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COMPOSITION FOR INHIBITING CORROSION IN TANKERS

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This invention relates to a composition for inhibiting the corrosion in the interior of tank ships or tankers and, more particularly, to an emulsion composition for inhibiting the corrosion in the interior of tankers.

One of the major problems in the shipping industry is the corrosion that occurs in the interior of tankers, in particular, tankers which carry light petroleum products such as gasoline, kerosene, and heating oils. These light petroleum products dissolve any oily or greasy material from the steel bulkheads and other supporting structures so that when the products are discharged from the ship their residual films evaporate readily from the interior steel surfaces, leaving a clean unprotected steel surface exposed. After discharging the cargo, usually about one-third of the total number of tanks of the tanker are filled with sea water to provide ballast and thereby render the ship seaworthy. This sea water ballast is exceedingly corrosive and the moist salt atmosphere is also exceedingly corrosive so that those tanks not carrying ballast are also subjected to severe corrosive conditions.

Many attempts have been made heretofore to solve the tanker corrosion problem, for example, the use of protective coatings, dehumidification of the non-ballasted tanks, cathodic protection, corrosion inhibitors incorporated in the seat water ballast or corrosion inhibitors included in the light product cargo itself. These solutions have met with only partial success. The protective coatings have been found to be unsatisfactory since difficulty has been encountered in providing a coating that would adhere to the surfaces to be protected and which would have a sufficiently long life to warrant the high initial cost. Dehumidification has been found to be only partially successful and, in addition, very expensive. Cathodic protection or inhibitors dissolved in the sea water ballast are satisfactory only for protecting those tanks carrying the ballast. Inhibitors dissolved in the light petroleum oil cargo have been found to be of little value in protecting the sea water ballasted tanks and the empty tanks exposed to the moist salt atmosphere and in addition such inhibitors are very costly.

It has been proposed also to apply a water-soluble corrosion inhibitor to the interior surfaces of a tanker by spraying such surfaces with a water solution. While this method has met with some success, it too has been found to be rather expensive and, in addition, difficulties have arisen from cargo contamination. Another proposal involved applying an aerosol fog of a corrosion inhibitor to the interior of a tanker, however, this method has been found also to be expensive.

A composition now has been found comprising an oil-in-water emulsion containing an oil-soluble corrosion inhibitor which may be sprayed directly onto the interior surfaces of the tanks of a tanker ship and which in particular provides excellent protection against moist salt atmosphere corrosion at a very low cost.

It is an object of this invention therefore to provide a corrosion inhibiting composition for the interior of tankers.

It is another object of this invention to provide a corrosion inhibiting composition for the interior of tankers which may be sprayed onto the surfaces to be protected.

It is another object of this invention to provide a corrosion inhibiting composition for the interior of tankers comprising an oil-in-water emulsion containing a corrosion inhibitor.

Other objects of this invention will be apparent from the description and claims that follow.

In accordance with the instant invention an oil-in-water emulsion is prepared in which the oil phase ranges from 1 percent by weight to 10 percent by weight of the emulsion and contains a mineral oil solution of an alkaline barium sulfonate together with an emulsifier and a water displacing agent.

The oil soluble alkaline barium sulfonate may be either the barium salts of petroleum sulfonic acids, i.e., the mahogany sulfonic acids, produced by the acid treating of petroleum oils or the barium salts of high molecular weight snythetic alkyl aryl sulfonic acids or mixtures of the petroleum sulfonates with the synthetic sulfonates.

The production of the alkaline barium salts of the mahogany acids is a well-known commercial process and includes the steps of acid treating a distillate cut generally having a viscosity of the order of 50 to 60 Saybolt seconds Universal at 210° F. produced from a Mid-Continent crude with successive quantities, "dumps," of sulfuric acid with settling and removal of sludge after each acid treat. The oil solution containing the oil-soluble sulfonic acids after the final sludge settling and removal step is air-blown to remove dissolved sulfur dioxide and thereafter the sulfonic acids are neutralized with an amount of barium oxide in excess of that required to produce a neutral sulfonate so that an alkaline barium sulfonate solution in the oil is produced.

In general temperatures ranging from 80° F. to 160° F. are employed during the acid treating steps and the neutralization step is often carried out at about 200° F. The alkaline barium sulfonate solution is finished by heating the solution to approximately 230° F. to volatilize the water, filtering through diatomaceous earth to produce a clear solution free of haze having a total base number of about 20 and a strong base number of about 20. This solution is treated with carbon dioxide to reduce the strong base number to a very low value, i.e. of the order of 2 leaving the total base number at 20, however.

