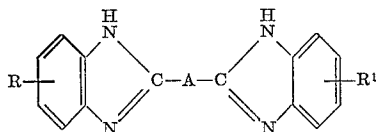


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3,222,285

NON-CORROSIVE DETERGENT COMPOSITIONS
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 mesne assignments, to Union Oil Company of California,
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This invention relates to a new class of corrosion inhibitors, viz., bisbenzimidazoles, bisbenzimidazolyl-alkanes and bis(benzimidazolyl)polyhydroxyalkanes represented by the formula



wherein R and R¹ are hydrogen or the same or different hydrocarbon radicals having 1 to 20 carbon atoms, there being 0 to 4 of such groups present in the molecule, and A is an alkylene group having 1 to 20 carbon atoms or an alkylene group of 1 to 20 carbon atoms having one or more hydroxy substituents, i.e., 1 to 20 hydroxyl groups.

More particularly this invention is based on the discovery that such compounds as 1,2-bis(2-benzimidazolyl)-1,2-dihydroxyethane; 1,4-bis(2-benzimidazolyl)-1,2,3,4-tetrahydroxybutane; 1,2-bis(2-benzimidazolyl)ethane; 1,2-bis(2-benzimidazolyl)octane and 1,2-bis(2-benzimidazolyl)methane when present in small quantities, in the order of 0.0001 to 0.2 g./100 ml. of solution, i.e., about 0.0001 to 0.2 weight percent, in aerated aqueous media, especially detergent compositions, are effective in reducing the corrosion of copper and other metals contacted by the solution.

Many commercial detergents contain builders, such as polyphosphates and pyrophosphates, to assist the washing action and prevent the formation of insolubles. Normally, in the use of detergent compositions in machinery such as found in laundries or factories, the coatings of corrosion products and other insolubles form a protective layer on the metal surfaces. The presence of builders or the use of highly effective detergents prevents or removes this coating and promotes corrosion of the metal surfaces. The innermetallic or associated complex of benzotriazoles of this invention are effective as corrosion inhibitors in aqueous solutions, aerated aqueous solutions, detergent solutions, and aerated detergent solutions to overcome this and related corrosion problems.

The detergent compositions with which the corrosion inhibitors of this invention can be used to contain any type of detergent, soap, builder or combination of these ingredients. Although the invention will be illustrated by the use of a mixed aryl alkyl sulfonate detergent composition, it is not to be limited thereto. The corrosion inhibitors of this invention can be used in metal-cleaning compositions, steam cleaners, skin detergents, car-washing compositions, metal-pickling solutions, lubricating oil compositions, cutting oils, grease emulsifiers, low-sudsing all-purpose emulsifier compositions or detergents for household use, dispersant or emulsion paints, latex paints, water-base inks, glues, galvanizing fluxes, electrolyte solutions, agricultural emulsifier formulations, anionic textile softeners, dye baths, warp-sizing compositions, textile and leather-treating compositions, dishwashing compositions, etc., that is, any of the known detergent- or surfactant-containing compositions.

Examples of various surfactants that may be contained in or be present in the aqueous environment to be inhibited by the compounds of this invention are the anionic and cationic surfactants such as dodecylbenzene sulfonic

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acid, salts of fatty acid tertiary amines, alkyl aryl sulfonate, sulfonated oil, alkyl aryl polyether alcohols, polyglycol esters, disodium N-octadecylsulfosuccinamate, ethanolated alkyl guanidine amine complexes, dihexyl ester of sodium sulfosuccinic acid, fatty carbamide derivatives, petroleum sulfonates, sulfated fatty alcohols, blends of alkalies and detergents, blends of nonionic and cationic agents, cetyl dimethyl benzyl ammonium chloride, alkyl polyoxyethylene glycol amide, sorbitan monolaurate, sorbitan sesquioleate, and others.

The foregoing synthetic detergents, emulsifiers and surfactants, along with ordinary soaps and alkalies including phosphates, carbonates, sulfates, acetates and mixtures of same, wherein the cation may be an alkali metal or an alkaline earth metal, are used in aqueous solutions in amounts ranging from about 0.1 g. to 10 gm./100 ml. of solution, or about 0.001 to 0.2% by weight having a pH of about 8 to 11, to make up a wide variety of cleaning, scouring, detergent and emulsifier compositions to which the corrosion inhibitors of this invention can be applied or incorporated. The invention also relates to the method of inhibiting the corrosion of metal parts in contact with detergent compositions by incorporating therein a corrosion-inhibiting amount of the compounds of this invention.

It becomes then a primary object of this invention to provide a new class of corrosion inhibitors of the foregoing formula.

