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DETERGENT COMPOSITION, NON-CORROSIVE TO METAL SURFACES

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This invention relates to a new class of corrosion inhibitors and corrosion-inhibiting compositions comprising or containing certain nitrated or nitrogen-containing mono-, di-, and polycarboxylic extract acids, and fractions thereof, prepared by nitrogen-dioxide oxidation of solvent extracts obtained in the solvent refining of mineral lubricating oils using a solvent selective for aromatic compounds. More particularly, this invention relates to a composition and method of inhibiting the corrosion of metals or alloys in contact with aerated, aqueous solutions, particularly aqueous detergent solutions which are prone to attack metal surfaces.

Metal surfaces, particularly copper and copper-alloy surfaces, are easily oxidized and corroded by contact with aerated solutions of commercial detergent compositions. Organic compounds containing nitrogen, oxygen, sulfur, and other members of Groups V and VI of the Periodic Table, such as amines, mercaptans, heterocyclic nitrogen compounds, etc., are widely used effectively in many aqueous environments to mitigate such corrosion.

Commercial detergent compositions, however, have presented an especially severe problem because of their polyphosphate contents. The polyphosphates tend to dissolve the copper or zinc from alloys such as brass, and to solubilize the metals as metal polyphosphate anions. Because the detergents prevent the deposition of protective films on the metal surfaces, little success has been realized heretofore in combating the corrosiveness of aqueous detergent solutions.

In accordance with this invention, we have discovered that certain complex, nitrated or nitrogen-containing mixed mono-, di-, and polybasic acids derived from solvent extracts obtained in the solvent refining of mineral lubricating oils are effective corrosion inhibitors in aqueous environments. This invention relates not only to a method of mitigating such corrosion, but also to a corrosion-inhibiting composition comprising a fluent mixture of said complex acids to be added to or incorporated in aqueous environments subject to corrosion, particularly aqueous detergent compositions containing or in contact with an oxygen-containing gas. Furthermore, the corrosion inhibitors of this invention have been found to be effective in small concentrations, in the order of 0.01 to 0.2 g./100 ml. solution or about 0.01 to 0.2 wt. percent.

In some applications higher concentrations may be used, e.g., 1% to 50% by weight based on the weight of detergent in the solution.

The primary object of this invention is to provide a new corrosion inhibitor.

Another object of this invention is to provide means for mitigating corrosion in the form of fluent mixtures containing an effective amount of a novel corrosion inhibitor.

Still another object of this invention is to provide a method of mitigating the corrosive action of aerated detergent solutions.

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

The novel corrosion inhibitors of this invention and the methods for their preparation are described in detail in copending application Serial Number 24,883, now abandoned, filed April 27, 1960, by John B. Braunwarth,

and application Serial Number 114,637, filed June 5, 1961, by Messrs. William L. Fierce and Roger L. Weichman.

It is known in the art that alkyl-substituted aromatic compounds can be oxidized to aromatic dicarboxylic acids and their esters by liquid-phase oxidation with a molecular-oxygen-containing gas. Terephthalic acid is prepared in this manner. When alkylated aromatic compounds contain several oxidizable alkyl groups, or when the alkyl substituent groups contain relatively longer chains, it is known that the oxidation of the first alkyl group to a carbonyl group takes place with more or less ease, but the subsequent oxidation of the resulting alkylated aromatic monocarboxylic acid to a dicarboxylic acid is much more difficult. The art has turned to the use of nitrogen dioxide, or compounds which release the NO_2 group, in anhydrous liquid phase with a molecular-oxygen-containing gas. In these processes, nitrogen dioxide is only used alone in the first stage oxidation to prepare the mono-carboxylic acid and oxygen is added to complete the oxidation. The use of this mixed NO_2=O_2 reaction mixture is most effectively executed with a catalyst and even then the yields are low on the order of 10% to 52% conversion, based on reactants charged per hour.

