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(71) Applicant: **KING INDUSTRIES, INC.**
Science Road
Norwalk Connecticut 06852(US)

(72) Inventor: **Gallacher, Lawrence Vincent**
136 Gregory Boulevard
Norwalk, CT 06851(US)

(74) Representative: **Roggero, Sergio et al**
Ing. Barzanò & Zanardo Milano S.p.A. Via
Borgonuovo 10
I-20121 Milano(IT)

(54) Amine dinonylnaphthalene sulfonates with corrosion inhibiting properties.

(57) Compositions comprising amine salts of alkylaromatic sulfonic acids, alone, or with a synergist, provide excellent corrosion inhibition and other significant characteristics such as demulsiblity, and are useful in applications where it is desirable to limit ash formation.

AMINE DINONYLNAPHTHALENE SULFONATES WITH CORROSION INHIBITING PROPERTIES

FIELD OF THE INVENTION

The present invention relates to ashless corrosion inhibiting compositions with excellent demulsibililty characteristics which include amine salts of dinonylnaphthalene sulfonates, alone or in combination with synergists.

BACKGROUND OF THE INVENTION

Lubricating oils and the like are commonly modified through the use of various additives or improvement agents for use in internal combustion engines, such as automotive, light aircraft and diesel engines. In particular, these lubricating oils require the use of additive agents to render them serviceable under the adverse environmental conditions frequently encountered in the operation of these engines.

Among the functions provided by such lubricant additives are detergency enhancement, corrosion-inhibition, oxidation stability, viscosity modification, anti-wear and extreme pressure protection, and the like. It is also well-known that oil-soluble metal sulfonates give enhanced corrosion protection, particularly in salt-containing environments, when combined with weak acids, such as carboxylic acids, and their ester and soap derivatives. Although not well understood, it is generally believed that this synergism involves mixed surface monolayers, analogous to mixed micelles. These oil-soluble metal sulfonates are useful as additives in fuels and in lubricating oil additives for engines. As additives for lubricating oils, the metal sulfonates retard the accumulation of sludge and thereby prevent engine fouling by virtue of their dispersant activity. They also function as corrosion inhibitors. However, since they contain metals, these conventional additives form ash deposits (i.e., solid residues) after combustion in the engine when added to the lubricating oil. Therefore, it is desirable to provide other additives which have similar desirable qualities without the presence of the ash-forming metal.

Dinonylnaphthalene sulfonic acid (HDNNS®, available commercially from King Industries, Inc. Norwalk, CT, U.S.A.) is well-known in the art as a replacement for petroleum sulfonic acids which are used in rubber plasticizers and processing aids, and the metal salts of this acid also have proven to be excellent for use in oil-soluble corrosion inhibitors.

It has been found that dinonylnaphthalene sulfonic acid and its salts form inverted micelles in non-polar media with the polar ends of the molecules turning inward. The extreme tendency of dinonylnaphthalene sulfonic acid salts to form miceller aggregates is consistent with a strong tendency to form monolayers at oil/air and oil/metal interfaces. The formation of very stable monolayers at oil/metal interfaces helps to explain why metal salts of dinonylnaphthalene sulfonic acid, particularly the barium, calcium and zinc salts, are effective oil-soluble corrosion inhibitors. The same characteristic contributes to the useful behavior of dinonylnaphthalene sulfonic acid salts, particularly the divalent metal salts, in acting as demulsifiers in oil media containing other surface-active compounds. However, these metal salts have the same previously-mentioned drawback of ash production.

Despite the known efficiency of amines and amine derivatives of carboxylic acids in inhibiting certain types of corrosion, relatively little work has been done with amine sulfonates as active corrosion inhibitors in lubricants and rust preventives. Ammonia and ethylene diamine salts of dinonylnaphthalene sulfonic acid have been commercially available for years (as NA-SUL® AS and NA-SUL® EDS/NA-SUL® LP from King Industries Inc., respectively), but there has been little development of applications for amine sulfonates. This is surprising, in view of growing interest in ashless additives.