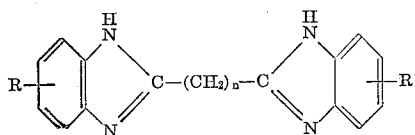
Another object of this invention is to provide corrosion inhibitors of the class defined herein, and compositions containing same.

Another object of this invention is to provide aqueous solutions of detergent compositions containing the herein-described compounds.

Another object of this invention is to provide a method of mitigating the corrosion of metals in contact with aerated aqueous solutions, especially aerated aqueous commercial detergent solutions.

These and other objects of this invention will be described or become apparent as the specification proceeds.

A sub-genus of compounds coming within the scope of this invention is the bisbenzimidazoles and bisbenzimidazolyl-alkanes having the formula



wherein R and R¹ are hydrogen atoms or the same or different hydrocarbon radicals having 1 to 20 carbon atoms and n is 0-20. Compounds of this sub-group are prepared by reacting dibasic acids, their anhydrides, dinitriles, or diesters with o-phenylene diamines in polyphosphoric acid medium. The reaction proceeds smoothly at 150-200° C. and is complete in 2 to 3 hours. The reaction mixture is poured onto ice-water and filtered. The precipitate is washed with H₂O, NaHCO₃ and water till free from acid. The yields of the products is generally high, varying from 60 to 95%. The bisbenzimidazolylalkanes thus prepared can be further purified by crystallization from solvents like ethanol, or benzene. These compounds have also been prepared by using 4N, hydrochloric acid instead of polyphosphoric acid, but in this case the reaction time is longer (10 to 12 hours) and generally the yields are poorer.

An example illustrating the preparation is:

EXAMPLE I

1,8-bis(2-benzimidazolyl)octane

Sebacic acid (20.2 g., 0.1 M) and o-phenylene diamine

(21.6 g., 0.2 M) were added with stirring to warm polyphosphoric acid (150 cc.) contained in a three-necked flask. The mixture was heated to 200° C. for 3 hours with stirring. It was then cooled and poured onto ice. A greyish precipitate appeared which was filtered and thoroughly washed with water followed by NaHCO₃ till free of acid. The product was dried in a vacuum desiccator and further purified by crystallization. The yield of 1,8-bis(2-benzimidazolyl)octane was 88%, M.P. 278° C.

Species of this sub-genus of compounds are:

1,2-bis(2-benzimidazolyl)ethane
1,3-bis(2-benzimidazolyl)propane

strated by a series of experiments with aqueous solutions of "Tide," a commercial detergent material containing alkylaryl sulfonates, sodium tripolyphosphate, sodium sulfate, and other components. First, a water solution of "Tide" (5 g./liter) was prepared. Then, a 50 ml. portion of this detergent solution was charged to each of seven flasks, two serving as controls, and the inhibitors prepared as above were placed in the remaining flasks at 0.1% w. concentration. Next, two polished brass strips (½" to 3") were placed in each of the seven flasks, and air was bubbled through the solutions at a rate of 20–30 cc./min. for a period of 72 hours while the temperature was held constant at 70° C. The results were as follows:

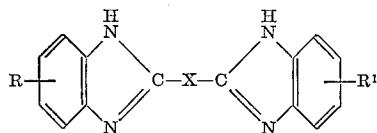
TABLE I

Test No.	Inhibitor	Percent Weight Loss or Gain*	Appearance After Test	Corrosion Rate* Inch per Year
1-----	None-----	2.17	Black-----	0.07467
2-----	1,2-bis(2-benzimidazolyl)-1,2-dihydroxyethane-----	0.00	Shiny-----	0.00000
3-----	1,4-bis(2-benzimidazolyl)-1,2,3,4-tetrahydroxybutane-----	0.00	do-----	0.00000
4-----	None-----	-2.01	Black-----	0.08526
5-----	1,2 Bis(2-benzimidazolyl)-ethane-----	+0.02	Shiny-----	0.00073
6-----	1,2 Bis(2-benzimidazolyl)-octane-----	+0.04	do-----	0.00176
7-----	1,2 Bis(2-benzimidazolyl)-methane-----	-0.04	do-----	0.00182

*Average of two coupons.

1,4-bis(2-benzimidazolyl)butane
1,5-bis(2-benzimidazolyl)pentane
1,20-bis(2-benzimidazolyl)eicosane
1,2-bis(4-isopropylbenzimidazolyl)ethane
1,3-bis(4-cyclopentylbenzimidazolyl)propane
1,9-bis(5-sec-butylbenzimidazolyl)nonane

Another sub-genus of compounds coming within the scope of this invention is the bis(benzimidazolyl)polyhydroxyalkanes of the formula



wherein R and R¹ are hydrogen or the same or different hydrocarbon radicals having 1 to 20 carbon atoms and X is an alkylene group having one or more, i.e., up to 20 hydroxyl groups.