These prior art processes are all based on pure starting materials, e.g., toluene, cumene, the various toluic acids, and the like. When an attempt is made to apply these prior art processes to more complex and impure starting materials, such as petroleum by-products, exemplified by solvent extracts, using the low-temperature techniques of the prior art, the acid numbers of the products and the conversion rates are too low for economic production. Thus, as disclosed in copending application Serial Number 24,883, in employing nitrogen dioxide alone at temperatures of 25° to 46° C. with 30 to 140 hours' contact time, the best product had an acid number of only 41.0. Since solvent extracts are extremely complex in nature, the discovery set forth in this copending application, that conducting the oxidation at temperatures of 100° C. to 200° C. results in less nitration and the formation of more carboxyl groups, is unique. The instant invention is based on the discovery that any of the complex oxidation products described in application Serial Number 24,883 are useful corrosion inhibitors regardless of the temperature of the reaction, and also that the purified, complex, oxidation products prepared therefrom by the process of copending application Serial Number 114,637 are effective corrosion inhibitors.

The starting materials for the preparation of the corrosion inhibitors of this invention comprise any source of complex, high-molecular-weight, polynuclear, aromatic radicals and heterocyclic nuclei, containing sulfur, nitrogen and oxygen in one or more rings, and containing oxidizable alkyl side-chains. A preferred source of this type of organic compound comprises solvent extracts obtained in the solvent extraction of mineral lubricating oils. Since the general process for solvent refining mineral lubricating oils is well-known, and described in both of said copending applications, it is only necessary herein to set forth some of the properties thereof, also disclosed in said copending applications, and give some examples.

The solvent extracts from lubricating oils used as starting materials for this invention have the following general properties and characteristics:

TABLE I

Characteristic:	Range of value
Gravity, ° API	7.3–18.3.
Gravity, Sp., 60/60° F.	0.9446–1.0195.

TABLE I—Continued

Characteristic—Continued	Range of value
Viscosity SUS at 210° F.	40–1500.
Viscosity index	Minus 153 to plus 39.
Pour point, ° F.	20–115.
Color, NPA	+2–5D.
Molecular weight, average	Above 300.
Sulfur, percent Wt.	Above 0.6.
Nitrogen, percent Wt.	Below 1.
Aromatic compounds, percent (including heterocyclics)	75–98.
Av. No. of aromatic rings/mean arom. mol.	1.7–3.5.

It is apparent that the yield and characteristics of the final oxidized acid products used in accordance with this invention may vary somewhat depending on the concentration and types of aromatic starting materials employed. The invention finds particular application to those solvent extracts containing from about 30% to 100% by weight of reactable aromatic and heterocyclic compounds of the type defined herein although the process is economically feasible using solvent extracts containing as little as 20% by wt. of such aromatic compounds. Solvent extracts are, accordingly, further characterized since the chemical and physical properties of this material, the complexity, etc., lends unique properties to the carboxylic acids produced therefrom. Thus, the average molecular weight of solvent extracts obtained in the preparation of 180–200 vis. neutral oils is about 340. These extracts contain about 75% to 87% of complex aromatic hydrocarbons and heterocyclics of aromatic character having an average of about 2.7 aromatic rings per aromatic molecule. The extracts obtained during the manufacture of 150–160 vis. bright stocks contain from 85% to 98% of complex aromatics and heterocyclics having an average of about 3.3 aromatic rings per aromatic molecule. When a typical solvent extract was subjected to carbon-type analysis using the method of Kurtz, King, Stout, Partikan and Skrabek (Anal. Chem., 28, 1928 (1956)), the results were: C_a—39%, C_n—30%, and C_p—31%. In this analysis the C_a and C_n include only the carbon atoms in the rings, while C_p includes the carbon atoms present as paraffins and as side-chains on the aromatic and naphthene rings. Extract No. 19 in Table III had an average molecular weight of 340, contained 84% aromatics (and heterocyclics of aromatic type), as determined by the silica gel procedure, showed 16% saturated hydrocarbons, etc., and contained 86.4% carbon and 10.7% hydrogen.

