United States Patent Office 3,078,223 Patented Feb. 19, 1963

3,078,223

REDUCING CORROSION IN PLANT EQUIPMENT

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No Drawing. Filed May 16, 1960, Ser. No. 29,154
9 Claims. (Cl. 208—348)

This is a continuation-in-part of my copending application Serial No. 850,049, filed November 2, 1959, now abandoned, and relates to a novel method of reducing corrosion in plant equipment. More particularly, the present invention is concerned with reducing corrosion caused by hot effluent products being removed from distillation zones.

In many petroleum refining operations, a petroleum fraction is subjected to distillation to separate the same into light and heavy products. The petroleum fraction generally contains acidic components which result in corrosion of the plant equipment. These acidic components either are present in the original petroleum feed and/or are formed at the high temperatures used in petroleum conversion reactions. The corrosion is particularly acute upon cooling of the hot effluent products withdrawn from a distillation zone.

This corrosion problem is exemplified in the case of a stabilizing column used to strip lighter components from the reaction products of a reforming operation. In the reforming operation, a gasoline or naphtha is subjected to contact with a reforming catalyst at a temperature of from about 800° to about 950° F. In the presence of hydrogen. Any suitable reforming catalyst is used and preferably comprises a composite containing platinum, more particularly an alumina-platinum composite and still more particularly an alumina-platinum-combined halogen composite. Other reforming catalysts include composites containing metals or compounds of metals in the left-hand columns of groups V, VI and VIII of the periodic table. Specific composites in this class are alumina-molybdenum oxide, alumina-molybdenum oxide-cobalt oxide, alumina-molybdenum oxide-nickel oxide, aluminum-palladium, alumina-palladium oxide, etc., as well as the corresponding sulfides thereof. The charge to reforming may be a full boiling range gasoline or a selected cut thereof, referred to as naphtha and having an initial boiling point within the range of from about 150° to about 350° F. and an end boiling point from about 325° to about 450° F. The reactor effluent products are cooled to separate hydrogen for reuse in the process, and the liquid products are subjected to stabilization to strip lighter components therefrom. The lighter components removed as an overhead from the stabilizing column contains acidic components, in this case particularly HCl, which then are passed through cooling equipment in order to condense liquid components. The charge to the stabilizer contains water and, upon cooling of the hot effluent products from the stabilizer, corrosion occurs in the cooling and receiving equipment. The cooling equipment is generally of the heat exchange type, in which the hot effluent overhead products from the stabilizer are passed in indirect heat exchange with a heat exchange medium of lower temperature. Considerable difficulty is encountered because of corrosion of the heat exchanger and the resultant necessity of replacing the internal equipment thereof. This in turn necessitates shutting down the stabilizer and, as can be seen, interferes with continuous plant operation.

Another example of corrosion problems encountered in plant equipment is in the prefractionation of a petroleum charge to separate the same into a selected fraction or fractions for subsequent catalytic conversion.

For example, a gasoline fraction may be subjected to fractionation to separate an intermediate or high boiling fraction for use as charge to a reforming operation of the type hereinbefore described. The fraction subjected to such separation contains acidic components and water and, upon cooling of the overhead products, corrosion of the cooling and receiving equipment occurs. This problem is acute and, as mentioned above, it results in too frequent shut-downs to replace the internals of the heat exchanger type coolers, the connecting piping and/or receiver, and necessitates discontinuing the prefractionator operation.

The above are two examples in which serious corrosion problems are encountered upon cooling of the hot effluent products of a distillation zone. The term "distillation" zone is used in the generic sense to include any type of fractionation, stripping, stabilization, etc. in which the overhead effluent products are subjected to cooling to separate a condenstae. In most cases a portion of the condensate is recycled to the upper portion of the distillation zone as a cooling and refluxing medium therein.

In the operation of the distillation zone of the class hereinbefore described, it is important that the pH of the overhead be controlled. For best operations, the pH should be within the limits of from about 5 to about 7 and still more particularly from about 6 to about 6.8. One method of controlling the pH is to introduce an inorganic alkaline agent into the overhead effluent products. Suitable inorganic alkaline agents include sodium compounds such as sodium hydroxide, sodium carbonate, disodium phosphate, trisodium phosphate, etc. or mixtures thereof. Other alkaline agents include the corresponding potassium compounds, lithium compounds, rubidium compounds, ammonium hydroxide, etc. or mixtures of one or more of these with the sodium compounds. These alkaline agents preferably are prepared as aqueous solutions and are injected into the hot effluent products leaving the distillation zone. It also is necessary to utilize a corrosion inhibitor and, for practical purposes, it is desirable to form a single solution of both the inorganic alkaline agent and the corrosion inhibitor, and to inject this combined solution into the hot effluent products. This avoids the necessity of utilizing separate pumping equipment which otherwise would be required in the case of a non-water soluble corrosion inhibitor.

