Water is usually included in the composition in a range of 20 to 80%, but when the composition is to be applied as an aerosol about 5 to 10% water is then advisable. The low boiling liquid hydrocarbon is one which boils in the gas oil range or below, e.g. kerosene, naphtha, gas oil, etc. A preferred hydrocarbon is "alkylate solvent"—the product formed when a C<sub>3</sub> or C<sub>4</sub> olefin is alkylated with isobutane. As an example, this product may have the following typical physical properties:

|                       |            |      |
|-----------------------|------------|------|
| Gravity, ° API        | -----      | 52.1 |
| 100 ml. distillation: |            |      |
| Initial B.P.          | ----- ° F. | 368  |
| 10%                   | ----- ° F. | 388  |
| 50%                   | ----- ° F. | 402  |
| 90%                   | ----- ° F. | 434  |
| End point             | ----- ° F. | 476  |
| Flash, Pensky-Martens | ----- ° F. | 145  |

The high boiling point petroleum hydrocarbon is of lubricating oil viscosity and preferably is a Mid-Continent neutral oil. Since the ammonium mahogany sulfonate is frequently made in oils of this type the quantity of high boiling petroleum hydrocarbon, if any, can be conveniently supplied to the composition by using the total mixture formed in the manufacture of the ammonium sulfonate.

The aromatic sulfonates useful in this invention are the oil-soluble NH<sub>4</sub>-aromatic sulfonates and oil-soluble sodium aromatic sulfonates of the benzene or naphthalene series, in which the aromatic ring is sulfonated and, in order to impart oil-solubility, the ring preferably also contains one or more alkyl substituents having up to a total of twenty carbon atoms. Such sulfonates can be made by the ammonium hydroxide or sodium hydroxide neutralization of sulfonated aralykyl hydrocarbons such as dinonyl naphthalene, and include neutralized sulfo-

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nated bottoms from the manufacture of dodecyl-benzene, neolene, etc. fractions. Typical aromatic sulfonates are described for instance in U.S. Patent 2,594,266. They can be obtained by the reaction of ammonia or sodium hydroxide with sulfuric acid-treated hydrocarbon oils. Such mahogany sulfonates possess appreciable solubility in both water and hydrocarbon oils. In manufacturing the supplement of the invention, the sulfonates may be employed as a concentrate in the oil from which they are derived. A typical concentrate for use in this composition has, for example, a sulfonate concentration of about 10% by weight and can be prepared by treating a Mid-Continent neutral oil with four successive dumps of oleum, a total of 120 pounds of the oleum being used for each barrel of oil. Following removal of the separable sludge after the last dump of oleum, the acid oil is blown with air to remove sulfur dioxide and settled to remove substantially the last trace of sludge. Thereafter the oil is mixed with 0.5% by weight of water and neutralized with an excess of anhydrous ammonia. Finally the oil is heated to a temperature of 280° F. to dehydrate it, and filtered to obtain the product.

Although the sulfonates are advantageously employed in the oil solution in which they may be prepared, the sulfonates can be recovered by extraction with a low molecular weight alcohol, such as isopropanol or ethanol, followed by distillation for use in the oil-free form. Aniline or a lower molecular weight oil-soluble alcohol, such as isopropanol, is advantageously added to sulfonate solution in small amounts to improve the stability thereof.

The petroleum wax may be paraffin or crystalline wax melting in the range from about 125 to 145° F.

The fatty acid mono esters of sorbitan useful in this composition are obtained by the esterification of sorbitan with fatty acids containing from 6 to 18, preferably at least 12, carbon atoms. The fatty acids can be those derived from various animal and vegetable oils and fats or synthetic fatty acids. Examples of suitable acids are caproic, caprylic, capric, lauric, myristic, palmitic, oleic, linoleic, linolenic, ricinoleic, stearic and dihydroxy stearic acids. Sorbitan is the partially dehydrated polyhydric alcohol 1,2,3,4,5,6-hexanehexol. The esters are made by reacting 1 mol of the polyhydric alcohol or 1 mol of the partially dehydrated alcohol with one to three mols of carboxylic acid or carboxylic acid mixtures either in the presence of or absence of a catalyst and/or hydrocarbon solvent. The catalyst may be acidic, for example, sulfuric or phosphoric acid, or alkaline, like sodium hydroxide. The ingredients are commingled and heated in a kettle or other container, preferably closed and equipped with suitable agitating means, at a temperature of 150 to 300° C. until the reaction reaches the desired stage. It is frequently desirable to maintain an atmosphere of inert gas such as nitrogen or carbon dioxide over the reacting mass or pass the inert gas through the reacting mass in order to assist removal of water and prevent discoloration of the esters formed. The reaction may also be carried out while refluxing hydrocarbon solvent, with means provided for trapping out the water formed. These esters are well-known to the art and methods for their preparation have been described for example in U.S. Patent 2,322,820. These esters are commercially available in the "Span" series. "Span 20" is sorbitan monolaurate; "Span 40" is sorbitan monopalmitate and "Span 60" is sorbitan monooleate. "Span 80" is a mixture of sorbitan mono fatty acids made from commercial fatty acid mixtures and contains sorbitan monostearate. In addition, these esters are available in less highly refined form in the "Atpet" series. "Atpet 100," for example, is a dark red oily liquid having a specific gravity of 0.98 to 1.00, a minimum viscosity at 25° C. of 900