The complexity of the types of compounds present, as based on these analyses, is illustrated by the following table:

TABLE II.—ESTIMATED CHEMICAL COMPOSITION OF SOLVENT EXTRACTS NOS. 19 AND 21 OF TABLE III

Type of compound:	Approx. percent in the extract
Saturated hydrocarbons	12.5
Mononuclear aromatics:	
Substituted benzenes	25.0
Dinuclear aromatics:	
Substituted naphthalenes	30.0
Trinuclear aromatics:	
Substituted phenanthrenes	10.0
Substituted anthracenes	5.0
Tetranuclear aromatics:	
Substituted chrysenes	0.5
Substituted benzphenanthrenes	0.2
Substituted pyrenes	0.2
Pentanuclear aromatics:	
Perylene	0.01
Sulfur compounds,* oxygen compounds, etc.	16.5

* Mainly heterocyclic compounds.

Any portion of the reactive aromatic constituents in solvent extracts may be isolated therefrom, or from other sources, to be used as starting materials for the present oxidation reaction. For example, solvent extracts may be distilled and selected portions thereof used as the starting materials. The content of reactive, complex, polynuclear, aromatic components, and heterocyclics, present in solvent extracts may vary depending on the type of solvent used, the extraction process and conditions, the mineral oil being treated, etc., although the general types of compounds present in the extract are not so varied. Extracts normally produced in the production of neutral oils and bright stocks will contain from about 30% to 90% of reactive complex aromatics as herein defined, and represent a preferred starting material because no further treatment is necessary to obtain economical yields of acids.

Table III following gives the physical and chemical charateristics of a number of solvent extracts from different sources, using different solvents, that can be used as the source of the complex radicals which characterize the nitroacids of this invention.

TABLE III.—SOURCES AND PHYSICAL CHARACTERISTICS OF SOLVENT EXTRACTS AND OTHER SOURCE HYDROCARBONS

Ext. No.	Crude Source	Solvent	API Grav.	Vis./210° F.	V.I.	° F. Pour	° F. Flash	° F. Fire	Percent C.R.	Percent Sulfur	Average Molecular Wt.
1	East Tex.	Phenol	11.1	282	−40	+55			7.2	2.66	
2	do	do	15.4	285	+39						
3	do	do	12.6	310.1	−1	+80			4.7	2.27	
4	do	do	14.6	313	+27	+90			4.7	2.2	
5	do	do	15.4	372	+5	+60			4.13	2.33	
6	do	do	13.7	355	+27	+80				2.18	
7	do	do	8.6	616	0	+70					
8	do	do	10.5	172.1	−101	+60				2.88	
9	Santa Fe Springs	do	10.2	371		+65	520	600			
10	Texas	Furfural	13.0	1,500		+85	470	515			
11	Penn.	Chlorex	12.2	1,365		+85	560	630			
12	Penn.	Nitrobenzene	10.0	1,500		+75	555	640			
13	Mid-Cont.	Propanecresol	14.4	1,500		+100	540	605			
14	do	Phenol	13.6	41.7	−82	+20					
15	do	Chlorex	13.6	200	−61	+75					
16	do	Phenol	8.9	569		+75					
17	do	Furfural	14.9	50.2	25	+20					
18	East Tex.	Phenol	13.5	341	17	+65	530	610	5.76	2.36	
19	do	do	11.1	61.5	−56	+40	435	475	0.42	2.7	340
20	do	do	13.7	360	+25	+65	550	630	5.5	2.3	590
21	do	do	7.7	71.1	−128	+35	420	495	0.86	3.2	340
22	do	do	7.3	796	−76	+65	520	610	7.7	3.0	

In order to demonstrate the preparation of nitro-acids to be used in accordance with this invention, several portions of a solvent extract having an original Acid No. of 6.9 was treated to oxidation with NO_2, using the prior art techniques as applied to pure alkyl aromatic starting materials. The results are shown in Table IV.

