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# STABILIZING FILMING AMINES

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The present inventon is directed to improvements in the stabilization of filming amines of the type employed in the protection of metal surfaces from corrosion by aqueous fluids.

It has long been known that high molecular weight aliphatic amines have highly effective protective film properties on metal surfaces. These materials have been extensively used in various systems such as steam generators, heat exchangers, evaporators, process water systems, coolers, steam return condensate systems, and the like. The insolubility of such materials, however, makes them difficult to feed into the system. Certain amine salts, particularly, acetates or the glycolates which have better dispersibility properties have been used in place of the free amine. However, the free amine may be precipitated when the salt is neutralized, and these salts cannot be fed with common alkaline water treatment chemicals since they are incompatible with these chemicals. Furthermore, the injection of the salts into the system involves serious difficulty because of their tendency to corrode mixing tanks and associated piping.

One of the most recent improvements in this art has been the development of amine emulsions for feeding the amine into the system. The best of these is described in United States Patent No. 2,956,889 issued to Wayne L. Denman. Briefly, this patent disclosed a water treating composition which included an aqueous aliphatic amine emulsion containing a high molecular weight filming amine in combination with a water soluble condensate of at least 5 mols of ethylene oxide with a high molecular weight amine as an emulsifying or dispersing agent. These alkaline emulsions are less corrosive to feed tanks and associated piping than are the acetate dispersions, and have some compatibility with boiler feed water chemicals. For this reason, alkaline amine emulsions can be fed to eitiher the feed line or the steam drum as well as to the steam header or line. In addition, the use of alkaline amine emulsions permits the incorporation of somewhat higher active amine contents as compared with the amine acetate.

The water treating material described in the Denman patent is frequently sold as a cutback material containing approximately 20% active material (amine plus dispersing agent) and the balance water. These products have the physical appearance of a firm paste. Feed solutions from such products are prepared by adding the required amount of water and heating with agitation until the paste melts and disperses. In the preferred method of preparing feed solutions, the above procedure is carried out at double the desired concentration, followed by dilution with an equal volume of cold water. The resulting cooling imparts stability to the feed solution. Various modifications of this general method have been used, but they all involve heating to melt or liquify the paste.

Cold mixing of the water cutback alkaline emulsions with water has been suggested, but this technique requires such extreme care that it was considered impractical. If the cold water is added to the concentrated emulsion too fast, or with insufficient agitation, lumps remain which may plug screens and pump check valves.

The present invention involves an improvement in the art of amine emulsions which permits rapid and spontaneous dispersion of the materials in cold water. I have found that the addition of certain polyhydroxyl phenolic



compounds, either free or combined, to the high molecular weight amines, preferably in conjunction with a nonanionic despersing agent, results in marked viscosity reduction and greatly increased ease of dispersion in cold water.

One of the objects of the present invention is to provide an improved method for introducing a filming amine into a corrosive aqueous fluid system.

Still another object of the invention is to provide an improved method for stabilizing filming amine compositions against breakdown in cold salt solutions.

A further object of the invention is to provide improved filming amine compositions which have reduced viscosity, and are easily dispersible in cold water.

A further object of the invention is to provide improved filming amine compositions which are stable on storage and which disperse readily in cold water without the necessity of melting or liquefaction.

While many different types of polyhydroxyl phenolic compounds can be used for the purposes of the present invention I particularly prefer to use phenolic lignin sulfonates or alkaline lignite compounds. Generally, lignin sulfonates are made by reacting wood chips with a solution of calcium, sodium, magnesium, or ammonium bisulfite. The product is a series of alkaline lignin sulfonates having a molecular weight usually in the range from 2,000 to 15,000 and containing from 2 to 4 monomeric units per atom of sulfur. These lignin sulfonates drastically reduce the viscosity of aliphatic amine dispersions, and make possible spontaneous dispersion of the amine emulsion concentrates in cold water with slight agitation. Furthermore, the susceptibility of the aliphatic amine emulsion to coagulation by polyvalent anions is reduced.