cp., an acid number of less than 7, a hydroxyl number of 160 to 185, a saponification number of 140 to 155 and a pour point of 50 to 85° F. "Atpet 200" is a sorbitan partial fatty ester. It is an amber-colored oily liquid having a specific gravity at 25° C. of approximately 1, a viscosity at 25° C. of approximately 1000 cp., an acid number of 4 to 8, a hydroxy number of 180 to 205, a saponification number of 135 to 150, and a pour point of approximately 0° F. "Span" and "Atpet" are trademarks of the Atlas Powder Company.

If desired antioxidants can be incorporated into the compositions of the present invention. The presence of an antioxidant is preferred mainly for the reason that it protects the linseed oil component of the novel composition against oxidation. Suitable antioxidants for use in the present invention are the alkyl substituted phenols such as 2,6-ditertiary butyl, 4-methyl phenol; 2,4,6-tritertiary butyl phenol; ortho tertiary butyl phenol; alkyl substituted nitrogen-containing phenols such as n,n-butyl-p-aminophenol; isobutyl-p-aminophenol and n,n-di-secondary butyl phenylene diamine. The above antioxidants are to be considered as merely exemplary and as not limiting the use of other antioxidants that are effective in hydrocarbons.

Germicides, likewise, if desired, can be used in the present invention. Use of a germicide is preferred, however, for the purpose of protecting the sulfonate component of the present invention against attack from bacteria. The germicides useful in our invention are those effective against bacteria known as the "sulfate reducing" or anaerobic type. The germicides include but are not limited to the following types: halogens, phenols, heavy metal salts, acids triphenylmethane dyes, amines and aldehydes. By a halogen type germicide we mean to include halogens such as iodine and organic halogen compounds such as organic chloramines, e.g. "Chloramine-T," a commercial germicide in which the active ingredient is sodium para-toluene sulfonchloramide, and chlorobenzenes, e.g. "Cuniphen 2722," a commercial germicide in which the active ingredient is 2,2'-methylenebis (4-chlorophenol). By a phenol type germicide we mean to include phenols such as ortho-cresol and thymol (1-methyl-3-hydroxy-4-isopropyl-benzene), and halogenated phenols such as chlorinated phenols, e.g. "Dowicide 6," a commercial germicide in which the active ingredient is tetrachlorophenol and "Nalco 21-S," a commercial germicide in which the active ingredient is trichlorophenolate and sodium pentachlorophenolate. By a heavy metal salt type germicide we mean to include heavy metal salts such as copper salts, e.g. "Cuprosee," a commercial germicide in which the active ingredient is copper citrate, and organic mercury compounds, e.g. mercurochrome. By an acid type germicide we mean to include acids such as boric acid and 2,4,5-trichlorophenoxy acetic acid. Examples of triphenylmethane dye type germicides include dyes such as malachite green. Examples of amine type germicides include amine type compounds such as "Nalco X-234," a commercial germicide comprising 1-(2-hydroxyethyl)-1-benzyl-2-tridecyl imidazolium nitrite in an alcohol co-solvent. It is non-phenolic and contains no heavy metals. Examples of aldehyde-type germicides include formaldehyde.

Although unnecessary, the use of anti-freezes in the present invention can be desirable particularly in cold climates. Suitable alcohol anti-freezes are the glycols such as ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol and the lower monohydric alcohols such as methyl, ethyl, propyl and butyl alcohol.