TABLE IV.—OXIDATION OF SOLVENT EXTRACTS WITH NO_2

Run No.	Temp.,°C.	Time, Hrs.	Wt. percent NO_2	Oxidized Extract Acid No.
1	46	30	3.5	7.9
2	25	140	7.5	10.0
3	25	140	13.0	14.0
4	25	140	69.9	34.0
5	25	140	72.0	41.0

All of the reactions were carried out in sealed glass tubes. The reaction tubes had a capacity of about 160 cc. and were formed of glass tubing having an outside diameter of 1¾ inches, one end of which was closed to a test-tube end and the other end was joined to a tube having an outside diameter of ⅜ inch.

The acids produced by Runs 1, 2 and 3 may be used as corrosion inhibitors in accordance with this invention, but the acids produced by Runs 4 and 5 are more effective. The product of Run No. 4 contained 3.8 weight percent of nitrogen, which, based on the average mol wt. of 330 for the extract oil, indicates that approximately one nitrogen atom had been added per molecule of solvent extract. In accordance with this invention, such an acid represents the first member of a series of preferred nitro-acids derived from solvent extracts which show unusual effectiveness as corrosion inhibitors. This effectiveness is shared by those complex nitro-extract acids having up to 4 or 5 nitro-groups or atoms of nitrogen per molecule, which corresponds roughly to the number of carboxyl groups present in the molecule.

Control of the degree of nitration is shown in the following series of experiments:

Example I

A 110-cc. stainless steel autoclave was charged witih 16.5 g. (0.05 mole) of Extract No. 19, 2 grams of concentrated sulfuric acid, and 14.5 g. of acetic acid. The mixture was cooled to 4° C. in an ice bath, and 2.5 g. (0.054 mole) of liquid nitrogen dioxide were added. The mixture was sealed in the autoclave and pressurized to 81 p.s.i.g. with oxygen. After being heated at 80° C. for 30 minutes, the mixture was cooled and poured into water. The organic phase was collected in benzene and washed with water until neutral, and the benzene solvent was removed by evaporation. The acid number of the product was 25.9 and the nitrogen content was 2.6 wt. percent.

TABLE V.—OXIDATION OF SOLVENT EXTRACT WITH NO_2

Run No.	Temp., °C.	Wt. percent NO_2	Wt. percent Nitrogen New Product	Acid No.	Mole percent Yield Based on NO_2	Mole percent Yield Per Pass
6	4–12	57	2.2	21	23	2.3
7	52	80	3.4	50	34	4.5
8	140	63	2.4	73	43	7.8

Although the conversion by nitrogen dioxide to acids was only 23.8%, and the molar yield per pass (based on nitrogen dioxide) was only 1.0%, the acids produced by Runs 6 and 7 may be used in accordance with this invention. The product of Run 8 is a preferred nitro-acid because the acid number is about 73 and about 2.5 wt. percent of nitrogen is present, indicating close to one nitrogen atom per molecule of extract.

Run No. 8 was conducted by placing 62 g. (0.19 mole) of Extract Oil No. 19 in a 200-cc. beaker and heating to 140° C. Nitrogen was slowly bubbled through the heated extract at the same time that gaseous nitrogen dioxide was bubbled through at a rate of 150 cc. per minute for 2.1 hours. At the end of this period, the mixture was cooled to room temperature. The mixture was washed with distilled water, dried, and found to contain 71 g. of acids. The results indicate that temperature of above about 100° C. with at least about 50% by weight of nitrogen dioxide are necessary for the reaction. The weight ratio of nitrogen dioxide to extract should be between 0.4/1 and 0.8/1, 0.6/1 being preferred.

As previously stated, this invention is also directed to the use of purified nitrated-acids, prepared in accordance with copending application Serial No. 114,367, as corrosion inhibitors. In accordance with said copending application, the NO_2-oxidized, complex, aromatic starting material, as just described in detail, is purified by water washing, the washed oil phase is contacted with an oil-insoluble alcoholic solution of ammonia, and the resulting ammonia salts are decomposed to produce substantially pure complex acids as the residue. The products so prepared are light brown solids, predominantly dibasic, and exhibit appreciably no solubility in ordinary solvents.