A water soluble corrosion inhibitor offers a number of advantages. In the first place, it will penetrate the aqueous phase and thereby serve to protect the inner surfaces of the piping and heat exchange equipment through which the hot effluent products pass. Secondly, the water soluble corrosion inhibitor will settle out in the water phase in a subsequent settler or receiver and thereby be withdrawn from the process. As another advantage, the water soluble corrosion inhibitor may be prepared as a solution in water which obviously is the least expensive solvent available. As hereinbefore set forth, the aqueous solution is prepared to contain both the alkaline agent and the corrosion inhibitor and this offers the improtant advantage of permitting simultaneous introduction of both of these materials in a single step.

While the water soluble corrosion inhibitor offers the advantages set forth above, the corrosion inhibitor must meet several stringent requirements. In the first place, the inhibitor must be water soluble and remain in solution in the aqueous menstruum. Secondly, the corrosion inhibitor must not cause emulsification problems which will interfere with the subsequent separation in the settler or receiver of a water phase from a petroleum phase. In addition, the corrosion inhibitor must be reasonable in cost in order to justify its use.

The present invention is based on discovery that an effective water soluble corrosion inhibitor may be prepared from certain by-product chemicals which are available commercially at a lower cost than pure chemicals. Surprisingly, it has been found that these lower cost, less highly refined and mixed by-product materials may be used in preparing effective water soluble corrosion inhibitors which meet the requirements hereinbefore set forth. Normally it would be expected that the use of these by-product materials would not satisfy the stringent requirements hereinbefore set forth and that substantially pure chemicals would be required for the preparation of satisfactory corrosion inhibitors. As will be shown in the appended examples, almost the reverse is true because a corrosion inhibitor prepared from a substantially pure chemical instead of the by-product material resulted in a highly gelled product which was difficultly soluble in water.

As will be hereinafter set forth in detail, the water soluble inhibitor for use in the present invention is prepared by the partial esterification of the condensation product of alkylene oxide with a polyamine residue. The use of the polyamine residue surprisingly offers advantages in the preparation of the inhibitor as set forth above. However, it also is an important and essential feature of the present invention that the esterification of the oxyalkylated polyamine residue is a partial esterification only and is effected using a critical mole ratio of acid to oxyalkylated polyamine residue. As will be shown by the examples appended to the present specifications, esterification in excess of the critical range herein specified results in an inhibitor which is not water soluble and therefore cannot be used for the purposes herein set forth.

In one embodiment the present invention relates to the method of reducing corrosion of plant equipment upon cooling of hot effluent products from a distillation zone and avoiding emulsification during subsequent separation, which comprises incorporating in said hot effluent products an inorganic alkaline agent and a water soluble inhibitor prepared by (1) condensing an alkylene oxide with a high boiling polyamine residue under conditions to replace each amine hydrogen of said polyamine residue with an oxyalkylene group, said residue remaining after distilling off lighter products formed in the manufacture of ethylene diamine, and (2) thereafter partially esterifying the resultant condensation product by reacting with not more than about 0.25 mole per mole of the oxyalkylated polyamine residue of a mixed carboxylic acid containing from about 16 to about 40 carbon atoms per molecule, and subsequently cooling said hot effluent products.

In a specific embodiment the present invention relates to a method of reducing corrosion of heat exchanger equipment during the cooling of hot overhead effluent products containing HCl from a hydrocarbon stabilization zone and avoiding emulsification during subsequent separation of aqueous and hydrocarbon phases which comprises incorporating in said hot overhead effluent products, prior to cooling thereof, an aqueous solution of both a sodium compound in a concentration to maintain a pH of from about 6 to about 6.8 in said effluent products and a water soluble corrosion inhibitor prepared by (1) condensing ethylene oxide with a high boiling polyamine residue under conditions to replace each amine hydrogen of said polyamine residue with an oxyethylene group, said residue remaining after distilling off tetraethylenepentamine and lighter products formed in the manufacture of ethylene diamine by the reaction of ethylene chloride and ammonia, and (2) thereafter partially esterifying the resultant condensation product by reaction with tall oil acid in a mole ratio of acid to oxyethylated polyamine residue of from about 0.1 to about 0.25:1, subsequently cooling said hot effluent products and thereafter separating an aqueous phase from a hydrocarbon phase.

