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COATING COMPOSITION AND METHOD

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This application is a continuation-in-part of application Serial No. 759,850, filed September 9, 1958, now abandoned.

The present invention concerns a novel supplement for wax-containing coating compositions which imparts long-lasting corrosion inhibiting properties to the composition. The resulting coating composition may be used on enameled metal surfaces as well as chromium-plated or stainless steel surfaces.

Much chrome plating is purely decorative and gives litle long-time corrosion protection. Moisture and corrosive agents seep into voids in the chrome plating and corrode the base metal underneath. The products of corrosion bleed out through the voids and produce an unsightly appearance. As a result, chrome-plated automobile bumpers and other non-enameled metal parts are apt to corrode quite badly especially when exposed to winter-time weather and road conditions. In the winter, salt used for deicing streets, soot, corrosives, and solids in the atmosphere tend to collect on automobiles. Infrequent washing of automobiles maintains an environment that is conducive to corroding chrome automotive parts and even stainless steel trim.

Stainless steels vary in their resistance to saline water corrosion. The grade often used in automotive trim, while more resistant to saline waters than mild steel, is not as corrosion resistant as desirable. Furthermore, the paint film is often imperfect where the trim is attached and conditions at the juncture of body and trim are ideal for crevice corrosion. The application of conventional paste waxes and liquid polishes to chrome plated and stainless steel parts generally does not provide a film thick enough or impervious enough to keep air, water, and corrodents from either the gaps or cracks in chrome plating or the surfaces of the stainless steel. Neither do they provide adequate protection against crevice corrosion.

It has now been discovered that a corrosion inhibiting supplement for automobile polish, comprising a mixture of an oil-soluble aromatic sulfonate and a fatty acid monoester of sorbitan in particular proportions may be incorporated in commercially available automobile liquid polishes and paste wax compositions to give these coating compositions greatly improved corrosion resisting properties. The supplement can be incorporated in the polishes or waxes in proportions of about 1–10% by weight, preferably about 2.0–6.5%.

The supplement has about 1–10, preferably about 1–5 parts by weight, of a sorbitan mono-fatty acid ester and about 1–5 preferably about 1–2 parts by weight of an oil-soluble aromatic sulfonate selected from the group consisting of oil-soluble ammonium aromatic sulfonates and oil-soluble sodium aromatic sulfonates. The sulfonate is usually available in solution in a petroleum oil such as lubricating oil. This solution frequently contains about 10% by weight of the sulfonate and the lubricating oil can be the native environment in which the sulfonate has been prepared. Where this preferred proportion of sulfonate prevails in the solution the proportions of ingredients in the supplement are approximately 5 to 10% of the sulfonate, 5 to 50% of the sorbitan mono-fatty acid ester and 45 to 90% of the high boiling mineral lubricating oil in which the ammonium sulfonate has been prepared.

The fatty acid monoesters of sorbitan useful in the supplement are obtained by the esterification of sorbitan by fatty acids containing from 6 to 18 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 can be 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. 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 150–300° 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 monoleate. "Span 80" is a mixture of sorbitan mono-fatty acids made from commercial fatty acid mixtures and contain 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 less than 7, a hydroxyl number of 160 to 185, a saponification number of 140–155 and a pour point of 50–85° 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 hydroxyl 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.

The aromatic sulfonates useful in this invention are the oil-soluble NH_4-aromatic sulfonates and the 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 respectively, by the ammonium hydroxide or sodium hydroxide neutralization of sulfonated aralkyl hydrocarbons such as dinonyl naphthalene, and include the neutralized sulfonated 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, commonly known as mahogany acids. Such 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 solution having, for example, a sulfonate concentration of about 10 percent by weight, 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 percent 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 ammonium mahogany sulfonates and sodium mahogany sulfonates are advantageously employed in the oil solution in which they are 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. In these circumstances the sulfonate may comprise about 9 to about 65% of the supplement of the invention with the rest sorbitan mono-fatty acid ester. The distillation procedure is disclosed in U.S. Patent No. 2,461,371. Aniline or a lower molecular weight oil-soluble alcohol, such as isopropanol is advantageously added to the sulfonate solution in small amounts to improve the stability thereof. Such ammonium mahogany sulfonate solutions of greater stability are disclosed in U.S. Patent Nos. 2,522,518 and 5,522,519.