The first step of the process comprises contacting the complex aromatic oil with nitrogen dioxide at a temperature above 100° C., but not exceeding 200° C., and preferably about 120° to 160° C., for at least about 2 hours. The proportion of nitrogen dioxide to complex aromatic hydrocarbon is that which is sufficient to produce the desired carboxylic acids, which proportion is preferably between about 40% by wt. to 80% by wt., based on the weight of said hydrocarbons. Large excesses of nitrogen dioxide are to be avoided in order to minimize the danger of an explosion.

One technique is to place about 0.2 mol of aromatic hydrocarbon in a reaction container and heat the oil to a temperature of about 140° C. Nitrogen is slowly bubbled through the heated oil at the same time gaseous nitrogen dioxide is bubbled through the oil at a rate of 150 cc. per minute. The introduction of nitrogen and nitrogen dioxide is continued for 2 to 3 hours. At the end of this time, the reaction mixture is cooled to room temperature and the foregoing purification steps are applied.

This technique is demonstrated by the following examples:

Example II

A 125-g. portion of bright stock extract, derived by phenol extraction in the manufacture of high-viscosity-index bright stock and having an acid number of 2.5, was charged to a 250-cc., three-necked flask equipped with fritted-glass bubbler, mercury-sealed stirred, and thermometer. The oil was heated to about 140° C. and maintained at that temperature for six hours while nitrogen (50 cc./min.), nitric oxide (80 cc./min.), and oxygen (40 cc./min.) were bubbled through it. The resulting product was cooled to room temperature and dissolved in toluene, after which it was extracted several times with a 2/1 mixture of methanol and water to remove water-soluble acids. After the solvent was stripped off, the washed reaction product was found to have an acid number of 29 and an average molecular weight of about 770. It weighed 146.5 g. The oxidation had increased the acid number from 2.5 to 29.

A 124.7-g portion of the washed oil solution was then taken up in benzene and contacted sequentially with three batches of solvent consisting of 6 parts (by volume) of concentrated ammonium hydroxide, 75 part of water, 150 parts of methanol, and 25 parts of carbon tetrachloride. The wash phases were combined, and the oil and wash phases were separately heated to constant weight on a steam bath. The oil had an acid number of

21.3 and an average molecular weight of 870, and weighed 118.3 g. The purified acids had an acid number of 151 (158, electrometrically), an average molecular weight of 670 (determined by boiling point elevation in tetrahydrofuran), and weighed 8.1 g. Because the total weight of these two products was slightly greater than the weight of starting material, it appears that a small amount of solvent remained in one or the other, or both, after they had been heated on the steam bath.

The acid product was solid, and had a light brown color after it was ground with mortar and pestle. It was not soluble to any appreciable extent in water, acetone, benzene, nitrobenzene, toluene, nitropropane, isopropanol, or hexane, but it was highly soluble in N,N-dimethylformamide. Because there were 1.9 equivalents of acid per mole, it is apparent that the product was predominantly dibasic.

Example III

Sixty-two grams (0.19 mole) of solvent extract No. 19 is placed in a 200-cc. beaker and heated to 140° C. Nitrogen is slowly bubbled through the heated solvent extract at the same time gaseous nitrogen dioxide is bubbled through at a rate of 150 cc. per minute for 2.1 hours. At the end of this period, the mixture is cooled to room temperature, and dissolved in toluene. The toluene solution is extracted several times with a 2/1 mixture of methanol and water to remove water-soluble acids. The solvent is stripped off and the reaction product, having an acid number of 73 (mole percent yield based on NO_2 of 43; mole percent yield per pass 7.8), is taken up in benzene and contacted sequentially with three batches of solvent consisting of six parts (by volume) of concentrated ammonium hydroxide, 75 parts of water, 150 parts of methanol, and 25 parts of carbon tetrachloride. The washed phases are combined, and the oil and wash phases are separately heated to constant weight on a steam bath. The oil, containing the oil-soluble acids, exhibits an acid number of about 20, and the purified acids exhibit an acid number of about 150, have an average molecular weight of about 670, and exhibit the solubility characteristics of the purified acids of Example II.