Alkaline lignite compounds are prepared by treatment of lignite, a type of peat coal with alkaline materials. The lignite itself is principally a combination of humic acids formed by the bio-degradation of vegetable tissue.

For the purposes of the present invention, the filming amines are those aliphatic primary amines which contain from 14 to 22 carbon atoms per molecule. The preferred dispersing or emulsifying agent is a condensate of at least 5 molecular proportions of ethylene oxide for each molecular proportion of an amine having 14 to 22 carbon atoms per molecule. The weight ratio of amine to the dispersing agent is in the range from 1 to 1 to 20 to 1, and the weight ratio of the amine plus the dispersing agent to the phenolic compound is in the range from 1 to 1 to 20 to 1. Within those broader ranges, the preferred ratio of amine to dispersing agent is within the range of 3 to 1 to 10 to 1. The preferred weight ratio of the combined amine and dispersing agent to phenolic compound is within the range of 4 to 1 to 1 to 1.

The following specific examples illustrate some of the variations possible in the practice of the present invention and the results achieved.

*Example A*

Approximately 100 grams of a cold tap water solution containing one gram each of sodium sulfite, disodium phosphate and sodium carbonate, was added cold with stirring to five grams of an emulsion containing 0.18 gram octadecylamine, 0.02 gram of a dispersing agent consisting of technical grade octadecylamine condensed with 50 mols of ethylene oxide, and 0.80 gram water per gram. The emulsion concentrate does not disperse uniformly, but floats with lumps.

*Example B*

One hundred grams of a cold tap water solution containing one gram each of sodium sulfite, disodium phosphate and sodium carbonate is added with stirring to 5.0 grams of an emulsion containing 0.18 gram octadecyl-

amine, 0.02 gram of the same dispersing agent is employed in Example A. 0.20 gram of a partially desulfonated sodium lignosulfonate and 0.60 gram water per gram of emulsion. This emulsion is thin and stably dispersed.

*Example C*

Two parts of a melted condensate of 50 mols of ethylene oxide with one mol of octadecylamine is dispersed in 79 parts of water at 170° F. Into this composition is dispersed 18 parts of melted technical grade octadecylamine, and the resulting emulsion cooled to 140° F. while stirring. The product is a viscous gel. One part of sodium lignosulfonate was added to this gel with stirring. The thick emulsion gel is thinned and is easily dispersible in cold water.

*Example D*

A procedure is carried out the same as in Example A except that 9 parts of sodium lignosulfonate is substituted for an equal portion of water. Also, a condensate of 50 mols of ethylene oxide with one mol of hydrogenated tallow amide was substituted for the amine ethoxylate. The resulting emulsion is thin and stable.

*Example E*

A procedure was carried out the same as in Example B except that a condensate of 50 mols of ethylene oxide with one mol of tallow fatty acids is substituted for the amine ethoxylate. The resulting emulsion is thin and stable.

*Example F*

A procedure was carried out the same as in Example B except that a 75% alcohol solution of hydrogenated tallow dimethyl quaternary ammonium chloride is substituted for the amine ethoxylate. The emulsion is thin and fairly stable.

*Example G*

A procedure is carried out the same as in Example B except that a condensate of ethylene diamine with propylene oxide and ethylene oxide ("Tetronic 908") having a base molecular weight of 4030 and containing 85% ethylene oxide to bring it to a total molecular weight of about 21,000 is substituted for the amine ethoxylate. The emulsion is thin and fairly stable.

*Example H*

A procedure is carried out the same as in Example B except that an alkyl phenol polyglycol ether (Poly Tergent G–300) is substituted for the amine ethoxylate. The emulsion is thin and fairly stable.

*Example I*

A procedure is carried out as in Example B except that sodium N-coco B-aminopropionate (Deriphate 151) is substituted for the amine ethoxylate. The emulsion is thin and fairly stable.