In prior art applications, amine sulfonates have been used as promoters in overbasing calcium or magnesium sulfonates. In this context, "over-based" means that the sulfonates contain an amount of magnesium substantially in excess of that required to form a neutral sulfonate. For instance, Sabol et al. in U.S. 4,201,682 over-based oil-soluble magnesium sulfonate compositions by one-step carbonation of a reaction mixture containing magnesium hydroxide. The sulfonate anion-affording materials used for the formation of the neutral magnesium sulfonate in the over-based product are oil-soluble sulfonic acids such as alkyl-substituted benzene or alkyl-naphthalene sulfonic acids. Similarly, Arnold et al. in U.S. 4,225,446 disclose an improved process for the preparation of fluid, highly basic magnesium sulfonates useful as lubricants for engines and as diesel fuel additives. the Arnold et al. process uses oil-soluble sulfonic acids prepared from alkyl or alkaryl hydrocarbons.

Also, Vaughan in U.S. 4,248,718 discloses overbased dispersants for lubricating oils having a very low ash content in comparison to the conventional overbased additives. These are prepared by reacting an ashless nitrogen-containing compound such as ammonia with a basically reacting metal compound, a suspending agent, a chalcogen compound such as carbon dioxide, and preferably a promoter such as ethanol.

In addition to the use of amine sulfonates as promoters in overbasing metal sulfonates, they have also been used as dispersants. For example, U.S. 3,960,937 discloses ashless additives for lubricating oils obtained by first reacting a petroleum sulfonic acid and a polyamine and then combining the product with a cyclic anhydride of a dicarboxylic acid.

Because the resultant compositions avoid the presence of an ash forming metal, they do not form deposits when used as detergent additives for lubricating oils such as engine oil or when added to oil which is mixed with gasoline in 2-stroke engines.

Finally, U.S. 3,979, 478 (Gallacher) discloses that when amino resins such as urea formaldehyde and melamine formaldehyde thermosetting resins are cured with high molecular weight polyalkylaromatic sulfonic acids, curing occurs much more rapidly at conventional temperatures than achieved previously.

It has now been unexpectedly discovered that amine dinonylnaphthalene sulfonates are very effective ashless corrosion inhibitors by themselves and show strong synergism when combined with carboxylic acid derivatives. Moreover, when careful attention is paid to the type of amine used surprising and unexpected enhancement of demulsibility is obtained. Thus, the particular amine dinonylnaphthalene sulfonates of this invention may be used in many corrosion inhibiting applications where metal sulfonates cannot be used and where ashless additives are nearly essential, such as in gasoline, fuel oil, and 2-cycle engine oil, while limiting any tendency to form stable emulsions which is bad.

SUMMARY OF THE INVENTION

According to the present invention there are provided corrosion-inhibiting compositions with good demulsibility characteristics comprising

(A) a salt of

i) an alkylaromatic sulfonic acid and;

ii) an amine having at least three carbon atoms and no oxygen atoms; and

(B) A liquid diluent therefor.

The present invention further contemplates such corrosion inhibiting compositions which further comprise a synergist such as a petroleum oxidate, an oil-soluble carboxylic acid, a metal or amine soap thereof, an ester thereof, an amide thereof, or a mixture of any of the foregoing.

In preferred embodiments, the alkylaromatic sulfonic acid is dinonylnaphthalene sulfonic acid, the nonyl radicals of which are highly branched.

It is also preferable that the amine component (ii) comprise an aliphatic monoamine, an aliphatic polyamine, or a substituted or unsubstituted aliphatic heterocyclic amine.

Among the features of the invention are articles comprising a metallic substrate normally susceptible to corrosion and, on at least a portion of the substrate, a protective layer of an ashless corrosion inhibiting composition defined above.