Example IV

Sixty-three grams (0.19 mole) of solvent extract No. 19 is placed in a reaction container and heated to 150° C. Nitrogen is slowly bubbled through the heated solvent extract along with gaseous nitrogen dioxide at a rate of about 100 cc. per minute for about three hours. The concentration of nitrogen dioxide is about 30% that of the nitrogen. At the end of this period, the mixture is cooled to room temperature and dissolved in xylene. The xylene solution is extracted several times with a 3/1 mixture of methanol and water to remove water-soluble acids. The solvent is stripped off and the reaction product, having an acid number of about 78, is taken up in benzene and contacted sequentially with three batches of a solvent comprising six parts by volume of concentrated ammonium hydroxide, 70 parts of water, 155 parts of ethanol and 25 parts of carbon tetrachloride. The washed phases are combined and the oil and wash phases are separately heated to constant weight on a steam bath. The oil, containing the oil-soluble acids, exhibits an acid number of about 25, and the purified acids exhibit an acid number of about 160 and have an average molecular weight of about 680. These acids exhibit the solubility characteristcs of the purified acids of Example II.

The effectiveness of the inhibitors so far described was demonstrated experimentally by a series of experiments with aqueous solutions of "Tide," a commercial detergent composition containing mixed aryl alkyl sulfonates, sodium tripolyphosphate, sodium sulfate, and other components.

First, a water solution of "Tide" (0.5 g. detergent/100 ml. solution) was prepared and divided into several flasks. Then portions of "nitrated extract acids," or fractions thereof, were added to the solutions in amounts equivalent to 0.1 g./100 ml. of solution. However, because these acids were only sparingly soluble in water, they did not dissolve completely. We estimate that the actual acid concentrations were in the range of about 0.01 g./100 ml. Finally, two brass strips (½" x 3") were immersed in the solutions in each flask, and air was bubbled through the solutions at a rate of 20–30 ml./min. for 72 hours while the temperature was maintained at 70° C. The weight losses from the brass strips were as given in the following examples.

Example V

In this example, the inhibitor, prepared in accordance with Run No. 8 of Table V and deoiled by extraction with boiling hexane, had an acid number of 90 and the following elemental analysis: carbon, 71.3% w.; hydrogen, 7.2% w.; nitrogen, 3.38% w.; and oxygen, 2.02% w. The weight loss from the strips in the inhibited solution averaged 0.0055 g. (0.51%), as compared with an average weight loss of 0.0254 g. (2.17%) from the strips in the uninhibited solution.

Example VI

In this example, the inhibitor, prepared in accordance with Run No. 8 of Table V and isolated by the method of Example III, had an acid number of 152 and contained 5.2% w. of nitrogen. The average weight loss from the coupons in the inhibited solution was only 0.0020 g. (0.16%), as compared with an average weight loss of 0.0198 g. (1.7%) from the coupons in the corresponding uninhibited solution.

The corrosion inhibitors of this invention are used 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 invention 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.

Examples of such synthetic detergents and emulsifiers that can be present in the aqueous environments to be protected by the corrosion inhibitors of this invention are dodecylbenzene sulfonic acid, salts of fatty acid tertiary amines, alkylaryl sulfonates, alkylaryl sulfonates having molecular weights of 465 to 480, alkylaryl polyether alcohols, polyglycol esters, disodium N-octadecylsulfosuccinamate, tetrasodium N-(1,2-dicarboxyethyl)-N - octadecylsulfosuccinamate, diamyl ester of sodium sulfosuccinic acid, ethanolated alkyl guanidine amine complexes, isopropyl naphthaline sodium sulfonate, alkali metal petroleum sulfonates, alkaline earth metal petroleum sulfonates, fatty amides, blends of alkalis and detergents, polyoxyethylated nonylphenols, polyoxyalkylene esters and sulfonates, and the like, which are either of anionic, nonionic, or cationic type. These detergents and emulsifiers are used in textile processing, electroplating, car washing, metal pickling, grease emulsifiers, emulsion paints, adhesives, cleaning compositions, dishwashing compositions, and the like. The corrosion inhibitors of this invention find application in the preparation, handling, and use of these type of detergent compositions.