As hereinbefore set forth and as will be shown in the appended examples, it is an important and essential feature of the present invention that the esterification of the oxyalkylated polyamine residue be effected using not more than about 0.25 mole of acid per mole of polyamine residue, and more particularly from about 0.1 to about 0.25:1 mole. The use of larger concentrations of acid results in products which are not water soluble and therefore will not offer the advantages of the water soluble inhibitor as previously described. The use of lesser concentrations of acid, on the other hand, will not produce the improved corrosion inhibitors.

In addition to the important requirement of critical mole ratio of acid and amine, it has been found that effective water soluble corrosion inhibitors are prepared through the use of by-product chemicals. The by-product chemical used as the amine portion and reactant in the preparation of the corrosion inhibitor of the present invention is the polyamine residue remaining after distilling off lighter products in the manufacture of ethylene diamine. Ethylene diamine is prepared by reacting ethylene chloride with ammonia. During the reaction, products boiling above ethylene diamine are inherently produced. In the recovery of the products from the ethylene diamine manufacture, ethylene diamine, diethylene triamine, triethylene tetramine and tetraethylene pentamine are distilled off and further separated to recover the individual polyamines as substantially pure chemical products. Remaining higher boiling products are recovered as a residue and, as hereinbefore set forth, it has been found that this residue is particularly suitable and apparently unique for use in preparing the corrosion inhibitor of the present invention. This polyamine residue is available commercially from a number of sources. One example is "Amine E–100" sold by the Dow Chemical Company. This polyamine residue has a specific gravity at 77°/77° F. of 0.956–0.962 and a boiling range at 760 mm. of 5% at 381° F. and at 80% of 437° F. A similar polyamine residue is available from Carbide & Carbon as "Polyamine H Special." In some cases a lighter polyalkylene-polyamine, particularly diethylene triamine and/or triethylene tetramine, is blended with the polyamine residue in small amounts, say from about 1% to about 15% by weight, in order to reduce the viscosity and to facilitate pumping and handling thereof. This may serve to increase the specific gravity at 77°/77° F. to an upper limit of about 0.999 or slightly higher.

The polyamine residue has a high basic nitrogen and accordingly more reserve alkalinity. Apparently this is one of the important properties of the polyamine residue which makes it particularly effective for use in preparing the corrosion inhibitor of the present invention. It is apparent that the polyamine residue is a complex mixture of polyamines and accordingly may vary in its specific composition. It has been found that the polyamine residue contains heterocyclic amine compounds including, for example, derivatives of poly-aminoethyl piperazines.

While the polyamine residue is peculiarly suitable for use as a reactant in preparing the corrosion inhibitor of the present invention, the polyamine residue must be further reacted in a specific manner to prepare the corrosion inhibitor. Accordingly, the polyamine residue is reacted with an alkylene oxide containing from 2 to 4 carbon atoms, and particularly ethylene oxide, under conditions to replace each of the amino hydrogens with an oxy-ethylene group. This is an important requirement in order that the inhibitor product meets the requirements hereinbefore set forth. This is readily accomplished by reacting the polyamine residue with the alkylene oxide at a temperature of from about 100° to about 300° F. and preferably from about 140° to about 195° F. in the presence of from about 5% to about 30% by weight

of water based upon the polyamine residue. Furthermore, the reaction is effected in the absance of a catalyst, as this has been found to limit the substitution of only one alkylene oxide group for each amino hydrogen. Accordingly, the alkylene oxide is reacted in a stoichiometric equivalent to the amino hydrogens of the polyamine residue. Generally an excess of alkylene oxide is used in order to insure complete reaction of all amino hydrogens. As hereinbefore set forth, in the absence of a catalyst, the substitution of the amino hydrogens will be limited to one alkylene oxide group per amino hydrogen. The reaction is effected readily by gradually adding the alkylene oxide to a heated and stirred mixture of the polyamine residue. The product is a black viscous liquid and in a preferred embodiment the water previously added is not removed and the intermediate product containing water then is further reacted in a manner to be hereinafter described. If advantages appear therefor, it is understood that the water may be removed but, as hereinbefore set forth, it generally is preferred to allow the water to remain.