DETAILED DESCRIPTION

The alkylaromatic sulfonic acid comprising component (i) can vary widely in chemical nature, so long as it has a minimum molecular weight of about 350. If a phenyl nucleus is present, these requirements can be met with a benzenesulfonic acid containing at least about one or two alkyl groups having a total of at least about 14 carbon atoms, e.g., didocecylbenzenesulfonic acid. Instead of a phenyl nucleus, the aromatic nucleus can be polycyclic, e.g., naphthyl, anthracyl, phenanthryl, etc. Many variations in the position of substitution are possible and contemplated and mixed positional isomers are included. The alkyl substituents can be straight or branched chain. Best results are obtained with maximum variations in substituent locations and with maximum branching.

The most preferred alkylaromatic sulfonic acids are branched alkyl-substituted naphthalenesulfonic acids. These are available, for example, by sulfonating polyalkylnaphthalenes. The polyalkylnaphthalenes can be made by alkylating naphthalene with olefins, for example, propylene trimer or tetramer, or alkyl halides, with a suitable catalyst, e.g., hydrogen fluoride or anhydrous aluminum chloride in a suitable solvent such as naphtha, sulfur dioxide, nitrobenzene or a mixture of benzene and nitrobenzene. See Robert G. King and George W. Thielcke, U.S. Pat. No. 2,764,548, assigned to the assignee of the present invention. Such a process produces naphthalene substituted with alkyl groups and, if a branched olefin is used, such as propylene trimer or propylene tetramer, obtained by polymerizing propylene with an acid catalyst such as phosphoric acid, then the alkyl groups will be highly branched as well. Sulfonation is accomplished by treating the alkylaromatic compound with a sulfonating agent. For example, dinonylnaphthalene is dissolved in an inert solvent, such as petroleum naphtha, hexane, heptane, octane, chlorinated solvents, and the like, and sulfuric acid, preferably oleum, is introduced into the solution at the desired temperature and with agitation. After reaction is complete, the sulfonic acid is recovered by separating and drawing off a heavy spent sulfonic acid layer and then extracting the sulfonic acid water to remove polysulfonic acids and residual sulfonic acid. A detailed technique for preparing dinonylnaphthalene sulfonic acid, didodecylnaphthalene disulfonic acid and isomers and analogs thereof, including the benzene analogs, is described in the King et al. patent, U.S. Pat. No. 2,764,548.

The nitrogen-containing compound corresponding to component (ii) serves as a source of supply of basic material in the additives of this invention. By "ashless" is meant a substance which after combustion has no non-volatile residue. This ashless nitrogen-containing compound can vary broadly. It will be an amine containing at least 3 carbon atoms and no oxygen atoms. Mixtures of different amines may also be used. In general, the amines will be selected from readily available aliphatic amines, polyamines, substituted and unsubstituted aliphatic heterocyclic amines, and the like.

Amines preferred for use in this reaction are aliphatic monoamines and polyamines having from at least 3 up to 50 carbon atoms in the aliphatic portion of the molecule, and aliphatic polyamines such as propanediamine and the like. Aliphatic monoamines include propylamine, octylamine, dicosoamine, decylamine, di(octyl)amine, tallowamine, eicosylamine, and the like. The amine may be derived from natural or synthetic sources using methods well known in the art. Preferred monoamines are C_{3-20} alkylamines and particularly preferred are the C_3-C_8 alkylmonoamines.

The polyalkylenepolyamines are prepared for example from ammonia and ethylenechloride or ethylene oxide and have a general repeating structure $H_2N(CH_2CH_2)_xH$ where x is 2-20. Especially preferred compounds are those where x is 2-6.

The aliphatic heterocyclic amines are those well known amines including substituted and unsubstituted piperidines, pyrrolidines and the like.

The ethyleneamines are those well known amines such as diethylenetriamine, triethylenetetramine, tetraethylenepentamine, pentaethylenehexamine and the like.