*Example J*

The procedure of Example B is carried out except that "Pluronic F-68" a condensate of propylene oxide having a base molecular weight of 1750 with 80% ethylene oxide is substituted for the amine ethoxylate. The resulting emulsion is thin and fairly stable.

*Example K*

A procedure is carried out the same as in Example B except that technical grade tetradecylamine is substituted for the octadecylamine. The emulsion is thin and stable.

*Example L*

A procedure is carried out the same as in Example B except that a commercial mixture of marine oil derived amines having carbon chains of 14 to 22 atoms (Adogen 101–D) is substituted for octadecylamine. The emulsion is thin and stable.



*Example M*

A procedure is carried out the same as in Example B except that calcium lignosulfonate is substituted for the partially desulfonated sodium lignosulfonate. The emulsion is thin and stable.

*Example N*

The procedure of Example B was carried out except that ammonium lignosulfonate was substituted for the partially desulfonated sodium lignosulfonate. The emulsion is thin and stable.

*Example O*

The procedure of Example B was carried out except that a water soluble alkaline lignite was substituted for the partially desulfonated sodium lignosulfonate. The emulsion is thin and stable.

The cold water dispersibility, viscosity reduction and stability while using various additives was determined and evaluated. With respect to the cold water dispersion characteristics, five grams of a concentrated 20% dispersion of a mixture of 9 parts of octadecylamine, one part of a dispersing agent consisting of a condensate of 50 mols of ethylene oxide with one mol of octadecylamine in water is manually stirred rapidly into 95 ml. of water at 60 to 70° F. When only slight dispersion results, and the bulk of the emulsion remains in lumps, the water dispersibility is rated poor. A rating of fair is given when a dispersion slowly forms but separates in less than three days, with some lumps remaining. A rating of good is given when the cold water dispersion is rapid and spontaneous, with no lumps present and is stable in excess of two months.

A rating of poor on viscosity reduction of the concentrate or 20% formulation is given when there is no reduction in viscosity compared to the viscosity of the original concentrate. A rating of fair is given when the viscosity reduction is somewhat less than free flowing at 80 to 100° F. A rating of good is given when the viscosity is reduced to that of a free flowing liquid.

The stability of the emulsion is determined on 1% dilutions of the 20% concentrated formulation. A rating of poor is given when the emulsion breaks in less than one day. A rating of poor is also given when the 20% concentrate thickens or hardens on aging at 80 to 100° F. up to two months storage. A rating of fair is given when the 1% emulsion breaks in varying periods between one day and two months. A rating of fair is also given if there is some viscosity increase in the 20% dispersion in two months. A rating of good is given when there is no separation or viscosity increase in either the 20% concentrate or 1% dispersion in periods up to two months at 80 to 100° F.

The following examples illustrate the results obtained when using materials coming within the scope of the present invention and those outside it. For purposes of convenience, there is provided the following definition of terms and identification of products:

*Myrobalans tannin.*—A pyrogallol type of tannin extracted from the wood of the quebracho tree, indigenous to Paraquay and Argentina. The extract is further treated with sulfite to prevent separation of the phlobaphenes. Only quebracho extract is so beneficated by this process. The final extract contains 63 to 67% tannin on a dry basis. The remainder are non-tannins.

*Myrobalans tannin.*—A pyrogallol type of tannin extracted from the unripe fruit or nuts of the various species of the tree *Terminala chebula,* indigenous to the Malay Archipelago. The nuts contained 30 to 40% tannin. On oxidation the product ellagic acid separates.

*Orzan S.*—Crown-Zellerbach's sodium ligno sulfonate of about 10,000 average molecular weight, only partially neutralized to give a pH of 4 in solution.

*Maracell E.*—Marathon's desulfonated, demethoxylated liquor from the vanillin process using sodium ligno sul-

fonate. The product is mostly phenolic material containing about 24% carbonate.