As hereinbefore set forth, ethylene oxide is preferred for use in reacting with the polyamine residue. In a broad embodiment, the alkylene oxide contains from 2 to 4 carbon atoms and thus includes propylene oxide and butylene oxide. Butylene oxide, when employed, preferably is a mixture of straight chain isomers as present in the butylene oxide mixture commercially available.

As hereinbefore set forth, the novel corrosion inhibitor of the present invention is prepared from low cost mixed chemicals. A preferred mixed chemical used in the next step of the process is tall oil acid which is a mixture of saturated and unsaturated fatty acids, rosin acid and also contains non-acidic materials such as esters, lactones, estolides, alcohols such as sterols, etc. This mixture is obtained by acidifying the black liquor skimmings formed in the pulping of wood, usually pine, by the sulfate (kraft) process. The black liquor produced during the pulping of wood is partially concentrated, then settled and the curdy soap skimmed from the top of the settling liquor. The skimmings are acidified with sulfuric acid (usually of 50 to 98% concentration) and the mixiture heated to about 100° C., followed by decantation of the liberated tall oil. The manufacture, purification, composition, etc., of tall oil is described in "Encyclopedia of Chemical Technology," volume 13, pages 572–7 (1954).

The crude tall oil may contain a mixture of unsaturated fatty acids such as oleic, lineoleic, lineolenic, and the like, rosin acids, all of which have not been identified, but some of which are of the abietic type or the pimaric type, alcohols such as sterol, esters of alcohols with the fatty acids and the rosin acids, lactones, hydrocarbons, and compounds which have not as yet been identified. During purification of the tall oil by many of the usual processes such as treatment with mineral acid, distillation under reduced pressure, solvent extraction, or other methods, a series of chemical reactions may occur among the tall oil constituents so as to modify further the composition of tall oil.

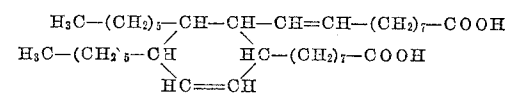
Either the crude tall oil acid or purified tall oil acid may be used. The properties of five commercial tall oil acids are shown in the "Encyclopedia of Chemical Technology" reference mentioned above.

In a preferred embodiment of the invention, the tall oil acid is low in rosin acid content. One commercially available tall oil acid is available commercially as "Indusoil L–5" and is said to have an acid number of 188–196, a saponification number of 190–198, a fatty acid content of 90% minimum, a rosin acid content of 5% maximum and a specific gravity at 60°/60° F. of 0.905–0.910. Another tall oil acid is available commercially as "Crofatol No. 1" and is said to have an acid number of 192 minimum, an iodine value of 125–135 and a rosin acid content of 1.5% maximum. Still another tall oil acid was "Aliphant 44–A" and was said to have an acid value of 192–198, an iodine value of 125–135, a rosin acid content of 1.5% maximum. The acid composition was said to be composed of 50% oleic acid, 46% linoleic acid, 2% palmitic acid, 1% stearic acid and 1% rosin acid. Here again it is noted that the mixed chemical may vary in its composition, but will contain 18 carbon atom fatty acids in a major concentration.

Another mixed by-product acid which may be used in accordance with the present invention is marketed commercially under the trade name of "VR–1 Acid." This is an acid residue produced by distilling, at about 270° C. under about 4 mm. of mercury pressure, the by-product acids obtained in the preparation of sebacic acid by fusing castor oil with alkali. Production of this residue is described in more detail in U.S. Patent 2,267,-269 to Cheetham et al. In the manufacture of sebacic acid from castor oil, the oil is heated with a caustic alkali. This splits the oil, forming octanol-2, methyl hexyl ketone, the alkali salt of sebacic acid, and the alkali salts of various other long-chained acids. The alcohol and ketone are readily removed from the reaction mixture by distillation. The alkali salts which remains then are dissolved in water and, upon slight acidification of the resulting solution, an oily layer separates. At a pH of about 6, the aqueous phase contains the alkali salt of sebacic acid, while the oily layer contains various other acids from the reaction. The term "by-product acids" is generally applied to the mixture of acids forming the oily layer.

These by-product acids then are separated into two parts. After these acids have been washed with a dilute mineral acid, such as sulfuric or hydrochloric, they are washed with water and dried. They then are distilled under reduced pressure. Fatty acids which are primarily monobasic carboxylic acids are taken off at 100° C. to 270° C. at pressures as low as 4 mm. This treatment leaves a residue which is a mixture of fatty acids, apparently primarily polybasic in character and including 36 carbon atoms per molecule acids. The residue is commercially available from Rohm & Haas Company under the trade name of VR–1 Acid and has an average molecular weight of 500–600, an acid number of 134–160, a saponification number of 174–179, an an iodine number of 53–60. A similar product sold by Wallace & Tiernan is "D–50 Acid."