Propyleneamines are a class of polyamines prepared by the reaction of acrylonitrile with an ethyleneamine, such as those described above and having the formula $H_2N(CH_2CH_2)_xH$ where x is 1 to 5, followed by hydrogenation of the resultant intermediate. For example, the products prepared from ethylenediamine and acrylonitrile would be $H_2N(CH_2)_3NH(CH_2)_2NH(CH_2)_3NH_2$.

The most preferred amines are diethylene triamine, triethylenetetramine, 2-methylpentanediamine, and 3-methylpiperidine.

Many diluents, both volatile and non-volatile, are suitable for use in the compositions of the present invention. The principle requisites desired in a diluent are that it acts as a solvent for the various components. If an oil, it should have a flash point of 385°-400° F. or above. A wide variety of oils, both natural and synthetic such as naphthenic bases, paraffin bases diesters and mixed-base oils may be used. Advantageously, the diluent oil is a naphthenic lubricating oil. Preferably this naphthenic lubricating oil has a viscosity range of 50-200 SUS at 100° F. Natural and synthetic solvents well known in this art such as poly-alpha-olefins, mineral spirits, kerosene, polyglycols, and the like, can also be used as the diluents.

It is within the scope of the present invention to use conventional synergists. These can comprise any of the carboxylic acids or derivatives and/or petroleum oxidates conventionally used as synergists with prior art metal sulfonates. In a preferred embodiment, the synergist comprises oxidized petrolatum.

In addition, when compositions according to the present invention are to be used as corrosion-inhibiting coatings for metals, it is possible to add suitable thickeners in effective amounts. The thickeners which can be used may be any of the well known thickeners of the prior art. Preferably, the thickener, if used, will comprise an oxidized polyethylene wax, a polyamide thixotrope, an overbased calcium sulfonate, an ethylene-vinyl acetate copolymer, and the like in an amount of, for example 0.01 to 5 percent by weight of the total composition.

The amine salts of the polyalkylaromatic polysulfonates may be prepared by any of the methods well known in the art. One such method of their preparation is set forth in previously-mentioned U.S. Patent No. 2,764,548.

The corrosion-inhibiting compositions in accordance with the present invention may be prepared by providing an effective amount of the dinonylnaphthalene amine sulfonate in the diluent. A concentrate can first be prepared and this may be further diluted with the same or another diluent or mixutre of such diluents. The relative amounts of the amine sulfonates may be varied widely. Generally, they are provided in similar proportions to the proportions of metal sulfonates used in the prior art. It is preferred, however, that a 50 percent active salt (in diluent oil) be diluted to from about 20 to 70 percent by weight with the diluent for use.

In general, the synergist may be added to the composition in proportions well known in the art as applied to the metal sulfonates. It is preferred, however, that the synergist and sulfonate be present in the composition at a combined amount from about 10 to about 99 percent by weight of the total composition.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The following examples illustrate the present invention. They are not to be construed to limit the claims in any manner whatsoever.

Comparative Examples 1-6 and Examples 7-21

Amine dinonylnaphthalene sulfonates in accordance with the present invention and of the prior art were prepared by direct neutralization of 38 percent active dinonylnaphthalene sulfonic acid in heptane with the appropriate amine, oil addition, and stripping with final adjustment to 50 percent active sulfonate content. The diluent oil used was a 75 second solvent-extracted naphthenic oil (Telura® 415, commercially available from Exxon Corp.). The particular amine dinonylnaphthalene sulfonates prepared are shown in Table 1. The first four amine dinonylnaphthalene sulfonates listed in Table 1 are based on the series $H_2N\text{-}(CH_2CH_2NH)_n\text{-}H$, where "n" varies from 0 to 3. Barium dinonylnaphthalene sulfonate was also prepared as a control sample corresponding to the prior art.