The synthetic oil soluble barium sulfonates are produced from the oil soluble sulfonic acids which in turn have been produced by the sulfonation of mixtures of mono- and dialkylated benzenes wherein the alkyl group attached to the benzene nucleus ranges between 15 and 24 carbon atoms in length and preferably between 17 and 21 carbon atoms in length with an average of about 18 carbon atoms in the alkyl group. The methods of alkylating benzene and the methods of sulfonating the alkylated benzenes are well known in patents and in technical literature. The synthetic oil-soluble alkaline barium sulfonates are fluids having an average molecular weight of about 1000 and are commercially available as a solution in mineral oil.

The emulsifying agents suitable for use in this invention may be either anionic, nonionic, or cationic. Anionic emulsifiers which have been found to be suitable include the sodium petroleum sulfonates, in particular, those having molecular weights of the order of 415 to 430. Nonionic emulsifiers which are useful are the polyethylene glycol esters of lauric acid, the polyethylene glycol esters of oleic acid, and similar compounds. Amines such as the polyoxyethylene lauric amido amines are suitable cationic emulsifiers. Anionic, nonionic and cationic emulsifiers capable of producing the desired oil-in-water emulsions of this invention are well known and have been described in considerable detail in literature, for example, one of the most recent and comprehensive compilations of such emulsions will be found

in "Soap and Chemical Specialties," December 1957, pages 61–68 incl.; January 1958, pages 45–62 incl.; February 1958, pages 53-70 incl.; March 1958, pages 59–75 incl.; and April 1958, pages 55–65 incl. It will be understood, of course, that not all of these emulsifiers are of identical effectiveness in producing oil-in-water emulsions. The important criterion is not the particular type of emulsifier or compound employed but instead that the emulsifier produce an emulsion which is stable for a time sufficiently long that it may be sprayed onto the desired location in the tanker.

In addition to the emulsifying agent and the alkaline barium sulfonate, it is necessary that the oil phase include an agent which will displace the water film from the surface of the metal to be protected. "Water displacing agents," as they are known, are characterized by having an appreciable power to wet the surface of a metal and at the same time be sufficiently soluble in oil so that, as they displace the water film from the metal surface, they will tend to cause an oil film to form thereon. Certain amine compounds are suitable as water displacing agents but, in particular, the product formed by condensing 1 mol of an octyl phenol with 5 mols of ethylene oxide in the presence of an alkaline catalyst is a particularly effective water displacing agent. This octyl phenol-ethylene oxide condensation product is sold commercially under the trade name, Plexol 305.

A screening test procedure was devised for measuring the effectiveness of an emulsion for protecting against sea water corrosion and sea air corrosion. This screning test procedure was utilized to determine which components are effective in the emulsions of this invention and also to determine the effect of varying the concentration of the components of the emulsions. Test panels consisting of shim stock two and one-half inches long by two inches wide by 0.020 inch in thickness were totally immersed in ASTM synthetic sea water for about 4 days until loose rust formed over a major portion of the surface of the panel. The loose rust was then washed from the panels with a jet of water and the prerusted panels were weighed, dipped for one minute in the emulsion to be tested, and drained for one hour. The panels were then half immersed in ASTM synthetic sea water for 4 days in a closed container so that the upper half of each panel was exposed to a saturated salt air atmosphere. After the 4-day contact with sea water the panels were half immersed for 3 days in a commercial home heating oil having a boiling range of from 325° F. to 630° F. Again the panels were contained in a closed container so that the upper half of each panel was exposed to atmospheric corrosion.

The seven days constituted one cycle and a second cycle was then started with the emulsion dipping step. Tests were run in duplicate for four cycles. At the end of the four cycles the panels were washed under hot water with mild rubbing to remove loose rust and were dried and weighed. Protection ratings were calculated for each emulsion tested taking zero weight loss (i.e. no change from the weight of the prerusted panels) as 100 percent protection and the weight loss of blank panels (i.e. with no emulsion protection) as zero percent protection.