Still another mixed by-product acid is being marketed commercially under the trade name of "Dimer Acid." Still another preferred acid is marketed commercially under the trade name of "Empol 1022." This dimer acid is a dilinoleic acid (36 carbon atoms per molecule) and is a represented by the following general formula:



This acid is a viscous liquid, having an apparent molecular weight of approximately 600. It has an acid value of 180–192, an iodine value of 80–95, a saponification value of 185–195, a neutralization equivalent of 290–310, a refractive index at 25° C. of 1.4919, a specific gravity at 15.5° C./15.5° C. of 0.95, a flash point of 530° F., a fire point of 600° F., and a viscosity at 100° C. of 100 centistokes.

For economic reasons, it is apparent that the use of the mixed by-product acids offers advantages. It is understood that other suitable mixed acids may be employed including, for example, crude oleic acids, referred to in the trade as red oil, etc. In addition to the economic advantage, the mixed acid also offer the advantage of producing a lower melting product and therefore improves the fluidity at lower temperatures. These mixed acids will comprise carboxylic acids having from about

16 to about 40 carbon atoms per molecule. The tall oils, for example, comprise principally acids containing 18 carbon atoms per molecule, but also may contain some lighter and heavier acids. The VR–1 and similar acids will comprise principally acids having 36 carbon atoms per molecule, but here again will contain some lighter and heavier acid. These mixed acids are being defined as containing from about 16 to about 40 carbon atoms per molecule and more particularly from about 18 to about 36 carbon atoms per molecule.

The mixed acid is reacted with the oxyalkylated polyamine residue prepared as hereinbefore set forth to form the corrosion inhibitor of the present invention.

As hereinbefore set forth, it is essential that the proportion of acid and oxyalkylated polyamine residue is within the critical ranges hereinbefore set forth. This reaction is effected in the absence of a catalyst by heating and stirring the mixture of the oxyalkylated polyamine residue and tall oil acid, for example, at a temperature of from about 215° to about 320° F. In general, this temperature should not be surpassed because excessive temperature produces side reactions and results in a product of undesirable properties. Water originally present in the reactants and that formed during the esterification reaction are continuously removed during the heating and reacting. The time of reaction may range from about 1½ to about 8 hours, after which the reaction product is allowed to cool and is recovered as a black viscous liquid.

While the water soluble corrosion inhibitor prepared in the above manner may be utilized as such, in a preferred embodiment it is prepared as an aqueous solution and, as hereinbefore set forth, is commingled with the alkaline agent. In one embodiment the solution contains from 30% to 70% by weight of active ingredient and the balance is solvent. In many cases, it is desirable to include an alcohol as part of the solvent and accordingly the solvent may comprise from about 10% to about 50% alcohol such as ethyl alcohol, isopropyl alcohol, butyl alcohol, etc. and the balance is water.

As hereinbefore set forth, in a preferred embodiment the alkaline agent is commingled with the corrosion inhibitor to form a mixed solution for single injection. The specific amount of alkaline agent and corrosion inhibitor to be used will depend upon the degree of acidity of the overhead effluent products. A suitable mixture was prepared to contain 500 grams of trisodium phosphate per pint of inhibitor solution containing 50% by weight of corosion inhibitor and a solvent consisting of isopropyl alcohol and water. It is apparent that additional water is used to make a free flowing stable solution. The amount of water is not critical because the water is subsequently separated from the hydrocarbon constituents of the overhead effluent products. Accordingly, excess water is readily removed from the process. In one method, the solution of corrosion inhibitor and alkaline agent are put in a suitable vessel and sufficient water commingled therewith to form the desired solution. In the example of one pint of corrosion inhibitor (50% active ingredient) and 500 grams of trisodium phosphate, about 5 or 6 gallons of water are used to form the final solution.

As hereinbefore set forth, the amount of corrosion inhibitor used varies with the acidity of the overhead effluent products. In general, the corrosion inhibitor, based on active ingredient, is used in a concentration of from about 0.00001% to about 0.01% by weight of the overhead effluent products and preferably from about 0.0001% to about 0.001% by weight. The alkaline agent is used in an amount to control the pH of the overhead effluent products from about 5.0 to about 7.0 and preferably from about 6.0 to about 6.8.