TABLE 1

AMINE SULFONATE SUMMARY	
All sulfonates are 50% active in naphthenic oil	
Designation	**Description**
AMM-S	50% Ammonium dinonylnaphthalene sulfonate (DNNS)
EDA-S	50% Ethylene diamine DNNS
DETA-S	50% Diethylene triamine DNNS
TETA-S	50% Triethylene tetramine DNNS
2-MPD-S	50% 2-Methylpentane diamine DNNS
3-MP-S	50% 3-Methylpiperidine DNNS
Comparison:	
BA-S	50% Barium DNNS

In the first series of tests, the six amine sulfonate preparations (at 50% active) were each diluted to 10% and 15% by weight in 75 second viscosity naphthenic oil. A third mixture was also made up consisting of 7.5% of the particular amine sulfonate preparation and 7.5% oxidized petrolatum with an acid value of 55 (ALOX® 600, ALOX Corporation), to evaluate possible synergistic behavior. As a comparison, equivalent mixtures were made using a 50% active barium dinonylnaphthalene sulfonate in oil (NA-SUL®BSN King

Industries). Cold-rolled steel panels, .032 inch, ground 1 side, were dip-coated with each mixture and allowed to drain vertically for 24 hours before being placed in the ASTM D-1748 humidity cabinet and B-117 salt-fog chamber. Two panels were used in each test, one with the ground side ("P") forward (humidity) or facing upward (salt fog), the other reversed (matte side, "M"). The time to failure was measured in hours for the designated side of each panel. The results are shown in Table 2.

TABLE 2

CORROSION TESTING OF AMINE SULFONATES IN OIL

EXAMPLE	MIXTURE	HOURS TO FAILURE			
		HUMIDITY		SALT FOG	
		P	M	P	M
1*	10% AMM-S	168	144	15	4
2*	15% AMM-S	312	312	13	7.5
3*	7.5% AMM-S/7.5% OX.PET.	312	216	16	15
4*	10% EDA-S	432	408	4	3
5*	15% EDA-S	456	408	4	3
6*	7.5% EDA-S/7.5% OX.PET.	408	264	13	8
7	10% DETA-S	648	508	4	3
8	15% DETA-S	648	648	6	4
9	7.5% DETA-S/7.5% OX.PET.	408	216	16	15
10	10% TETA-S	432	288	4	3
11	15% TETA-S	456	456	6	6
12	7.5% TETA-S/7.5% OX.PET.	288	288	14	8

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*Comparative Example

TABLE 2 cont'd

CORROSION TESTING OF AMINE SULFONATES IN OIL

		HOURS TO FAILURE			
		HUMIDITY		SALT FOG	
EXAMPLE	MIXTURE	P	M	P	M
13	10% 2-MPD-S	912	696	3	1
14	15% 2-MPD-S	912	816	3	1
15	7.5% 2-MPD-S/7.5% OX.PET.	504	336	16	14
16	10% 3-MP-S	432	432	1	1
17	15% 3-MP-S	528	288	1	1
18	7.5% 3-MP-S/7.5% OX.PET.	312	288	15	15
	REFERENCE				
19	10% BA-S	576+	408	4	3
20	15% BA-S	576+	432	7.5	6
21	7.5% BA-S/7/5% OX.PET.	288	264	16	15

The following conclusions can be made based on these results: (1) In humidity, the oxidate has a negative effect; in salt fog, the oxidate has a powerful synergistic effect. (2) Certain amine sulfonates, notably DETA-S and 2-MPD-S, give excellent performance in humidity, comparable to the reference barium sulfonate. (3) The amine sulfonates by themselves vary widely in salt-fog performance. However, in the presence of the oxidate, they are comparable to each other and to the barium sulfonate.

Examples 22-25

The ratio of 2-MPD-S to oxidate was varied in three steps from 1:2 to 2:1 in oil and mineral spirits. Also, the oxidate alone was evaluated in oil. The results are shown in Table 3.