The two ingredients of the supplement may be incorporated in commercial wax-containing liquid or paste waxes in minor amounts separately or as a blend. The resulting compositions contain preferably 0.25–2% sorbitan mono-fatty acid ester and 0.05–1% of the aromatic sulfonate. To add the supplement constituents as a blend, Atpet 200, for example, may be easily mixed with the ammonium or sodium mahogany sulfonate oil solution, for example, by heating to 110 to 120° F. with stirring. A blend of 25 percent by weight of Atpet 200 and 75 percent by weight of a 10 percent oil solution of ammonium mahogany sulfonate, for example, is a dark oily mixture with a viscosity similar to SAE 20 lubricating oil. A special complete formulation has been developed which uses the supplement and not only provides greatly enhanced corrosion resisting properties to surfaces to which it is applied, but also greatly enhanced durability of an unexpected nature. This complete formulation is described in copending application Serial No. 759,849, filed September 9, 1958.

One of the commercial liquid preparations reported in Tables I and II to which the novel supplement may be added is described in U.S. Patent No. 2,250,667 as follows:

	Percent
Gum tragacanth	0.18
Formaldehyde	1.06
Water	71.04
Methyl cellulose	0.14
Glycerine	2.91
Diatomaceous earth	11.10
Beeswax	0.28
Carnauba wax	0.02
Neutral oil	12.38
Amyl acetate	0.19
Ferric oxide	0.20
Turkey red oil	0.50
	100.00

Another automobile polish tested reportedly has the following ingredients:

	Percent
Sodium carboxymethyl cellulose	0.75
Neutral oil	13.00
Blown castor oil	0.75
Diatomaceous earth	13.00
Water	69.00
Sulfonated castor oil	0.50
Formaldehyde	0.50
Glycerine	2.00
Paraffin wax	0.50
	100.00

Still another reported is:

	Percent
Dimethyl polysiloxane	1.00
Oxidized microcrystalline wax	3.00
Light petroleum naphtha	96.00
	100.00

In order to determine the effectiveness of the supplement of the invention, tests were performed on commercially available automotive polishes and "wax" compositions and on some original formulations containing the supplement.

Such formulations may contain, besides about 1–10% of the supplement, about 1–10% petroleum wax, which may be paraffin or crystalline wax having a melting point of about 125–145° F., 20–98% low-boiling liquid hydrocarbon and 0–80% water. The low-boiling hydrocarbon is usually one which boils in the gas oil range or below, e.g. kerosene, naphtha, gas oil, etc. An alkylate solvent made by alkylating C_3–C_4 olefins with isobutane is preferred which may have for example, the following typical physical properties:

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

Preferably such formulations contain approximately 50–80% water, 10–30% low-boiling hydrocarbon solvent, 1–6% of the petroleum wax and 2.0 to 6.5% of the supplement. When such a formulation is to be applied as an aerosol, the water content is preferably 5–10% and the low boiling hydrocarbon solvent 80–95%. Also if desired, the formulation may contain anti-freeze agents, germicides and anti-oxidants in effective amounts.

The presence of an antioxidant is preferred mainly for the reason that it protects the oil components 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.

Use of a germicide is preferred 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 chlor-

amines, e.g. "Chloramine-T," a commercial germicide in which the active ingredient is sodium paratoluene 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-isopropylbenzene), 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 trichlorophenate and sodium pentachlorophenate. By a heavy metal salt type germicide we mean to include heavy metal salts such as copper salts, e.g. "Cuprose," 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 imidazolinium 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 antifreezes in the present invention can be desirable particularly in cold climates. Suitable alcohol antifreezes 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.

In the preparation of the above water-base formulations, the non-aqueous constituents are mixed at a temperature of at least about 135° F., preferably about 150° F., and the resulting mixture then agitated with water at a temperature of at least about 135° F. It is particularly preferred in these preparations to add slowly about 50 to 80%, more preferably 60 to 70%, water at a temperature about 150° F. to a mixture of the non-aqueous constituents rather than adding the mixture of non-aqueous constituents to the water. When water is added to the non-aqueous constituents a water-in-oil emulsion results which allows the preparation to coat chrome plate or stainless steel with an inhibitor film that repels water and affords long lasting protection from rusting. When the non-aqueous constituents are added to the water, however, an oil-in-water emulsion results. Chrome plate and stainless steel coated with this emulsion are more easily washed free of the protective inhibitor film causing rusting to occur more rapidly.

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 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°, 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.