It is preferred to have the ingredients present in the approximate ranges:

|                                         | Percent  |
|-----------------------------------------|----------|
| Water -----                             | 50 to 80 |
| Low boiling hydrocarbon-----            | 10 to 30 |
| High boiling petroleum hydrocarbon----- | 1 to 5   |
| Boiled linseed oil-----                 | 2 to 7   |

|                                     | Percent     |
|-------------------------------------|-------------|
| Petroleum wax-----                  | 1 to 5      |
| Sorbitan mono gatty acid ester----- | 0.1 to 1.5  |
| Aromatic sulfonate-----             | 0.1 to 0.5  |
| 5 Anti-freezes -----                | 2 to 15     |
| Anti-oxidant -----                  | 0.05 to 0.5 |
| Germicide -----                     | .1 to 1     |

A specific formulation of the composition of the invention is:

|                                         | Percent |
|-----------------------------------------|---------|
| Ammonium mahogany sulfonate-----        | 0.3     |
| Sorbitan mono fatty acid ester-----     | 1.0     |
| 135-137° F. M.P. paraffin wax-----      | 2.0     |
| 15 Boiled linseed oil-----              | 4.0     |
| High boiling petroleum hydrocarbon----- | 2.7     |
| Low boiling hydrocarbon-----            | 25.0    |
| Water -----                             | 65.0    |
|                                         | 100.0   |

The above specific formulation can also include about 0.05 to 0.5% of an anti-oxidant, .1 to 2% of a germicide and 2 to 15% of an anti-freeze.

The following examples and tests are included to further illustrate the present invention.

A suggested way to prepare these coating compositions is first to mix the non-aqueous materials at about 150° F. and then add this mixture slowly to highly agitated water at about 150° F. and mix until an emulsion is formed. It is preferred, however, to mix the non-aqueous constituents to a temperature of at least about 135° F. and to add to this mixture with rapid stirring the water heated to a temperature greater than about 135° F.

#### EXAMPLE I

Table I below shows the results of tests comparing the corrosion resistant qualities of the composition of the invention with other coating compositions.

Chrome plated automobile license plate fasteners were selected as test specimens. Metallographic examination determined the chrome plating to be a typical automotive chrome-plated product as to its thickness and application. The license plate fasteners were used both new and also after pre-rusting. The pre-rusted (old) specimens were reconditioned by acid cleaning to a corrosion-product-free surface before application of the polish. Because of a limited supply of stainless steel automobile porthole grilles, most of the testing was done with automobile license plate fasteners, but tests performed on the stainless steel specimens gave comparable results. The test specimens were exposed until failure, that is, until more than a trace of rust was observed, under three different conditions: (1) the regular MIL-L-3150 salt fog cabinet, wherein ASTM synthetic sea water is fogged into a cabinet maintained at 95° F.; (2) the same cabinet with the same conditions except deionized water was used instead of the synthetic sea water; and (3) immersion in ASTM synthetic sea water.

The formulations reported in Table I are as follows. Formula I consisted of an emulsion containing 1% Atpet 100, 3% of a solution containing 10% ammonium mahogany sulfonate in the petroleum lubricating oil in which it was manufactured, 2% paraffin wax (M.P. 135 to 137° F.), 44% alkylate, solvent and 50% water. III is an emulsion containing 1% Atpet 100, 3% of the ammonium mahogany sulfonate solution of formulation I, 4% boiled linseed oil, 2% paraffin wax (M.P. 135 to 137° F.), 40% alkylate solvent and 50% water. II is a formulation containing 4% of a mixture containing 75% of the 10% ammonium mahogany sulfonate of Formulation I and 25% Atpet 100, 4% boiled linseed oil and 92% alkylate solvent. These formulations were compared with each other by coating a chrome-plated automobile license plate fastener with each and subjecting it

to the test conditions described. Half a dozen fasteners were also coated each with a different automobile polish purchased at retail in the Chicago area. Typical test results for such a fastener are also reported, as well as the corrosive effects of the test conditions on a license plate fastener which was not given any additional polish coating.