TABLE 3

EFFECT OF 2-MPD-S/OXIDATE RATIO ON SALT-FOG PERFORMANCE IN OIL AND MINERAL SPIRITS							
EXAMPLE	MIXTURE	OIL DILUENT			MINERAL SPIRITS		
		THICKNESS MILS	SALT-FOG		THICKNESS MILS	SALT-FOG	
			P	M		P	M
22	10% -MPD-S/5% OX.PET.	0.10	24	20	0.05	3	4
23	7.5% 2-MP-S/7.5% OX.PET.	0.10	24	24	0.05	3	8
24	5% 2-MPD-S/10% OX.PET.	0.10	24	24	0.05	2	8
25	15% OX.PET.	0.10	2	2	----	---	---

The film thickness (in mils), was determined by weighing before and after film removal after 24 hours vertical draining, not including the lower edge where an extra "bead" is normally left.

These results together with the results shown in Table 2 confirmed the amine sulfonate/oxidate synergism, but failed to show a ratio effect. This could be the result of experimental uncertainty in the short-time failure range. In any event, it seems to be more than a simple matter of film thickness, and may be related to a greater film mobility in the oil-based coatings.

Examples 26-29

Examples 26-29 are directed to the effects of film thickness in oil-based systems. A 2-MPD-S/oxidate system (7.5% of each) is provided as the constant active component. Four thickeners were used: an oxidized polyethylene wax (Polymekon 300, Bareco); a polyamide thixotrope used in conventional hard coatings (DISLON® 6500, King Industries, Inc.); an overbased calcium sulfonate (SACI 200A, Witco); and an ethylene-vinyl acetate copolymer (AC-400, Allied). An attempt was made to obtain equivalent thickening with each additive using diluent oil alone, in order to get equivalent coating thickness. The results are set forth in Table 4.

TABLE 4

EFFECT OF THIXOTROPES ON 7.5% 2-MPD-S/7.5%OX.PET. PERFORMANCE IN SALT-FOG

EXAMPLE	% THIXOTROPE	DISPERSION METHOD	COATING THICKNESS,MILS*	SALT FOG,HOURS	
				P	M
26	2.8% oxidized polyethylene	Dissolve 90° C, cool	0.3	84	84
27	2.5% polyamide	Heat to 70° C high shear	1.9	484	390
28	25% overbased calcium sulfonate	Blend	0.35	48	55
29	8.5% ethylene-vinyl acetate copolymer	Dissolve 100° C, cool	0.35	72	48

* Average thickness excluding bottom 3/4" of panels.

As Table 4 shows, this was not particularly successful, but did give major improvements in salt-spray performance in every case. The most striking improvement was obtained with the polyamide thixotrope, which also gave by far the thickest coating. In order to see if the thixotrope has a beneficial effect by itself in oil, an additional two panels were coated with 2.5% polyamide in oil and subjected to salt-fog testing. The coating thickness was 4.1 mils, and the panels failed in 2 hours.

Examples 30-37

In order to evaluate combinations of amine sulfonates, other acid synergists and thickeners, all in oil, another series of formulations was prepared, panels were coated, and salt spray tests were performed. Again, coating thickness was measured without including the bottom draining edge of the panels. In addition, the average thickness including the bottom edge on several panels was determined in order to see if there was a significant "bead" effect. The other synergists evaluated in place of the oxidate were tetrapropenyl succinic acid (TPSA) and the monomethyl ester of hexadecenyl succinic acid (MHDSA). The results are shown in Table 5.