Species of this sub-genus of compounds are:

1,3-bis(2-benzimidazolyl)-1,2-dihydroxypropane
1,3-bis(2-benzimidazolyl)-1,2,3-trihydroxypropane
1,5-bis(2-benzimidazolyl)-1,2,3,4,5-pentahydroxypentane
1,3-bis(2-benzimidazolyl)-2-hydroxypropane
1,1-bis(2-benzimidazolyl)-hydroxymethane
1,4-bis(2-benzimidazolyl)-2-hydroxybutane
1,4-bis(2-benzimidazolyl)-2,3-dihydroxybutane
1,4-bis(2-benzimidazolyl)-1,2-dihydroxybutane

This subgroup of corrosion inhibitors is prepared by reacting about 2 moles of an o-phenylene-diamine with one mole of a hydroxy dibasic acid, the reaction proceeding with or without the presence of a catalyst such as polyphosphoric acid. The reaction is conducted at temperatures of about 100° to 200° C. The following example is illustrative.

EXAMPLE II

One mole (206 g.) of diethyl tartrate was heated for two hours at 125°–150° C. with two moles (216 g.) of o-phenylenediamine, in the presence of 125 gms. of polyphosphoric acid. The reaction mixture was allowed to cool and was poured into ice water. Then, the product was filtered off, washed with a 5% solution of sodium bicarbonate, followed by water and recrystallized from ethanol. There was a nearly quantitative yield of 1,2-bis(2-benzimidazolyl)-1,2-dihydroxyethane.

The effectiveness of our inhibitors has been demon-

Two blank runs are shown because these determinations were run on different days and the usual procedure is to have a separate control sample for each determination.

As illustrated by the foregoing examples, this invention is directed to compounds and method for inhibiting corrosion of metal surfaces in contact with aqueous environments. The effectiveness of the inhibitors has been demonstrated in relation to aqueous solutions of commercial detergents containing builders such as polyphosphates and alkali metal sulfates. The following experiments demonstrate that the presence of these builders, particularly the phosphates, is a causation of corrosion and the surfactant agent, i.e., dodecylbenzene sodium sulfonate itself does not contribute to the corrosion.

In these experiments, pure synthetic dodecylbenzene sodium sulfonate and reagent grade sulfate, phosphate, metasilicate, pyrophosphate and tripolyphosphate salts were used and the procedure in the foregoing experiments was followed:

TABLE II

Blend No.	Component	Wt. Percent	Corrosion Wt. Percent Loss	Corrosion inch/year
#1-----	DBSS-----	100	0.25 (gain)	-----
#2-----	DBSS-----	40	0.11 (gain)	-----
#3-----	Sodium sulfate-----	60	-----	-----
	DBSS-----	40	0.04	0.0009
	Sodium sulfate-----	20	-----	-----
#4-----	Trisodium phosphate-----	40	-----	-----
	DBSS-----	40	0.07	0.0017
	Sodium sulfate-----	20	-----	-----
#5-----	Sodium metasilicate-----	40	-----	-----
	DBSS-----	40	1.04	0.041
	Sodium sulfate-----	20	-----	-----
#6-----	Sodium pyrophosphate-----	40	-----	-----
	DBSS-----	40	1.33	0.051
	Sodium sulfate-----	20	-----	-----
#7-----	Sodium tripolyphosphate-----	40	-----	-----

*DBSS—abbreviation for dodecylbenzene sodium sulfonate.

Within this environment, that is, for example, blend No. 5 in Table II, the presence of about 0.2 g. of 1,2-bis(2-benzimidazolyl)-1,2-dihydroxyethane or 0.2 g. of 1,2-bis(2-benzimidazolyl)ethane will reduce the corrosion weight percent loss to about 0.4 to 0.35 or 0.16 to 0.12 inch per year. These results are significant since the concentration of pyrophosphate or polyphosphate in the blends tested in Table II are above the concentrations of

these builders in commercial detergent compositions which are about 5 to 20% by weight.

In addition to the examples of synthetic detergents and emulsifiers that can be present in the environments to be protected by the corrosion inhibitors of this invention, other examples are alkaryl sulfonates having molecular weights of 465 to 480, tetrasodium N-(1,2-dicarboxyethyl)-N-octadecylsulfosuccinamate, diamyl ester of sodium sulfosuccinic acid, isopropyl naphthalene sodium sulfonate, alkali metal petroleum sulfonates including sodium, potassium, lithium, cesium, petroleum sulfonates, polyoxyethylated nonylphenols, polyoxyalkylene esters and sulfonates, and the like.