ASTM synthetic sea water provides a solution containing inorganic salts in proportions representative of ocean water. The process by which this water is made can be found on page 295 of the November 1957 Book of ASTM Standards on Petroleum Products and Lubricants. This standard synthetic sea water has a pH of 8.2 and contains:

| Compound—                            | Gms./l. |
|--------------------------------------|---------|
| NaCl                                 | 24.54   |
| MgCl <sub>2</sub> ·6H <sub>2</sub> O | 11.10   |
| Na <sub>2</sub> SO <sub>4</sub>      | 4.09    |
| CaCl <sub>2</sub>                    | 1.16    |
| KCl                                  | 0.69    |
| NaHCO <sub>3</sub>                   | 0.20    |
| KBr                                  | 0.10    |
| H <sub>3</sub> BO <sub>3</sub>       | 0.03    |
| SrCl <sub>2</sub> ·6H <sub>2</sub> O | 0.04    |
| NaF                                  | 0.003   |

Table I

TEST RESULTS, CHROME AUTOMOTIVE PARTS

| Test specimens           | Failure time, days |     |           |     |                      |     |
|--------------------------|--------------------|-----|-----------|-----|----------------------|-----|
|                          | Salt fog           |     | Water fog |     | Salt water immersion |     |
|                          | New                | Old | New       | Old | New                  | Old |
| Formula:                 |                    |     |           |     |                      |     |
| I                        | 17+                | 5   | 13+       | 7   | 15                   | 6   |
| II                       | 10                 | 3   | 11        | 5   | 5                    | 5   |
| III                      | 14+                | 8   |           | 11+ | 30                   | 30  |
| Conventional auto polish | 2                  | 1   | 4         | 2   | 1                    | 1   |
| No treatment             | 1                  | 1   | 2         | 1   | 1                    | 1   |

<sup>1</sup> No rust or only a trace of rust when test was discontinued.

Table II

RESULTS OF CHROME PRESERVATIVE TESTS ON CARS

| Make of automobile | Treatment and bright metal trim condition |                                                  |  |         |                                                                                                                    |
|--------------------|-------------------------------------------|--------------------------------------------------|--|---------|--------------------------------------------------------------------------------------------------------------------|
|                    | Coating                                   | Driver's side                                    |  | Coating | Passenger's side                                                                                                   |
| Chrysler           | III                                       | No change since start of test                    |  | B2      | Chrome-plated die casting erupted further.                                                                         |
| Cadillac I         | III                                       | do                                               |  | B1      | Do.                                                                                                                |
| Ford I             | III                                       | do                                               |  | C2      | Stainless steel trim spotted.                                                                                      |
| Chevrolet I        | III                                       | do                                               |  | None    | Rust on wrap-around portion of front and back bumpers; rust on bumper over tailpipe; stainless steel trim spotted. |
| Chevrolet II       | A1                                        | Light patches of rust on rear bumper             |  | III     | Good condition.                                                                                                    |
| Buick              | B2                                        | Chrome-plated die casting erupted further        |  | III     | No change since start of test. <sup>1</sup>                                                                        |
| De Soto            | None                                      | Patches of rust on bumper over tailpipe          |  | III     | Good condition.                                                                                                    |
| Plymouth I         | B2                                        | Good condition                                   |  | None    | Patches of rust on rear bumper below license plate.                                                                |
| Plymouth II        | A3                                        | do                                               |  | do      | Rusted areas on rear bumper; chrome-plated die casting erupted.                                                    |
| Cadillac II        | A2                                        | Chrome-plated die casting erupted <sup>2</sup>   |  | III     | Good condition.                                                                                                    |
| Lincoln            | II                                        | Good condition except for a residual sticky film |  | A3      | Chrome-plated die casting erupted.                                                                                 |
| Ford II            | A3                                        | Good condition                                   |  | II      | Good condition except for a residual sticky film.                                                                  |

<sup>1</sup> A section of plating on the right rear fender was completely peeled off and was heavily rusted before the test.  
<sup>2</sup> A section of plating on the left front fender was completely peeled off but apparently did not rust.

It can easily be seen that Formulations II and III which contain boiled linseed oil give far longer-lasting corrosion protection to chrome-plated surfaces than the average commercially sold automobile polish, and Formulation III also gives markedly better protection than Formulation I, which did not contain boiled linseed oil, or Formulation II, which did not contain water or wax. Formulation II, which did not contain wax, was found to be difficult to apply. Formulation III, however, was satisfactory as to its application characteristics.