TABLE 5

FOG PERFORMANCE OF VARIOUS AMINE SULFONATE/SYNERGIST/THIXOTROPE COMBINATIONS IN OIL

EXAMPLE	MIXTURE	AVERAGE THICKNESS, MILS		HOURS TO FAILURE	
		W/O LOWER EDGE	W/LOWER EDGE	P	M
30	7.5% 2-MPD-S 7.5% OX.PET. 1.5% Polyamide	200	---	264	264
31	7.5% 2-MPD-S 7.5% OX.PET. 5% OX. Polyethylene	0.52	---	100	76
32	7.5% DETA-S 7.5% OX.PET. 1.5% Polyamide	2.25	---	288	288
33	7.5% DETA-S 7.5% OX.PET. 5% OX. Polyethylene	0.50	0.78	100	76
34	7.5% DETA-S 4.5% MHDSA 1.5% Polyamide	1.88	1.73	225	225
35	7.5% DETA-S 4.5% MHDSA 5 Ox Polyethylene	0.61	0.70	76	88
36	7.5% DETA-S 4.5% TPSA 1.5% Polyamide	2.17	2.02	264	246
37	7.5% DETA-S 4.5% TPSA 5% OX. Polyethylene	0.68	0.86	150	144

Broadly, these results show a strong dependence of salt fog performance on coating thickness. It is also apparent that MHDSA and TPSA are effective synergists in combinations with amine sulfonates. Comparison with Table 4 shows the polyamide to be less here in terms of time to failure at equivalent thickness. This is probably the result of the method of dispersing the polyamide thixotrope. In the Table 5 mixtures, the goal was to pre-dissolve the polyamide by heating a 3% polyamide/oil mixture, then cooling, adding the other ingredients, and shearing with a Cowles disperser. Unfortunately, the mixtures were heated to 105° C, not a high enough temperature to achieve a clear solution, and the final formulation gave grainy uneven coatings. In a subsequent experiment, uniform 1% polyamide coatings 1.10 mils thick were produced by pre-dissolving the polyamide in oil at 120° C, then cooling, combining ingredients, and shearing at 70° C.

Comparison Examples 38-39 and 44-46 and Examples 40-43

Examples 38-43 show the demulsibility of amine sulfonates in oil, as compared to reference Example 44-46.

A demulsifier is a surface-active material which de-stabilizes emulsions. In lubricating oil, water-in-oil emulsions can form readily as a result of water contamination, and "demulsibility", the tendency for such emulsions to break in the absence of shear, is an important characteristic. One of the more widely used demulsibility tests is ASTM D-1401 (American Society of Testing Materials), in which 40 ml each of water and oil are mixed in a grauated cylinder and then allowed to separate. The cylinders are observed at 5 minute intervals, and the time required to reach 3 ml or less of emulsion layer is taken as a measure of the demulsibility.

In running the test, the additive is run at a series of concentrations in an oil base containing a surface-active material which tends to promote emulsification. A standard light paraffinic base was used which contained approximately 0.5% zinc dioctyldithiophosphate. The 50% active amine sulfonates were each tested at 0.1%, 0.5%, 1.0% and 2.0%. The results are given in Table 6.

TABLE 6

THE DEMULSIBILITY OF EXPERIMENTAL AMINE SULFONATES IN THE ASTM D-1401 TEST					
EXAMPLE	WT.% 50% ACTIVE SULFONATE: SULFONATE TYPE	TIME IN MINUTES TO 3 ML. EMULSION			
		0.1	0.5	1.0	2.0
38*	AMM-S	40	10	15	NO SEP.
39*	EDA-S	60	5	15	NO SEP.
40	DETA-S	60	5	10	15
41	TETA-S	30	5	5	10
42	2-MPD-S	30	10	15	10
43	3-MP-S	---	15	10	10
	REFERENCE:				
44	BARIUM DNNS	23	15	10	10
45	CALCIUM, DNNS	18	5	10	10
46	BARIUM ALKYL BENZENE SULFONATE	23	34	60	60+

Demulsibility results obtained with three 50% active barium and calcium sulfonates are shown for comparison.

Typically, an ammonium or EDA sulfonate, both of which are outside the present invention exhibit slow separation at very low concentrations, rapid separation at intermediate concentrations and very slow separation at high concentrations (Comparative Example 38 and 39). A normal divalent metal dinonylnaphthalene sulfonate shows moderate separation time at low levels, which improves and levels off with increasing concentrations. Monovalent metal dinonylnaphthalene sulfonates generally separate more slowly with increasing concentration, and alkyl benzene sulfonates behave similarly.