The following examples are introduced to illustrate further the novelty and utility of the present invention but not with the intention of unduly limiting the same.

EXAMPLE I

368 grams of polyamine residue (Amine E–100) and 60 grams of water were stirred in a 3-necked flask while held in a water bath at a temperature of about 160° F. 319 grams of ethylene oxide were gradually introduced into the reaction flask. The reaction was mildly exothermic. Heating and stirring of the reactant were continued while the temperature was held at about 175° F.

The oxyethylated polyamine residue prepared in substantially the same manner as described above was reacted with tall oil acid (Aliphat 44–A). 73.5 grams of the oxyethylated polyamine residue were mixed with 30 grams of the tall oil acid and the mixture heated in an oil bath until the flask reached a temperature of 320° F. The flask was open at the top so that the water originally introduced and formed in the reaction was allowed to escape. The product was recovered as a black viscous liquid.

Solutions of the products formed in the above manner were prepared to contain one gram of the corrosion inhibitor, two grams of sodium hydroxide and 250 cc. of water. The solution remained clear after standing for 24 days at room temperature.

EXAMPLE II

Oxyethylated polyamine residue was prepared in substantially the same manner as described in Example I, except that the polyamine residue used in this example is "Polyamine H Special," which is similar in properties to the "Amine E–100" described in Example I and previously in the specifications. A number of separate esterification products were prepared by reacting the oxyethylated polyamine residue with tall oil acid (Indusoil L–5). In these preparations the mole proportion of acid to oxyethylated amine residue was varied as shown in the following table:

Table I

Preparation No.	Oxyethylated Polyamine Residue (Grams)	Acid (Grams)	Mole Ratio Acid: Amine
A	36.8	45	0.422:1
B	36.8	30	0.283:1
C	73.5	30	0.14.:1

Preparation A was insoluble in water. It will be noted that the mole ratio of acid to amine is above the critical upper limit of 0.25 acid to amine mole ratio hereinbefore set forth.

Preparation B was a very viscous material and therefore not desirable for use in accordance with the present invention.

Preparation C was completely soluble in water. It will be noted that the ratio of acid to amine is within the desired range of 0.1 to 0.25 heretofore set forth.

EXAMPLE III

Additional compositions similar to those described in Example II are prepared to comprise effective corrosion inhibitors which are water soluble and accordingly are comprised within the present invention.

Table II

Preparation No.	Oxyethylated Polyamine Residue (Grams)	Acid (Grams)	Mole Ratio Acid: Amine
D	73.6	52	0.25
E	73.6	42	0.20
F	73.6	38	0.18
G	73.6	26	0.12
H	73.6	22	0.10

EXAMPLE IV

The inhibitor as prepared in the manner described in Example I was evaluated as a corrosion inhibitor in the following manner: In this test a steel metal coupon of about ¾" x 6" x 1/16" is suspended in the vapor space of a one liter flask containing 300 cc. of a heptane fraction and 50 cc. of corrosive water having a pH of 1.5, the flask being equipped with a reflux condenser at the top. Hydrogen sulfide is continuously introduced into the lower portion of the flask. The flask is maintained at a temperature of 212° F. and the rising vapors pass over the test coupon, are collected at the top of the flask and the condensate passes downward over the test coupon. A continuous stream of water commingles with the condensate and passes over the test coupon. The test is continued for 16 hours, after which the loss in weight due to corrosion is determined by weighing.

The following table reports the results of a run in the absence of a corrosion inhibitor and two runs in which an inhibitor prepared as described in Example I is added to the water which passes over the test coupon. In one case, the inhibitor was added in a concentration of 0.1% by weight of the water and in the other case in a concentration of 0.05% by weight of the water.

Table III

Inhibitor	Weight of Strip		
	Initial, g.	Final, g.	Loss, mg.
None	8.8350	8.8094	25.6
0.1% by weight of inhibitor described in Example I	9.1017	9.0982	3.5
0.05% by weight of inhibitor described in Example I	9.2982	9.2915	6.7

From the data in the above table, it will be noted that the corrosion was reduced considerably in the samples containing the inhibitor of the present invention.