Road tests.—Cars were field tested in the Chicago metropolitan area during the winter months. The trim

on one side of each of twelve automobiles was treated, once a month, either with Formulation III, a commercial wax, polish or cleaner, or given no treatment. The Chrysler, Cadillac I, Ford I, Chevrolet I, Buick and Plymouth I were coated about November 1 and the other models received their initial treatment in the latter part of December. Various combinations of the composition of the invention, commercially sold polishes, and no treatment were thus tested side by side. The commercial waxes and polishes tested are identified in the table below as A3, B2, etc., the brands of the same manufacturer or distributor being given the same letter and different numbers. Liquid polishes have been given odd numbers, while paste "waxes" are given even numbers. All the cars were washed at least every two weeks and generally at least once a week. The trim was always free of dust and dirt before any of the coatings was applied. Two of the cars were used to evaluate the experimental Formula II product described above. Table II shows the treatment given each car and condition of the bright metal in the following May.

The trim of these cars received much better care than average and one would not expect much deterioration. However, close inspection of the trim shows that frequent washing alone will not prevent trim corrosion and the use of presently available commercial products, while slowing down the corrosion process, will not consistently arrest it completely. Chrome-plated die casting appears to be the most easily corroded of all bright metal trim and the composition of the invention gives excellent corrosion protection to automobile bright metal trim.

Formulation IV, an emulsion of 30% water, 60% alkylate solvent, 3.5% paraffin wax (M.P. 130-132° F.), 2.5% boiled linseed oil, 3% ammonium mahogany sulfonate concentrate (10% sulfonate, remainder petroleum lubricating oil) and 1% Span 80, and Formulation V, an emulsion of 50% water, 3% paraffin wax having a melting point of 138 to 140° F., 0.5% Span 80, 0.1% ammonium mahogany sulfonate, 6% boiled linseed oil and the rest alkylate solvent also give satisfactory performance in preventing corrosion of chromium plated automotive parts.

In accordance with the preferred method of the present invention the non-aqueous constituents are first mixed together at a temperature greater than about 135° F. Then the water, heated to a temperature greater than about 135° F. is added to the mixture. It is advantageous that the water be added slowly to assure a water-in-oil emulsion. If added too rapidly an oil-in-water emulsion might result producing an inferior corrosion preventive. The mixing speeds and temperatures employed have a definite effect on the emulsion stability and corrosion preventive properties of the coating composition of the

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present invention. The non-aqueous constituents should be heated above about 135° F. to assure solution of the paraffin wax. A temperature of about 150° F. is generally chosen to make sure complete solution is obtained before the water is introduced. The water when added should be at a temperature above about 135° F., preferably about 150° F. Formulations wherein the water is less than 135° F. when added are not as stable or as effective as corrosion preventives as the formulations where the water was 135° F. or higher. Furthermore, formulations limited to about 50 to 80% water are not only the most stable emulsions but possess best corrosion preventive properties. Also, as will be demonstrated, when faster mixing speeds are used a better product results.

To illustrate the advantages of adding water to the non-aqueous constituents in accordance with the preferred method of preparation rather than the non-aqueous constituents to the water, Examples II to V are included.

#### EXAMPLE II

Formulations containing 2% paraffin wax (135 to 137° F., M.P.), 4% of a mixture composed of 75% of a solution containing 10% ammonium mahogany sulfonate in the petroleum lubricating oil in which it was manufactured and 25% Atpet 200, 4% boiled linsed oil, various amounts of water, with the balance alkylate solvent, were prepared either by adding the non-aqueous constituents to the water or adding the water to the non-aqueous constituents. In all cases the non-aqueous constituents were mixed together at 150° F. and the temperature of both the water and non-aqueous constituents before admixture was 150° F. Addition, whether of water to hydrocarbons or hydrocarbons to water was conducted slowly to assure an emulsion. Mixing of the non-aqueous constituents and water was conducted at a speed of 12,000 r.p.m. and continued until the temperature fell to 130° F. These formulations were compared with each other by (1) coating metal panels with the different formulations and subjecting the panels to the regular MIL-L-3150 salt fog cabinet test wherein ASTM synthetic sea water is fogged into a cabinet maintained at 95° F. and (2) by measuring the percent of separation of water and oil from the formulation after three weeks of storage.

The results are illustrated in Table III.