In view of the above-mentioned experimental results, it may be concluded that the amine sulfonates in oil show a strong synergistic response in mixtures with carboxylic acids in salt-fog testing, just as metal sulfonates do, despite generally poorer performance when used alone in oil. Film thickness is also very important, but not in thickened oil films in the absence of rust inhibitors. On the other hand, several of the experimental amine sulfonates showed excellent efficiency in humidity tests.

All but two sulfonates, those based on ammonia and ethylene diamine, have excellent demulsibility characteristics, comparable at all but the lower concentrations to divalent metal DNNS sulfonates.

All of the above-mentioned patents are incorporated herein by reference.

Many variations of this invention well suggest themselves to those skilled in the art in light of the above detailed description. For example, didodecylnaphthalene disulfonic acid and the like may be used as the polyalkylaromatic polysulfonic acid instead of dinonylnaphthalene disulfonic acid. All such obvious variations are within the full intended scope of the appended claims.

Claims

1. An ashless corrosion-inhibiting composition with good demulsibility characteristics comprising
(A) a salt of
i) an alkylaromatic sulfonic acid; and
ii) an amine having at least three carbon atoms and no oxygen atoms; and
(B) a liquid diluent therefor.

2. A composition as defined in Claim 1, wherein said diluent comprises a synthetic oil, a natural oil, a volatile solvent or a mixture of any of the foregoing.

3. A composition as defined in Claim 1 wherein said component (i) comporise dinonylnaphthalene sulfonic acid, the nonyl radicals of which are highly branched.

4. A composition as defined in Claim 1 wherein component (ii) comprises an aliphatic monoamine, an aliphatic polyamine, or a mixture thereof.

5. A composition as defined in Claim 4 wherein said component (ii) comprises diethylenetriamine, triethylenetetramine, 2-methylpentanediamine or 3-methylpiperidine or a mixture of any of the foregoing.

6. A composition as defined in Claim 1 further comprising a synergist selected petroleum oxidate, an oil-soluble carboxylic acid derivative selected from a carboxylic acid, a metal or amine soap thereof, an ester thereof, an amide thereof or a mixture of any of the foregoing.

7. A composition as defined in Claim 6 wherein said component (ii) comprises diethylenetriamine, triethylenetetramine, 2-methylpentanediamine or 3-methylpiperidine or a mixture of any of the foregoing.

8. A corrosion inhibiting composition as defined in Claim 1 comprising from about 20 to about 70 percent by weight of said salt (A) and said diluent (B).

9. An ashless corrosion inhibiting composition as defined in Claim 6 comprising from about 10 to about 99 percent by weight of said salt (A) and said synergist.

10. An article comprising a metallic substrate normally susceptible to corrosion and, on at least a portion of said substrate, a protective layer of a corrosion inhibiting composition as defined in Claim 1.

11. An article comprising a metallic substrate normally susceptible to corrosion and, on at least one portion of said substrate, a protective layer of a corrosion inhibiting composition as defined in Claim 6.

12. An article as defined in Claim 10 wherein said component (i) comprises dinonylnaphthalene sulfonic acid, the nonyl radicals of which are highly branched.

13. An article as defined in Claim 10 wherein said component (ii) comprises an aliphatic monoamine, an aliphatic polyamine or a mixture thereof.

14. As ashless corrosion inhibiting composition as defined in Claim 1 wherein (i) comprises dinonylnaphthalene sulfonic acid and (ii) comprises diethylenetriamine, triethylenetetramine, 3-methylpiperdine, 2-methylpentanediamine or a mixture of any of the foregoing.

15. An ashless corrosion inhibiting composition as defined in Claim 6 wherein component (ii) comprises an aliphatic monoamine, an aliphatic polyamine or a mixture thereof.