A stable emulsion (S–1) was prepared which contained 2% paraffin wax (M.P. 135–137° F.), 1% Atpet 100, 3% ammonium mahogany sulfonate (10% concentrate in petroleum lubricating oil), 44% low-boiling petroleum hydrocarbon solvent, and 50% water. Mild steel panels, polished to a smooth finish of 6 to 12 micron surface roughness, were coated with the above formulation. The panels were exposed in a JAN–H 792 specification humidity cabinet maintained at 120° F. and 100% relative humidity for 14 days, but showed no rusting. Another formulation (S–2) containing 2% paraffin wax (M.P. 135–137° F.), 1.5% Atpet 100, 0.45% ammonium mahogany sulfonate, about 4% high boiling petroleum hydrocarbon and the rest low-boiling hydrocarbon solvent was applied to test panels and after exposure for 14 days in the same humidity cabinet showed only minor amounts of rust. If the wax content of this formulation was increased to 6% wax, no rusting at all occurred during a comparable exposure period, but the wax content was so high that at room temperature the preparation was solid. A formulation S–4 containing 0.5% of sodium mahogany sulfonate, 2% paraffin wax (M.P. 135–137° F.), 1% Atpet 200, about 2.5% high boiling petroleum hydrocarbon, about 25% low-boiling hydrocarbon solvent and about 65% water was applied to test panels and after exposure for 14 days in the humidity cabinet test showed no rust. By low-boiling hydrocarbon is meant 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_3 or C_4 olefin is alkylated with isobutane. The high-boiling petroleum hydrocarbon is one of lubricating viscosity and preferably is a Mid-Continent neutral oil.

Chrome-plated automobile license plate fasteners were selected as test specimens for the other tests. 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 prerusting. The prerusted (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 Buick porthole grilles, most of the testing was done with the 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.

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.	Compound	Gms./l.
$NaCl$	24.54	$NaHCO_3$	0.20
$MgCl_2 \cdot 6H_2O$	11.10	KBr	0.10
Na_2SO_4	4.09	H_3BO_3	0.03
$CaCl_2$	1.16	$SrCl_2 \cdot 6H_2O$	0.04
KCl	0.69	NaF	0.003

The formulation "S–3" consisted of an emulsion containing 1% Atpet 100, 3% ammonium mahogany sulfonate concentrate (10% in petroleum lubricating oil), 2% paraffin wax (M.P. 135–137° F.), 44% low-boiling petroleum hydrocarbon solvent and 50% water. This formulation and commercial automotive polishes with and without the supplement of the invention were compared with each other by coating a chrome-plated automobile license plate fastener with each subjecting it to the test conditons described.

Table I reports the corrosive effects of the test conditions on a license plate fastener which was not given any additional polish coating as well as the effects of the addition of 4% of the supplement on commercially available liquid automobile polishes and paste waxes. These commercial automobile waxes and polishes are identified in the table below as A3, B2, etc., the brands of the same manufacturer being given the same letter and different numbers. Liquid polishes have been given odd numbers, while paste "waxes" are given even numbers.

It is apparent from these test results that wax-containing coating compositions in liquid or paste form, containing the supplement of the present invention, can impart great corrosion resistance to chrome-plated automotive parts. The wax may be a hydrocarbon or an ester-type wax.

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 the following examples are included.

Example I

Formulations containing 2% paraffin wax (135–137° 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 linseed 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. 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 II.

TABLE I

Test specimen	Chrome automotive part failure time, days											Mild steel panels, percent rusted at 14 days [1]	
	Salt fog				Water fog			Salt water immersion					
	New		Old		New	Old		New		Old		No	Yes
4% supplement added	No	Yes	No	Yes	No	No	Yes	No	Yes	No	Yes		
Coating composition:													
B2 paste	1–	8		3		1–		1	4		3	100 hvy	10 lt.
B1 liquid	1–				4	2		2		1		50 med	15 lt.
A3 liquid	2	5	1	3	6	2		1–	31		3	100 hvy	10 lt.
A1 liquid	3	7	2	3	6	1		1–	3			50 med	5 lt.
D2 paste	3		1–									100 hvy	Trace.
A2 paste					3	1–		1–				80 med	3 lt.
D1 liquid							1–					100 v. hvy	30 lt.
C2 paste												90 hvy	Trace.
No treatment	1		1–		2	1–		1–		1–		100 v. hvy	
S3	[2] 7+		5		[2] 13+	7		15		6			Zero.

[1] MIL–C–8188B specs; panels polished to a 6–12 micron surface roughness and exposed at 120° F. and 100% relative humidity in a JAN–H 792 spec cabinet.

[2] No rust or only a trace of rust when test was discontinued.