EXAMPLE V

As hereinbefore set forth, it is important that the corrosion inhibitor does not cause emulsification and thereby interfere with the separation of the hydrocarbon and aqueous phases in the receiver. The emulsification was evaluated in the following manner: In a 50 ml. volumetric flask, 50 mg. of the corrosion inhibitor is dissolved to volume with water. The desired amount of corrosion inhibitor is removed by pipetting and is diluted with water to give 100 grams of solution. For example, 2 ml. of the above solution will give a concentration of 20 parts per million in 100 grams of water. 30 ml. from the 100 grams of solution are poured into a glass stoppered 100 cc. graduate. 70 ml. of a heptane fraction is added. The graduate is shaken vigorously for 2 minutes and then allowed to stand for 10 minutes. The amount of emulsion at the interface is noted.

When evaluated in the above manner, the interface was very clean and showed no emulsion.

EXAMPLE VI

Another corrosion inhibitor was prepared in substantially the same manner described in Example I except that the tall oil acid was Indusoil L–5. The properties of this acid have been hereinbefore set forth. The product was recovered as a black viscous liquid and was prepared as a 50% solution of active ingredient in a solvent consisting of 40% isopropyl alcohol and 60% water. The properties of the solution are as follows:

Specific gravity at 60° F	1.0095
Kinematic viscosity at 100° F, cst	43.38
Universal viscosity at 100° F, secs	201.7
Tag open cup flash point, ° F	84

EXAMPLE VII

As hereinbefore set forth, it is essential that the polyamine residue be reacted with alkylene oxide prior to esterification with the tall oil acid. An additive was prepared by reacting the polyamine residue (Amine E–100) and tall oil acid but the product was a gel and could not be readily handled. The solubility in water was not satisfactory.

EXAMPLE VIII

Another additive was prepared in the manner described in Example VI except that tetraethylene pentamine was used instead of the polyamine residue. When evaluated in the emulsification test described in Example IV, the emulsification tendency was rated at 1 ml. at the interface. In contrast to this, the inhibitor prepared according to Example I was rated at less than 0.5 and was reported as very clean.

EXAMPLE IX

Another corrosion inhibitor was prepared substantially in the same manner as Example I except that VR–1 Acid was used in the esterification step. When evaluated in the same manner as described in Example IV, 0.05% by weight of the inhibitor served to reduce the weight loss from 25.6 mg. to 7.7 mg. Here again it will be noted that the inhibitor serves to considerably reduce corrosion of the metal coupon.

EXAMPLE X

As hereinbefore set forth, a particular advantage of the water soluble corrosion inhibitors of the present invention is that they may be prepared as a combined solution with alkaline agents. A 50 percent by weight active ingredient solution of the inhibitor prepared as described in Example I in a solvent consisting of 70% water and 30% isopropyl alcohol was prepared. One pint of this solution and 500 grams of trisodium phosphate were placed in a 6 gallon drum and additional water was added thereto to fill the drum. About one-half of the resultant solution was added per day to the hot overhead effluent products of a prefractionator used to separate a naphtha into an overhead fraction, having an end boiling point of about 200° F., and a heavier fraction for use as charge to a reforming operation. The charge rate is about 1400 barrels per day and the prefractionator is maintained at a pressure of about 40 pounds per square inch with a bottoms temperature of about 400° F. and a top temperature of about 200° F.

The charge to the prefractionator is saturated with water and also contains HCl. This resulted in excessive corrosion of the coolers used to condense the overhead products from the prefractionator. Corrosion of this equipment is reduced by injecting the combined solution of trisodium phosphate and corrosion inhibitor into the overhead products prior to cooling thereof, thereby considerably increasing the life of this equipment.

EXAMPLE XI

The naphtha charge separated as a bottoms product in the prefractionator described in Example IX is subjected to reforming in the presence of an alumina-platinum-combined halogen catalyst and hydrogen at a temperature of about 900° F. The reactor effluent products are condensed to separate hydrogen for recycle from liquid, the liquid being subjected to stabilization to strip out lighter components. The stabilizer is operated at a pressure of about 300 pounds, utilizing a temperature at the bottom of 425° F. and at the top of about 150° F. The hot overhead effluent products are cooled and collected in a receiver, wherefrom normally gaseous components are separated from condensate. A water layer collects at the bottom of the receiver and is separately withdrawn.

Considerable corrosion was encountered in such an

operation and this was followed by analyzing the iron and copper content, as well as the pH, of the water being withdrawn from the receiver. In one operation in which no additive was incorporated in the overhead effluent products, the pH of the water sample was 4.1 and it contained 93.6 parts per million of iron and 5.5 parts per million of copper. About one-half of the corrosion inhibitor-trisodium phosphate solution prepared as described in Example IX was injected daily into the overhead effluent products prior to cooling. This served to increase the pH of the overhead products, as determined by analysis of the water withdrawn from the receiver, to between 6.2 and 6.8 and to reduce the iron to as low as 1.6 parts per million and the copper to as low as 0.6 part per million. It must be appreciated that the acidity of the charge to the stabilizer continuously changes and accordingly the pH of the overhead effluent products and the iron and copper concentrations of the water fluctuate. However, it will be noted that there was a considerable reduction in the corrosion of the cooling and receiving equipment through which the overhead effluent products pass.