Accordingly, this invention contemplates non-corresive fluent mixtures of an inert solvent and the corrosion in-

hibitors 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 suspensible amount, of the corrosion inhibitors.

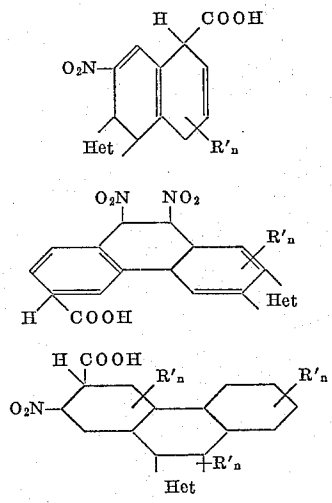
Suitable solvents, inert as regards any reactivity toward the corrosion inhibitors but exhibiting a corrosive action to metal under the conditions of use, include water, liquid hydrocarbons, lubricating oils, neutral lubricating oils, bright stock, solvent extracts from the solvent refining of mineral 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 0.01 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.

Expressed on a weight percent basis, a corrosion-inhibiting amount can be from about 0.01 to 0.2 wt. percent, or about 0.01% to about 5.0% or about 10% by weight for solutions, suspension, and concentrates, depending on the nature of the carrier composition (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.

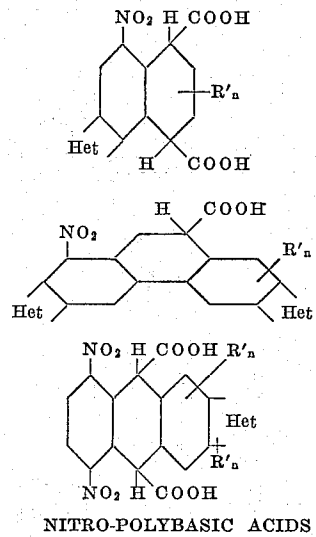
The invention also contemplates a method of inhibiting the corrosion of metals or alloys in contact with a corrosive fluid (gaseous or liquid) atmosphere by incorporating an effective and corrosion-inhibiting amount of the corrosion inhibitors disclosed herein. The method is carried out by adding or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

In order to graphically illustrate the complexity of the nitrated or nitrogen-containing aromatic and heterocyclic acids which comprise the active corrosion inhibitors of this invention, the following simplified structures are given, omitting the positioning of the numerous alkyl, cycloalkyl substituents and heterocyclic nuclei present in the molecules:

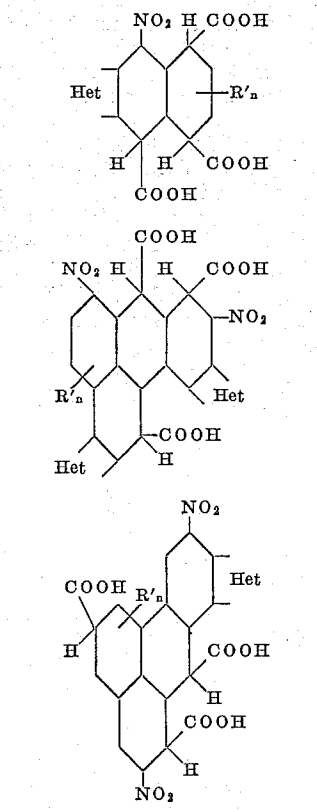
NITRO-MONOBASIC ACIDS



NITRO-BASIC ACIDS



NITRO-POLYBASIC ACIDS



wherein R' comprises alkyl and/or cycloalkyl substituents having a sum of about 15 to 22 carbon atoms in each formula, *n* is the number of such alkyl group, which may be from 3 to 10, and "Het" illustrates one or more S-, N-, or O-containing heterocyclic rings in the molecule. The molecular weight of the acids is in the range of about 346 to 728, indicating the presence of about 1 to 3 NO_2 groups.