The corrosion inhibitors of this invention find application in the preparation, handling and use of the various types of detergent compositions disclosed herein whether in aqueous, inert, solvent, paste, fluid, or solid and semi-solid form.

Accordingly, this invention contemplates non-corrosive fluent mixtures of an inert solvent and the corrosion inhibitors disclosed herein, or fluent mixtures of a detergent in an inert solvent and the corrosion inhibitors, and also solid or semi-solid compositions such as soaps and greases. The fluent mixtures can be in the form of solutions, suspensions, or concentrates containing a small amount, a soluble amount or a suspendable amount, of the corrosion inhibitors.

Suitable solvents, inert as regards any reactivity toward the corrosion inhibitors but exhibiting a corrosive action to metal under the conditions of use, include water, liquid hydrocarbons, lubricating oils, neutral lubricating oils, bright stock, solvent extracts from the solvent refining of mineral lubricating oils, naphthas, kerosene, gasoline, grease, vegetable, animal and fish oils, synthetic esters, cleaning solvents and the like, containing or not containing detergents, emulsifiers or other addends. The corrosion-inhibiting amounts may vary from 0.0001 to 0.2 g./100 ml. of the composition for most purposes, but larger amounts up to about 10 g./100 ml. of composition may be used, in solutions, suspensions, semi-solids and concentrates, depending on the nature or carrier compositions (whether solid, semi-solid or liquid) used therewith, and the solubility or suspendability of the corrosion inhibitor therein. The inhibitors of this invention may be dissolved or suspended in an inert solid, semi-solid, fluid or fluid composition as a concentrate to be added or incorporated in a final composition by blending, grinding, dilution, etc. Cleaning pads composed of soap or detergent compositions and steel wool, copper mesh or wire mesh are specific examples of solid or semi-solid carrier compositions to which the corrosion inhibitors of this invention can be added.

The invention also contemplates a method of inhibiting the corrosion of metals or alloys in contact with a corrosive fluid (gaseous or liquid) atmosphere by incorporating an effective and corrosion-inhibiting amount of the corrosion inhibitors disclosed herein. The method is carried out by adding or introducing the corrosion inhibitor

per se or as a fluent mixture into systems in contact with such corrosive atmospheres. The rate of introduction or the amount of corrosion inhibitor used is varied in accordance with the demands of the system in order to accomplish the intended result.

The corrosion inhibitors of this invention are used and applied in the same manner as prior art corrosion inhibitors are used to combat the deterioration of metal surfaces in contact with a corrosive environment. The metal surfaces to be protected may be ferrous metals, alloys, plated metals, tin, iron, aluminum, brass, copper, bearing metals, castings, machine parts and the like which are in contact with aqueous environments or aerated aqueous environments, or aerated aqueous commercial detergent environments. The corrosive atmospheres counteracted by the corrosion inhibitors of this may contain acids, alkali, salts, organic materials, solvents, water and emulsifiers, ordinary soaps, modern detergents and the like. The corrosion inhibitors of this invention are particularly effective against the corrosive action of aerated aqueous solutions that are used in many processes, and are also particularly effective against the corrosive action of aqueous solutions of synthetic detergents and emulsifiers.

The embodiments of this invention in which an exclusive property or privilege is claimed are defined as follows:

1. A detergent composition consisting essentially of a major portion of water, about 0.0001 to about 0.2% by weight of a corrosion inhibitor of the group consisting of 1,2-bis(2-benzimidazolyl)-1,2-dihydroxyethane, 1,4-bis(2-benzimidazolyl)-1,2,3,4-tetrahydroxybutane, 1,2-bis(2-benzimidazolyl)ethane, 1,8-bis(2-benzimidazolyl)octane and 1,1-bis(2-benzimidazolyl)methane and about 0.1 to 10% by weight of a detergent composition consisting essentially of an alkyl aryl sulfonate detergent and about 5 to 20% by weight, based on said detergent composition, of at least one substance of the group consisting of sodium pyrophosphate and sodium tripolyphosphate.

2. A detergent composition in accordance with claim 1 in which said corrosion inhibitor is 1,2-bis(2-benzimidazolyl)-1,2-dihydroxyethane.

3. A detergent composition in accordance with claim 1 in which said corrosion inhibitor is 1,2-bis(2-benzimidazolyl)ethane.

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