In the examples which follow the alkaline barium sulfonate employed was produced from petroleum mahogany sulfonic acids by treating a petroleum distillate cut having a viscosity of about 55 Saybolt seconds Universal at 210° F. with two 5 percent treats of 91 percent sulfuric acid and then with two 7.5 percent treats of 104 percent (fuming) sulfuric acid with settling and separation of sludge after each treat. After removing the sulfur dioxide by air blowing the product was neutralized with a barium oxide aqueous slurry in an amount about twice that required to produce the neutral sulfonate. The sulfonate oil solution was finished as has been described hereinbefore so that the finished oil solution contained approximately 16 percent by weight of barium sulfonate. The anionic emulsifier, sodium petroleum sulfonate, was the commercial product, consisting of a 60 weight percent concentration in mineral oil having a molecular weight of about 400. The nonionic emulsifier sold under the trade name, Nonisol 100, was the polyethylene glycol (glycol 400) ester of lauric acid. The catonic emulsifier sold under the trade name, Amine O, was the oleic acid derivative of a heterocyclic tertiary amine. The water displacing agent used was Plexol 305, i.e., the condensation product of 1 mol of octyl phenol with 5 mols of ethylene oxide. Emulsions containing 1 percent by weight of the oil phase were prepared and tested according to the screening test procedure. The composition of the oil phase in weight percent and the test results are set forth in the table.

Emulsion Example Number	Composition of Oil Phase in Weight Percent				Percent Protection
	Alk. Ba Sulf. Sol.	Na Petr. Sulf.	Water Displ. Agent (Plexol 305)	Other	
1	73	25	2		82
2	50	25	2	23—Lubricating oil distillate (100 Saybolt Seconds Universal at 100° F.).	57
3	30	25	2	43—Lubricating oil distillate (100 Saybolt Seconds Universal at 100° F.).	59
4	20	25	2	53—Lubricating oil distillate (100 Saybolt Seconds Universal at 100° F.).	37
5	75	25	0		39
6	73	25	0	2—Heterocyclic t-amine laurate (water displacing agent).	85
7		25	2	73—neutral barium sulfonate.	61
8		25	2	73—calcium sulfonate, 15 percent solution in oil.	53
9	88	0	2	10—Nonisol 100 (nonionic emulsifier).	96
10	88	0	2	10—Amine O (cationic emulsifier).	94
11	88	0	2	10—Sodium Oleate (anionic emulsifier).	87
12	0	25	2	73—Lubricating oil distillate (80 Saybolt Seconds Universal at 210° F., 2,100 Saybolt Seconds Universal at 100° F.	55
Blank	0	0	0		0

It is generally accepted that a corrosion inhibiting compound should give a protection level of 80 percent or more. On this basis it will be seen from the results set forth in the table that it is necessary to employ a water displacing agent in the composition of this invention (comparing Example 1 with Example 5). It will also be seen that by comparing Example 1 with Example 6 the water displacing agent may be the other recognized agents of this type as well as Plexol 305. Comparison of Example 1 with Example 7 shows that it is necessary to employ the alkaline barium sulfonate rather than the neutral barium sulfonate produced by merely neutralizing the sulfonic acids with a stoichiometric quantity of the barium oxide. Anionic, cationic or nonionic emulsifiers are effective as shown by Examples 1, 9, 10, and 11. Comparison of Examples 1, 2, 3, and 4 shows that the alkaline barium sulfonate oil solution should be at least about 70 percent by weight. Example 8 demonstrates that the calcium salt of the petroleum sulfonic acids cannot be used in the composition of this invention. Example 12 was included to show that the inhibiting effect obtained with the composition of this invention is not due to viscosity of the oil since, if a petroleum oil having the same viscosity as that of the barium sulfonate oil solution is substituted for the barium sulfonate solution, the resulting composition is

completely ineffective for giving adequate corrosion inhibition.

It was noted visually that the emulsions of Examples 1, 6, 9, 10, and 11 had rather poor stability, that is, they tended to break after standing for a few days. The emulsions of Examples 2, 3, 4, 5, 7, 8, and 12, however, showed good stability, that is, they did not break after standing for several days or even weeks. This observation supports the conclusion that the quality of the emulsion is important with respect to the amount of corrosion protection that the emulsion will give. If the stability of the emulsion is very good the protection is poor since the emulsion does not break and deposit the corrosion inhibiting oil film on the exposed steel surface. If, however, the emulsion stability is rather poor and the emulsion shows a tendency to break, the protection that it gives is very good since if the emulsion breaks readily the oil film is deposited on the steel surface and the steel is thereby given a corrosion inhibiting protective film. Accordingly, therefore, it is necessary only that the emulsion be sufficiently stable such that it can be sprayed onto the surfaces to be protected and thereafter it is desirable that the emulsion break readily in order to provide the exposed surface with the protective coating.