Table III

| Percent water used | Water-in-oil emulsion |                                         |     |                                                        | Oil-in-water emulsion |                                         |       |                                                        |
|--------------------|-----------------------|-----------------------------------------|-----|--------------------------------------------------------|-----------------------|-----------------------------------------|-------|--------------------------------------------------------|
|                    | Sample #982-          | Three weeks' storage, percent separated |     | MIL-L-3150, salt fog results, percent rust at 72 hours | Sample #982-          | Three weeks' storage, percent separated |       | MIL-L-3150, salt fog results, percent rust at 72 hours |
|                    |                       | Water                                   | Oil |                                                        |                       | Water                                   | Oil   |                                                        |
| 80.....            | 249                   | 2                                       | 5   | 5                                                      | 250                   | 45                                      | 5     | 35                                                     |
| 70.....            | 166                   | 2                                       | 2   | 3                                                      | 172                   | 35                                      | Trace | 10                                                     |
| 65.....            | 165                   | None                                    | 2   | None                                                   | 171                   | 25                                      | Trace | 1 35                                                   |
| 60.....            | 157                   | None                                    | 7   | 1                                                      | 158                   | 20                                      | Trace | 2 75                                                   |
| 55.....            | 159                   | None                                    | 10  | 6                                                      | 160                   | 15                                      | Trace | 2 75                                                   |
| 50.....            | 161                   | None                                    | 15  | 25                                                     | 162                   | 10                                      | Trace | 2 80                                                   |
| 45.....            | 163                   | None                                    | 20  | 50                                                     | 164                   | 5                                       | Trace | 2 35                                                   |

<sup>1</sup> Test stopped at 48 hours.

<sup>2</sup> Test stopped at 24 hours.

#### EXAMPLE III

Formulations containing 2% paraffin wax (135 to 137° F., M.P.), 4% of a mixture composed of 75% of a solution containing 10% ammonium mahogany sulfonate on the petroleum lubricating oil in which it was made and 25% Atpet 200, 4% boiled linsed oil, various amounts of water ranging from 25 to 80% with the balance alkylate solvent were prepared by adding water to the non-aqueous constituents as described in Example II. As in Example II the formulations were given the 3 week storage stability and the salt fog cabinet test. These results are given in Table IV.

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Table IV

| Sample #982- | Percent water used | Stability, 3 weeks' storage, percent separated |     | MIL-L-3150, salt fog test results, percent rust at 72 hrs. |
|--------------|--------------------|------------------------------------------------|-----|------------------------------------------------------------|
|              |                    | Water                                          | Oil |                                                            |
| 249.....     | 80                 | 2                                              | 5   | 5                                                          |
| 166.....     | 70                 | 2                                              | 2   | 3                                                          |
| 165.....     | 65                 | None                                           | 2   | None                                                       |
| 157.....     | 60                 | None                                           | 7   | 1                                                          |
| 159.....     | 55                 | None                                           | 10  | 6                                                          |
| 161.....     | 50                 | None                                           | 15  | 25                                                         |
| 163.....     | 45                 | None                                           | 20  | 1 50                                                       |
| 173.....     | 35                 | None                                           | 50  | 1 30                                                       |
| 178.....     | 25                 | None                                           | 60  | 2 90                                                       |

<sup>1</sup> Test stopped at 48 hours.

<sup>2</sup> Test stopped at 24 hours.

#### EXAMPLE IV

The formulation of Example II having 65% water and 25% alkylate solvent was prepared in accordance with the method of Example II but using water of various temperatures during formulation. The test results are found in Table V.

Table V

| Sample No. 982- | Temperature, ° F. |             | Stability, 3 weeks' storage percent oil separated | MIL-L-3150 salt fog test results, percent rust at 72 hours |
|-----------------|-------------------|-------------|---------------------------------------------------|------------------------------------------------------------|
|                 | Water             | Hydrocarbon |                                                   |                                                            |
| 180.....        | 75                | 150         | 5                                                 | 10                                                         |
| 181.....        | 100               | 150         | 4                                                 | 3                                                          |
| 182.....        | 125               | 150         | 3                                                 | 2                                                          |
| 183.....        | 135               | 150         | 2                                                 | None                                                       |
| 165.....        | 150               | 150         | 2                                                 | None                                                       |

#### EXAMPLE V

Formulations containing 2% paraffin wax (135 to 137° F., M.P.), 4% of a mixture of 75% of a solution containing ammonium mahogany sulfonate in the petroleum lubricating oil in which it was made and 25% Atpet 200, 4% boiled linsed oil, 65% water and 25% alkylate solvent were prepared in accordance with the method of Example I using various mixing speeds during admixture of the water with the non-aqueous constituents. The formulations were tested as in the previous examples. Results of the tests are shown in Table VI.