*Marasperses.*—Marasperse is Marathon's registered name for products manufactured from the higher molecular weight fractions of ligno sulfonate, hetero-disperse polymers derived from the sulfite process of wood pulp digestion. The basic structure is a condensed alkyl phenol, phenylfuran substituted with phenolic, methoxy, hydroxy and sulfonic groups (1,000 to 20,000 molecular weight). Oxy groups are arranged in the ortho position.

*Marasperse CB.*—The calcium-sodium salt of ligno sulfonate, highly desulfonated as a by-product of the vanillin process.

*Marasperse C.*—The calcium-sodium salt from the basic calcium lgino sulfonate precipitated at pH 8 to 9 sulfite liquor.

*Marasperse N.*—The sodium salt from the basic calcium ligno sulfonate precipitated from spent sulfite liquor.

*Super treat.*—American Colloid Company's registered name for a product derived from the mineral leonardite which consists of water insoluble mixed humic acids of an average molecular weight of 400. These humic acids have the basic structure of anthracene with carboxyl, hydroxyl, carbonyl, methyl, toluyl and ether substituents. The phenolic characteristic predominates wtih phenolic hydroxyl and ketones displaced in the para positions. In Super Treat the insoluble humic acid is rendered soluble by leaching with alkaline solution and drying to give a product containing 25% free hydroxide plus humic acid salts and ten to fifteen percent insolubles. The dispersing power of the humic acid salts is sufficient to disperse the insolubles in the fine ground product.

*Armeen 18D.*—Armour Chemical Company's distilled, high stearyl primary amine.

*Ethomeen 18/60.*—Armour Chemical Company's ethoxylated high stearyl amine. On the average, ethoxylation is carried to the extent of 50 moles ethylene oxide for each mole of high stearyl amine.

In the following tests, a concentrated alkaline octadecylamine emulsion was prepared as follows. To 800 grams of Chicago tap water at 170° F. was added 18 grams of Ethomeen 18/60 followed by 182 grams of Armeen 18D with agitation. Heat was applied, if necessary, to raise the temperature to 170° F. and the agitation was continued. Then, the material was allowed to cool with agitation to 140° F. and packaged in a wide mouth closed container. This material is referred to in the succeeding examples as a concentrated alkaline octadecylamine emulsion.

*Example 1*

Dissolve 4 grams of 50% sodium hydroxide solution in 90 grams of concentrated alkaline octadecylamine emulsion. Mix in 6 grams of powdered myrabolam extract, heat to 150° and cool. Now add 5 grams of the above mixture (cold) with stirring to 95 grams Chicago tap water. The emulsion stability is rated as fair.

*Example 2*

Dissolve 4 grams of 50% sodium hydroxide solution in 86 grams of concentrated alkaline octadecylamine emulsion. Mix in 10 grams of powdered myrabolam extract, heat to 150° F. and cool. Now add 5 grams of the above mixture (cold) with stirring, to 95 grams cold Chicago tap water. The emulsion stability is rated as fair.

*Example 3*

A preparation of Example 1 using Super Treat in place of myrabolam extract. The emulsion stability is rated as extra good.

*Example 4*

Preparation of Example 2 using Super Treat in place of myrabolam extract. The emulsion stability is rated as extra good.



*Example 5*

The preparation of Example 1 using quebracho extract in place of myrabolam extract. The emulsion stability is rated as good.

*Example 6*

The preparation of Example 2 using quebracho extract in place of myrabolam extract. The emulsion stability is rated as good.

*Example 7*

The preparation of Example 1 using Maracell E extract in place of myrabolam extract. The emulsion stability is rated as fair to good.

*Example 8*

The preparation of Example 2 using Maracell E extract in place of myrabolam extract. The emulsion stability is rated fair to good.

*Example 9*

A preparation of Example 1 using Marasperse C in place of myrabolam extract. The emulsion stability is rated as fair.

*Example 10*

The preparation of Example 2 using Marasperse C in place of myrabolam extract. The emulsion stability is rated as fair.