Having thus described the invention, the only limitations attaching thereto appear in the appended claims. The term "solvent extracts" as used herein is meant to include the extract product obtained in the solvent refining of mineral lubricating oils, or fractions thereof, by solvent extraction using a solvent selective for aromatic compounds.

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

1. A detergent composition normally tending in aerated

aqueous solution to corrode metals consisting essentially of a water-soluble mixed aryl sulfonate detergent, a water-soluble metal polyphosphate and as the sole corrosion inhibiting agent about 0.01 to about 10% by weight of nitrogen-containing mixed mono-, di-, and poly-carboxylic acids derived from solvent extracts obtained in the solvent extraction of mineral lubricating oils using a solvent selective for aromatic compounds, said acids being prepared by reaction of said solvent extracts with nitrogen dioxide at a weight ratio of nitrogen dioxide to solvent extracts of about 0.4/1 to 0.8/1 and a temperature of about 100° to 200° C. for at least about 2 hours and characterized by having a molecular weight of about 346 to 728 and an average of about 1.7 to 3.5 aromatic rings per mean aromatic molecule.

2. A detergent composition in accordance with claim 1 in which said water-soluble synthetic detergent is mixed arylalkyl sulfonate and said water-soluble metal polyphosphate is sodium tripolyphosphate.

3. A detergent composition in accordance with claim 1 in which said mixed polycarboxylic acids are prepared by reacting said solvent extract and nitrogen dioxide at a temperature of about 140° C. for about 2.1 hours and said complex acids have an acid number of about 73 and contain about 2.4 wt. percent of nitrogen.

4. A detergent composition in accordance with claim 1 in which said corrosion inhibiting agent comprises the oil-soluble complex carboxylic acid portion of said reaction product of said solvent extracts and nitrogen dioxide, obtained by treating said mixed complex carboxylic acid reaction product with an aqueous-alcoholic-ammonia solution to form an aqueous phase containing the ammonium salts of the water-soluble complex acids and an oil phase of the ammonium salts of the oil-soluble complex acids, said phases are separated and the oil phase is heated to decompose said oil-soluble ammonium salts to the free complex acids.

5. A detergent composition normally tending in aerated aqueous solution to corrode metals consisting essentially of a water solution of mixed arylalkyl sulfonates, sodium tripolyphosphate and sodium sulfate and as the sole corrosion inhibiting agent about 0.1 g. to 0.01 g./100 ml. of said water solution of complex dicarboxylic acids derived from phenol extract obtained in the solvent extraction of mineral lubricating oils to prepare bright stocks, said complex acids being prepared by reacting said phenol extract with about 150 cc./min. of nitrogen dioxide at a temperature of about 140° C., dissolving the reaction product in an aromatic solvent, washing the aromatic solvent solution with a 2/1 mixture of methanol and water, recovering a first washed aromatic solvent phase, treating said aromatic solvent phase with a solvent consisting of about 6 parts by volume of concentrated ammonium hydroxide, 75 parts by volume of water, 150 parts by volume of methanol and 25 parts by volume of carbon tetrachloride to produce a second washed aromatic solvent phase containing ammonium salts of said acids, heating the second washed aromatic solvent phase to decompose the ammonium salts and recover purified oil-soluble complex dicarboxylic acids therefrom having an acid number of about 151 and an average molecular weight of about 670.

6. A detergent composition in accordance with claim 5 in which the complex dicarboxylic acids recovered have an acid number of about 152 and contain about 5.2% by weight of nitrogen.

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