Table VI

| Sample No. 982- | Stirrer speed, r.p.m. <sup>1</sup> | Stability, 3 weeks' storage, percent oil separated | MIL-L-3150, salt fog test results, percent rust at 72 hours |
|-----------------|------------------------------------|----------------------------------------------------|-------------------------------------------------------------|
| 189.....        | 200                                | 15                                                 | 5                                                           |
| 190.....        | 2,000                              | 6                                                  | Trace                                                       |
| 191.....        | 3,300                              | 3                                                  | None                                                        |
| 192.....        | 4,000                              | 2                                                  | None                                                        |
| 193.....        | 5,000                              | 2                                                  | None                                                        |
| 165.....        | 12,000                             | 2                                                  | None                                                        |

<sup>1</sup> Brookfield counter rotating mixer with 1½" blades. Approximate stirring speeds shown.

Examination of the test data shows the following:

The data of Table II demonstrates that much more corrosion protection is afforded when the water is added to the non-aqueous constituents than when the reverse procedure is used. The preparation containing 65% water when prepared by adding water to the oil protected the mild steel panels 72 hours in the MIL-L-3150 salt fog test, while the same formulation prepared by adding the oil to the water allowed the panels to rust 35% in 48 hours. When other amounts of water, i.e. 50% to 80%, are present the differences in corrosion protection are also quite pronounced.

The data of Table IV demonstrates that 65% water content is the optimum for emulsion stability as well as corrosion preventive qualities. As the content of water decreases or increases both the emulsion stability and corrosion preventive qualities worsen. For optimum stability and activity the water content should be about 55 to 80%.

The effects of mixing speeds and temperatures are evident from Tables V and VI. The formulations in Table V wherein the water was less than 135° F. when added were not as stable or as effective as corrosion preventives as the formulations where the water was 135° F. or higher. It is demonstrated in Table VI that when faster mixing speeds are used a better product results.

#### EXAMPLE VI

Formulations containing 2% paraffin wax (135 to 137° F., M.P.), 0.5% of the sulfonate indicated below in petroleum lubricating oil, 25% Atpet 200, 4% boiled linseed oil, 65% water with the balance alkylate solvent were prepared by adding the water to the non-aqueous constituents. Metal panels were coated with each of the formulations and subjected to the salt fog cabinet test. The results were as follows:

Table VII

MIL-L-3150 SALT FOG TEST RESULTS AND STABILITY INSPECTION

| Sulfonate                                    | Percent of panel rusted at— |          |          | Percent oil separated at three weeks |
|----------------------------------------------|-----------------------------|----------|----------|--------------------------------------|
|                                              | 24 hours                    | 48 hours | 72 hours |                                      |
| RD-119 <sup>1</sup> .....                    | None                        | None     | None     | 2                                    |
| RD-119 <sup>2</sup> .....                    | 1                           | 6        | 15       | 10                                   |
| C-base <sup>3</sup> .....                    | 70                          | (a)      | (a)      | -----                                |
| NaSul ammonium sulfonate <sup>4</sup> .....  | 50                          | (a)      | (a)      | -----                                |
| Bryton ammonium sulfonate <sup>5</sup> ..... | 10                          | 30       | (b)      | -----                                |
| Na aromatic sulfonate.....                   | 2                           | 4        | 7        | 3                                    |

<sup>1</sup> 10% concentrate ammonium mahogany sulfonate in Mid-Continent neutral oil from which it was derived.

<sup>2</sup> 10% concentrate ammonium mahogany sulfonate in Sweet Texas Distillate from which it was derived.

<sup>3</sup> Oil-soluble sulfonic acid prepared by the sulfonation of the bottoms produced in the manufacture of monododecyl benzene which bottoms consist essentially of didodecyl benzene along with a minor amount of other polyalkylated benzene molecules.

<sup>4</sup> Ammonium hydroxide neutralized sulfonated dinonyl naphthalene.

<sup>5</sup> Neutralized sulfonate bottoms from the manufacture of benzene.

<sup>a</sup> Test stopped at 24 hours.

<sup>b</sup> Test stopped at 48 hours.

The results show that of all the sulfonates, better corrosion resistance in a salt water environment is obtained when ammonium mahogany sulfonate is employed. This is not to be construed as meaning that the other sulfonates are poor corrosion inhibitors, however, for all of the sulfonates give satisfactory rust inhibiting properties outside of a salt environment.