*Example 11*

The preparation of Example 1 using Marasperse CB in place of myrabolam extract. The emulsion stability is rated as fair.

*Example 12*

The preparation of Example 2 using Marasperse CB in place of myrabolam extract. The emulsion stability is rated as fair.

*Example 13*

A preparation of Example 1 using Marasperse SN in place of myrabolam extract. The emulsion stability is rated as fair.

*Example 14*

The preparation of Example 2 using Marasperse SN in place of myrabolam extract. The emulsion stability is rated as fair.

*Example 15*

The preparation of Example 1 using Orzan S in place of myrabolam extract. The emulsion stability is rated as fair.

*Example 16*

The preparation of Example 2 using Orzan S in place of myrabolam extract. The emulsion stability is rated as fair.

*Example 17*

The preparation of Example 1 using phenol in place of myrabolam extract. Viscosity reduction is rated as good and spontaneous dispersion is rated as poor. No rating is given to emulsion stability.

*Example 18*

The preparation of Example 2 using phenol in place of myrabolam extract. Viscosity reduction is rated as good, spontaneous dispersion is rated as poor and no rating is given to emulsion stability.

*Example 19*

The preparation of Example 1 using hydroquinone in place of myrabolam extract. Viscosity reduction is rated as good, spontaneous dispersion is rated as good and emulsion stability is rated as poor.

*Example 20*

The preparation of Example 2 using hydroquinone in place of myrabolam extract. The viscosity reduction is

rated as good, spontaneous dispersion is rated as good and emulsion stability is rated as poor.

*Example 21*

The preparation of Example 1 using resorcinol in place of myrabolam extract. Viscosity reduction, spontaneous dispersion and emulsion stability are all rated as fair.

*Example 22*

The preparation of Example 2 using resorcinol in place of myrabolam extract. Viscosity reduction, spontaneous dispersion and emulsion stability are all rated as fair.

*Example 23*

The preparation of Example 1 using pyrogallol in place of myrabolam extract. Viscosity reduction, spontaneous dispersion and emulsion stability are all rated as good.

*Example 24*

The preparation of Example 2 using pyrogallol in place of myrabolam extract. Viscosity reduction, spontaneous dispersion and emulsion stability are all rated as good.

*Example 25*

The preparation of Example 1 using gallic acid in place of myrabolam extract. Viscosity reduction, spontaneous dispersion and emulsion stability are all rated as good.

*Example 26*

The preparation of Example 2 using gallic acid in place of myrabolam extract. Viscosity reduction, spontaneous dispersion and emulsion stability are all rated as good.

*Example 27*

The preparation of Example 1 using salicylaldehyde in place of myrabolam extract. Viscosity reduction is rated as good, spontaneous dispersion is rated as good and emulsion stability is rated as poor (hardens on aging).

*Example 28*

The preparation of Example 2 using salicylaldehyde in place of myrabolam extract. Viscosity reduction is rated as good, spontaneous dispersion is rated as good and emulsion stability is rated as poor (hardens on aging).

*Example 29*

The preparation of Example 1 using salicylic acid in place of myrabolam extract. Viscosity reduction and spontaneous dispersion are rated as poor and no rating is given to emulsion stability.

*Example 30*

The preparation of Example 2 using salicyclic acid in place of myrabolam extract. Viscosity reduction and spontaneous dispersion are rated as poor and no rating is given to emulsion stability.

*Example 31*

Preparation of Example 1 using p-aminophenol in place of myrabolam extract. Viscosity reduction is rated as fair, spontaneous dispersion is rated as poor and no rating is given to emulsion stability.

*Example 32*

Preparation of Example 2 using p-aminophenol in place of myrabolam extract. Viscosity reduction is rated as fair, spontaneous dispersion is rated as poor and no rating is given to emulsion stability.

*Example 33*

A preparation of Example 1 using p-cresol in place of myrabolam extract. Viscosity reduction and spontaneous dispersion are rated as poor and no rating is given to emulsion stability.