Formulation "S–5," an emulsion of 30% water, 63% alkylate solvent, 2% paraffin wax (M.P. 130–132° F.), 3% ammonium mahogany sulfonate concentrate (10% sulfonate in petroleum lubricating oil) and 1% Span 80, and formulation "S–6," an emulsion of 50% water, 45.5% alkylate solvent, 3% paraffin wax having a melting point of 138–140° F., 0.5% Span 20, 1% ammonium mahogany sulfonate (10% in petroleum lubricating oil) give satisfactory performance in preventing corrosion of chromium-plated and stainless steel automotive parts. Formulation "S–7" is an emulsion of 1% Atpet 200, 3% ammonium mahogany sulfonate (10% in petroleum lubricating oil), 4% boiled linseed oil, 2% paraffin wax, 25% low-boiling petroleum hydrocarbon and 65% water.

TABLE II

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	[1] 50	164	5	Trace	[2] 35

[1] Test stopped at 48 hours. [2] Test stopped at 24 hours.

Example II

A water-in-oil emulsion containing 2% paraffin wax (135–137° F., M.P.), 4% of a mixture composed of 75% of a solution containing 10% of ammonium mahogany sulfonate in the petroleum lubricating oil in which it was made and 25% Atpet 200, 4% boiled linseed 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 I. As in Example I the formulations were given the 3 week storage stability and the salt fog cabinet test. These results are given in Table III.

TABLE III

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

[1] Test stopped at 48 hours. [2] Test stopped at 24 hours.

Example III

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 IV.

TABLE IV

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 IV

Formulations containing 2% paraffin wax (135–137° 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 linseed 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 V.

TABLE V

Sample No. 982–	Stirrer speed, r.p.m.[1]	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

[1] Brookfield counter rotating mixer with 1⅜" blades. Approximate stirring speeds shown.

Examination of the test data shows the following:

The data in Table II demonstrates that 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 II 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 III and IV. The formulations in Table III 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 IV that when faster mixing speeds are used a better product results.

Example V

Formulations containing 2% paraffin wax (135–137° 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 was 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 VI.—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 [1]	None	None	None	2
RD–119 [2]	1	6	15	10
C-base [3]	70	[a]	[a]	----------
NaSul ammonium sulfonate [4]	50	[a]	[a]	----------
Bryton ammonium sulfonate [5]	10	30	[b]	----------
Na aromatic sulfonate	2	4	7	3

[1] 10% concentrate ammonium mahogany sulfonate in Mid-Continent neutral oil from which it was derived.
[2] 10% concentrate ammonium mahogany sulfonate in Sweet Texas Distillate from which it was derived.
[3] 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.
[4] Ammonium hydroxide neutralized sulfonated dinonyl naphthalene.
[5] Neutralized sulfonate bottoms from the manufacture of benzene.
[a] Test stopped at 24 hours.
[b] 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 VI

A formulation containing 2% paraffin wax (135–137° 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 the antioxidant, 2,6-ditertiary butyl-4-methyl phenol, 0.5% of ortho cresol as a germacide 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 VII

To the formulation of Example VI was added 5.0% of ethylene glycol. This formulation was tested as in Example VI and similarly no rust was detected.

It is to be understood that the antioxidant, germacide and antifreeze employed in Examples VI and VII could be replaced by any of those listed in the specification. Similarly, the ammonium mahogany sulfonate can be replaced by a sodium aromatic sulfonate.

It is claimed:

1. A water-in-oil emulsion consisting essentially of 50–80% water, 10–30% low-boiling petroleum hydrocarbons, 1–6% petroleum wax having a melting point of 125–140° F., and 2.0 to 6.5% of a mixture containing 4 to 6% of a sulfonate selected from the group consisting of ammonium mahogany sulfonate and sodium mahogany sulfonate, 5–50% of a sorbitan mono-fatty acid ester and the rest a high-boiling petroleum hydrocarbon.

2. The emulsion of claim 1 containing 0.25 to 2% sorbitan mono-fatty acid ester and 0.05–1% of the mahogany sulfonate.

3. The method of preventing the corrosion of chromium-plated metal which comprises coating the chromium-plated metal with the emulsion of claim 5.

4. A method of preparing the water-in-oil emulsion of claim 5 which comprises heating 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.

5. A water-in-oil emulsion consisting essentially of about 50 to 80% water, about 10 to 46.7% liquid petroleum hydrocarbon, 0.3 to 10% wax, about 0.05 to 1% of a sufonate selected from the group consisting of oil-soluble ammonium aromatic sulfonates and oil-soluble sodium aromatic sulfonates, and about 0.05 to 5% of a sorbitan mono-fatty acid ester.

6. The emulsion of claim 5 wherein the sulfonate is a mahogany sulfonate and the mono-fatty acid ester is sorbitan monooleate present in an amount of about 0.25 to 2%.

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