I claim as my invention:

1. A method of reducing corrosion of plant equipment upon cooling of hot effluent products from a distillation zone and avoiding emulsification during subsequent separation, which comprises incorporating in said hot effluent products a mixed solution of an inorganic alkaline agent and a water soluble corrosion inhibitor prepared by (1) condensing an alkylene oxide containing from 2 to 4 carbon atoms with a high boiling polyamine residue under conditions to replace each amine hydrogen of said polyamine residue with an oxyalkylene group, said residue being the residual material remaining after distilling off tetraethylene pentamine and lighter products formed in the manufacture of ethylene diamine by the reaction of ethylene chloride with ammonia, and (2) thereafter partially esterifying the resultant condensation product by reacting with a mixed carboxylic acid containing from about 16 to about 40 carbon atoms per molecule in a mole ratio of acid to oxyalkylated polyamine residue of from about 0.1 to about 0.25:1, and subsequently cooling said hot effluent products.

2. A method of reducing corrosion of cooling and receiving equipment through which hot effluent products from a distillation zone pass and avoiding emulsification during separation, which comprises incorporating in said hot effluent products a mixed solution of an inorganic alkaline agent and a water soluble corrosion inhibitor prepared by (1) condensing ethylene oxide with a high boiling polyamine residue under conditions to replace each amine hydrogen of said polyamine residue with an oxyethylene group, said residue being the residual material remaining after distilling off tetraethylene pentamine and lighter products formed in the manufacture of ethylene diamine by the reaction of ethylene chloride with ammonia and (2) thereafter partially esterifying the resultant condensation product by reacting with tall oil acid in a mole ratio of acid to oxyethylated polyamine residue of from about 0.1 to about 0.25:1, and subsequently cooling said hot effluent products.

3. A method of reducing corrosion of cooling and receiving equipment through which hot effluent products from a distillation zone pass and avoiding emulsification during separation, which comprises incorporating in said hot effluent products a mixed solution of an inorganic alkaline agent and a water soluble corrosion inhibitor prepared by (1) condensing ethylene oxide with a high boiling polyamine residue under conditions to replace each amine hydrogen of said polyamine residue with an oxyethylene group, said residue being the residual material remaining after distilling off tetraethylene pentamine and lighter products formed in the manufacture of ethylene diamine by the reaction of ethylene chloride with ammonia, and (2) thereafter partially esterifying the resultant condensation product by reacting with a dicarboxylic acid containing 36 carbon atoms per molecule in a mole ratio of acid to oxyethylated polyamine residue of from about 0.1 to about 0.25:1, and subsequently cooling said hot effluent products.

4. A method of reducing corrosion of cooling and receiving equipment upon cooling of overhead effluent products from a distillation zone and avoiding emulsification during subsequent separation, which comprises incorporating in said effluent products prior to cooling thereof a mixed aqueous solution of both a sodium compound and a water soluble corrosion inhibitor prepared by (1) condensing ethylene oxide with a high boiling polyamine residue under conditions to replace each amine hydrogen of said polyamine residue with an oxyethylene group, said residue being the residual material remaining after distilling off tetraethylene pentamine and lighter products formed in the manufacture of ethylene diamine by the reaction of ethylene chloride ammonia, and (2) thereafter partially esterifying the resultant condensation product by reacting with tall oil acid in a mole ratio of acid to oxyethylated polyamine residue of from about 0.1 to about 0.25:1, and subsequently cooling said hot effluent products.

5. The method of claim 4 further characterized in that said sodium compound is sodium hydroxide.

6. The method of claim 4 further characterized in that said sodium compound is trisodium phosphate.

7. The method of claim 4 further characterized in that said distillation zone is a prefractionator to separate light components from a naphtha charge for catalytic reforming.

8. The method of claim 4 further characterized in that said distillation zone in a stabilizer used to strip light components from the effluent products of a reforming operation.

9. The method of claim 4 further characterized in that said sodium compound is introduced in a concentration to maintain the pH of said effluent products within the range of 6.0 to 6.8.

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