From a large number of tests it has been found that the alkaline barium sulfonate oil solution should range from 70 weight percent to 89 weight percent of the oil phase of the emulsion and preferably from 72 weight percent to 88 weight percent with the alkaline barium sulfonates ranging between 15 and 30 weight percent of the oil solution in which they are contained. The emulsifying agent should range preferably from 10 weight percent to 26 weight percent of the oil phase of the emulsion and the water displacing agent should range from 1 weight percent to 4 weight percent of the oil phase and preferably the water displacing agent should amount to about 2 weight percent of the oil phase.

The oil phase of the emulsion should range between 1 weight percent and 10 weight percent. Amounts less than 1 weight percent give insufficient protection whereas with amounts greater than 10 weight percent oil phase in the emulsion the film of oil deposited on the interior surface of the tanker is sufficiently heavy such that it will cause a problem with respect to cargo contamination. The best results have been obtained when the oil phase has ranged between 3 weight percent and 7 weight percent of the emulsion.

The emulsion compositions of this invention can be utilized very economically since they can be sprayed onto the interior surfaces of the cargo tanks through existing Butterworth equipment. The express spray which drains to the bottom of the tank can be collected and utilized to spray another tank and thus there is little or no loss.

I claim:

1. A composition for inhibiting the corrosion in the interior of tankers consisting of an oil-in-water emulsion in which the oil phase ranges from 1 weight percent to 10 weight percent based on the weight of the emulsion, said oil phase consisting essentially of from 70 weight percent to 89 weight percent based on the weight of the oil phase of a mineral oil solution of alkaline barium salts of oil soluble sulfonic acids wherein the alkaline barium salts range between 15 and 30 weight percent of the

mineral oil solution, from 10 weight percent to 26 weight percent of an emulsifying agent consisting essentially of oil soluble sodium salts of petroleum sulfonic acids and from 1 weight percent to 4 weight percent of the condensation product of 1 mol of octyl phenol with 5 mols of ethylene oxide.

2. A composition for inhibiting the corrosion in the interior of tankers consisting of an oil-in-water emulsion in which the oil phase ranges from 3 weight percent to 7 weight percent based on the weight of the emulsion, said oil phase consisting essentially of from 72 weight percent to 88 weight percent based on the weight of the oil phase of a mineral oil solution of alkaline barium salts of oil soluble sulfonic acids wherein the alkaline barium salts range between 15 and 30 weight percent of the mineral oil solution, from 10 weight percent to 26 weight percent of an emulsifying agent consisting essentially of oil soluble sodium salts of petroleum sulfonic acids and about 2 weight percent of the condensation product of 1 mol of octyl phenol with 5 mols of ethylene oxide.

3. A composition for inhibiting the corrosion in the interior of tankers consisting of an oil-in-water emulsion in which the oil phase ranges from 1 weight percent to 10 weight percent based on the weight of the emulsion, said oil phase consisting essentially of from 70 weight percent to 89 weight percent based on the weight of the oil phase of a mineral oil solution of alkaline barium salts of oil soluble sulfonic acids wherein the alkaline barium salts range between 15 and 30 weight percent of the mineral oil solution, from 10 weight percent to 26 weight percent of a nonionic emulsifying agent consisting essentially of the polyethylene glycol ester of lauric acid and from 1 weight percent to 4 weight percent of the condensation product of 1 mole of octyl phenol with 5 moles of ethylene oxide.

4. A composition for inhibiting the corrosion in the interior of tankers consisting of an oil-in-water emulsion in which the oil phase ranges from 1 weight percent to 10 weight percent based on the weight of the emulsion, said oil phase consisting essentially of from 70 weight percent to 89 weight percent based on the weight of the oil phase of a mineral oil solution of alkaline barium salts of oil soluble sulfonic acids wherein the alkaline barium salts range between 15 and 30 weight percent of the mineral oil solution, from 10 weight percent to 26 weight percent of a cationic emulsifying agent consisting essentially of the oleic acid derivative of a heterocyclic tertiary amine and from 1 weight percent to 4 weight percent of the condensation product of 1 mole of octyl phenol with 5 moles of ethylene oxide.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,007,880 November 7, 1961

Harold A. Hartung

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, line 34, for "seat" read -- sea --; column 3, lines 30 and 31, for "screning" read -- screening --; column 4, line 8, for "catonic" read -- cationic --; column 5, line 51, for "express" read -- excess --.

Signed and sealed this 17th day of April 1962.

(SEAL)
Attest:

ESTON G. JOHNSON
Attesting Officer

DAVID L. LADD
Commissioner of Patents

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