*Example 34*

The preparation of Example 2 using p-cresol in place of myrabolam extract. Viscosity reduction and spontaneous dispersion are both rated as poor and no rating is given to emulsion stability.

*Example 35*

The preparation of Example 1 using catechol in place place of myrabolam extract. Viscosity reduction is rated as fair, spontaneous dispersion is rated as good and emulsion stability is rated as fair.

*Example 36*

The preparation of Example 2 using catechol in place of myrabolam extract. Viscosity reduction is rated as fair, spontaneous dispersion is rated as good and emulsion stability is rated as fair.

In Examples 1 to 36 sodium hydroxide was added to each example, regardless of whether the phenolic material used was free or combined. The following examples illustrate the preparation of cold water dispersible formulations without adding sodium hydroxide as such.

*Example 37*

Add 2.0 grams of Ethomeen 18/60 to 79 grams hot Chicago tap water (180° F.), stir in 18 grams of Armeen 18D and cool to 150° F. with stirring. Now slowly add 1 gram of Super Treat with agitation. Cool to substantially room temperature and package. Disperse 5 grams of the above concentrate (cold) in 95 grams cold Chicago tap water. The viscosity of the concentrate is reduced slightly from that of the 20% concentrate alone and the spontaneous dispersibility and stability in cold water is improved moderately over the 20% concentrate.

*Example 38*

A preparation made as that of Example 37 except that the concentrate is made with 3 grams of Super Treat and 77 grams Chicago tap water instead of 1 gram of Super Treat and 79 grams of Chicago tap water. Viscosity reduction, cold water dispersibility and stability are all rated as good.

*Example 39*

A preparation made as that of Example 37 except the concentrate is made with 5 grams of Super Treat and 75 grams Chicago tap water instead of 1 gram Super Treat and 79 grams Chicago tap water. Viscosity reduction, cold water dispersibility and stability are all rated as good plus.

In Examples 1 to 39, as well as the concentrated emulsions of Examples A to D, the final product is readily dispersible in cold water, but is a firm paste at an octadecylamine content of 18%. It has been found that the addition of 5% to 40% of a 25% polyacrylate solution to this concentrated emulsion results in improved emulsion stability and marked thinning at octadecylamine contents of 18%. Among the polyacrylates suitable for this purpose are "Good-rite K705" (an ammonium polyacrylate marketed by B. F. Goodrich) and "K708" (a sodium polyacrylate marketed by the same concern). Both these materials are based upon polyacrylic acids having molecular weights of 80,000 to 90,000. The molecular weight of the polyacrylic acids may be as low as 10,000 but should not be as high as 200,000.

The improved compositions of the present invention can be added to aqueous fluids in widely varying concentrations, depending upon conditions. Amounts as little as 1 part per million or less will be effective in some cases, and amounts up to 100 parts per million may be required in others. Generally speaking, amounts in excess of 100 parts per million are not necessary, and may be uneconomical.

It should be evident that various modifications can be made to the described embodiments without departing from the scope of the present invention.

I claim as my invention:

1. A corrosion inhibiting composition characterized by stability in cold water solutions consisting essentially of, in admixture, a primary aliphatic amine containing from 14 to 22 carbon atoms per molecule, a dispersing agent consisting of an ethoxylated amine condensate containing at least 5 molecular proportions of ethylene oxide for every molecular proportion of an aliphatic amine containing from 14 to 22 carbon atoms per molecule, and a phenolic lignin sulfonate having a molecular weight of 2,000 to 15,000, and containing from 2 to 5 monomeric units per atom of sulfur, the weight ratio of amine to dispersing agent being from 1 to 1 to 20 to 1, and the weight ratio of amine plus dispersing agent to phenolic lignin sulfonate being from 1 to 1 to 20 to 1.



2. The composition of claim 1 in which said primary aliphatic amine is octadecylamine.

3. The composition of claim 1 in which said condensate is a condensate of approximately 50 mols of ethylene oxide with 1 mol of octadecylamine.

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