#### EXAMPLE VII

A formulation containing 2% paraffin wax (135 to 137° F. melting point wax), 4% boiled linseed oil, 4% of a mixture composed of 75% of a solution containing 10% ammonium mahogany sulfonate in the petroleum lubricating oil in which it was manufactured and 25% Atpet 200, 0.3% of 2,6-ditertiary butyl-4-methyl phenol, 0.5% of ortho cresol, 65% water with the balance alkylate solvent

was prepared. Metal panels were coated with formulation and subjected to the salt fog test for 72 hours. No rust was found.

#### EXAMPLE VIII

To the formulation of Example VII was added 8.0% of ethylene glycol. This formulation was tested as in Example VII and similarly no rust was found.

It is to be understood that the anti-oxidant, germicide and anti-freeze employed in Examples VII and VIII could be replaced by any of those listed in the specification. Similarly, the ammonium mahogany sulfonate can be replaced by a sodium aromatic sulfonate.

We claim:

1. A coating composition consisting essentially of about 0.05% to 1% of a sulfonate selected from the group consisting of oil-soluble ammonium aromatic sulfonate and an oil-soluble sodium aromatic sulfonate, about 0.25% to 2% sorbitan mono fatty acid ester, about 1% to 10% petroleum paraffin wax having a melting point of about 125 to 145° F., about 0.5 to 10% boiled linseed oil, up to about 9% high-boiling petroleum hydrocarbon, about 1-80% low-boiling hydrocarbon and about 5-80% water.

2. A coating composition consisting essentially of about 0.05% to 1% of a sulfonate selected from the group consisting of oil-soluble ammonium aromatic sulfonate and an oil-soluble sodium aromatic sulfonate, about 0.25% to 2% sorbitan mono fatty acid ester, about 1% to 10% petroleum paraffin wax having a melting point of about 125 to 145° F., about 0.5 to 10% boiled linseed oil up to about 9% high-boiling petroleum hydrocarbon, about 1-80% low-boiling hydrocarbon and about 5-80% water, about .05 to 1% of an anti-oxidant to protect said linseed oil against oxidation and 0 to 1.0% of a germicide to protect said sulfonate from bacterial attack.

3. A coating composition consisting essentially of approximately 50 to 80% water, 10 to 30% low-boiling hydrocarbon, 1 to 5% petroleum lubricating oil, 2 to 7% boiled linseed oil, 1 to 5% petroleum paraffin wax (melting point 125 to 145° F.), 0.1 to 1.5% sorbitan mono fatty acid ester and 0.1 to 0.5% of a sulfonate selected from the group consisting of oil-soluble ammonium aromatic sulfonate and oil-soluble sodium aromatic sulfonate.

4. A coating composition consisting essentially of approximately 50 to 80% water, 10 to 30% low-boiling hydrocarbon, 1 to 5% petroleum lubricating oil, 2 to 7% boiled linseed oil, 1 to 5% petroleum paraffin wax (melting point 125 to 145° F.), 0.1 to 1.5% sorbitan mono fatty acid ester and 0.1 to 0.5% of a sulfonate selected from the group consisting of oil-soluble ammonium aromatic sulfonate and oil-soluble sodium aromatic sulfonate, about .05 to 1% antioxidant to protect said linseed oil against oxidation and about .05 to 0.5% of a germicide to protect said sulfonate against bacterial attack.

5. A coating composition comprising the following ingredients in approximately the following proportions:

|                                          | Percent |
|------------------------------------------|---------|
| Ammonium mahogany sulfonate .....        | 0.3     |
| Sorbitan mono fatty acid ester .....     | 1.0     |
| 135-137° F. M.P. paraffin wax .....      | 2.0     |
| Boiled linseed oil .....                 | 4.0     |
| High-boiling petroleum hydrocarbon ..... | 2.7     |
| Low-boiling hydrocarbon .....            | 24.7    |
| Water .....                              | 65.0    |
| Anti-oxidant .....                       | 0.3     |

6. A method of preparing the coating composition of claim 1 which comprises mixing the non-aqueous constituents to a temperature of at least about 135° F. and adding to said mixture with rapid stirring the water heated to a temperature greater than about 135° F.

7. A water-in-oil emulsion composition consisting essentially of approximately 50 to 80% water, 10 to 30%

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low-boiling hydrocarbon, 2 to 7% boiled linseed oil, 1 to 5% petroleum paraffin wax (melting point 125 to 145° F.), 0.5 to 1.5% sorbitan mono fatty acid ester and 0.1 to 0.5% of a sulfonate selected from the group consisting of oil-soluble ammonium aromatic sulfonate and oil-soluble sodium aromatic sulfonate. 5

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