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METHOD OF PREVENTING CORROSION

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This invention relates to a novel method of preventing corrosion of plant equipment used in the refining of an organic liquid. More particularly it is directed to a process in which an organic liquid is subjected to distillation and a distilate product is collected and then subjected to treatment with an alkaline agent, after which it is sent to storage.

A serious problem encountered during the refining of oils is corrosion of the plant equipment. During distillation of oils containing acidic components, corrosion occurs in the internal surfaces of the distillation column and in the internal fractionating equipment including, for example, baffle plates, bubble decks, side-to-side pans, etc. Acidic components are removed from the distillation zone along with the distillate product and cause corrosion of the heat exchangers, coolers, condensers, etc. and of the receiving tanks, as well as of the connecting piping, through or into which the distillate product passes. The distillate product is treated with an alkaline reagent in order to remove the acidic components and then it is passed to storage. Corrosion of the storage tanks also is encountered due to the presence of water and air therein. The corrosion is further increased because all of the acidic components are not completely removed during the alkaline treatment.

Distillation, alkaline treatment and storage of oil are performed on oil from various sources. For example, heavy petroleum distillates, including crude oil, topped crude, reduced crude, gas oil, etc., are subjected to cracking, either in the presence or absence of a catalyst, in order to form lower boiling materials and particularly gasoline. The product from the cracking is subjected to distillation to separate a gasoline fraction, as well as other fractions including a fuel oil or diesel fuel fraction, lubricating oil fraction, etc. The gasoline generally is recovered as an overhead fraction from the distillation zone, while the fuel oil, lube oil and other fractions may be recovered as side cuts from the distillation zone. These fractions then are cooled, condensed and sent to collecting equipment. The cracked products contain sulfur or sulfur compounds and other acidic components which subsequently are removed in an alkaline treating step, after which the product is sent to storage. Another illustration of a system employing distillation, alkaline treating and storage equipment includes the reforming of a gasoline fraction, in which a gasoline fraction is subjected to treatment, either in the presence or absence of a catalyst, in order to improve the anti-knock characteristics thereof, and the reformed product then is subjected to distillation to separate a reformed gasoline fraction. The reformed gasoline fraction then is subjected to alkaline treatment and subsequently sent to storage. Still another illustration includes the distillation of crude oil or other heavy oil to separate a gasoline fraction and/or a fuel oil or diesel fuel fraction, as well as a lubricating oil or other fraction, and one or more of these fractions is subjected to alkaline treatment for

removal of acidic components and then the treated oil is sent to storage.

Regardless of the source of the oil subjected to distillation and subsequent alkaline treatment, corrosion of the equipment is encountered with oils containing corrosive components. In accordance with the present invention, a particular type of corrosion inhibitor is introduced into the distillation zone to thereby retard corrosion of the distillation zone and internal equipment. At least a portion of the corrosion inhibitor is retained in the distillate product and thereby serves to prevent corrosion of the heat exchangers, coolers, condensers, receiving tanks and piping through or into which the distillate product is passed. The corrosion inhibitor employed in this step of the process is an oil soluble basic corrosion inhibitor and therefore is not removed during subsequent treatment of the distillate product with an alkaline agent. Following the alkaline treatment, an organic acid is commingled with the distillate product in a concentration sufficient to form a salt of the basic corrosion inhibitor, and the resulting salt serves as an inhibitor to retard corrosion of the storage equipment into which the treated oil is passed.

It has been found that the basic corrosion inhibitor is effective in retarding corrosion of the distillation, connecting cooling and collecting equipment but it is not effective in retarding corrosion of the storage equipment. The reason why the basic corrosion inhibitor is not effective in retarding corrosion of the storage tanks is not completely understood. One possible explanation is that the distillation, cooling and collecting is effected in the absence of air, whereas the storage of the oil is effected in the presence of air. Air is introduced into the storage tanks during gaging of the tanks or in other ways. Furthermore, some alkaline treating processes employ air or oxygen during the treating step, and the air or oxygen may be retained in the treated product. Applicant does not intend to be limited to this specific explanation. Regardless of the reason, this phenomenon has been demonstrated in actual refinery runs.

The present invention offers numerous advantages. In the first place, a basic corrosion inhibitor is employed in the first step of the process and is not removed during the alkaline treating step of the process as would be the case if an acid or even a neutral corrosion inhibitor were employed. Following the alkaline treatment, an organic acid is commingled with the distillate product and the resultant salt serves as an effective inhibitor to retard corrosion of the storage equipment into which the distillate product is passed. Thus, through the use of an inexpensive organic acid, effective inhibition of corrosion of the storage equipment is obtained.

In one embodiment the present invention relates to a method of preventing corrosion of distillation and connecting collecting equipment and of subsequent storage equipment used in the refining of an organic liquid, wherein said organic liquid is subjected to treatment with an alkaline agent between the collecting and storage thereof, which comprises effecting said distillation in the presence of a basic corrosion inhibitor which is in part retained in a distillate product of said distillation, whereby the corrosion of said distillation and of said collecting equipment is retarded, thereafter subjecting said distillate product to treatment with an alkaline agent and retaining at least a portion of said basic corrosion inhibitor in said distillate product, thereafter commingling an organic acid with the treated distillate product containing the basic corrosion inhibitor in a concentration sufficient to form a salt of the basic corrosion inhibitor, and passing the resultant mixture into storage equipment, said salt serving as an inhibitor to retard corrosion of said storage equipment.

As hereinbefore set forth, the present invention is used in preventing corrosion of distillation and condensing, cooling and collecting equipment, as well as of subsequent storage equipment used in the handling of oil containing corrosive components regardless of the source of said oil. The basic corrosion inhibitor may be added directly to the distillation zone or it may be commingled with the oil being supplied thereto. A preferred method is to inject the basic corrosion inhibitor into the upper portion of the distillation zone. It is believed that the corrosion inhibitor forms a film on the inner surface of the metal and thereby prevents attack by water, water vapor, hydrogen sulfide or other acidic components. The basic corrosion inhibitor is retained in part in the product and this, in turn, serves to retard corrosion of the piping, cooler, condenser, heat exchanger and receiving tanks through and into which the distillate product is passed.

Any suitable basic corrosion inhibitor may be employed in accordance with the present invention. One class of basic corrosion inhibitor comprises substituted imidazolines including particularly 2-heptadecyl imidazoline. Other substituted imidazolines include 2-hexyl imidazoline, 2-heptyl imidazoline, 2-octyl imidazoline, 2-nonyl imidazoline, 2-decyl imidazoline, 2-undecyl imidazoline, 2-dodecyl imidazoline, 2-tridecyl imidazoline, 2-tetradecyl imidazoline, 2-pentadecyl imidazoline, 2-hexadecyl imidazoline, 2-octadecyl imidazoline, 2-nonadecyl imidazoline, etc. The imidazoline may contain other substituents attached thereto, the other substituents being selected from alkyl, cycloalkyl or aryl groups as well as such groups containing oxygen, nitrogen or sulfur. Another class of basic corrosion inhibitor comprises oil soluble alkyl amines including decyl amine, undecyl amine, dodecyl amine, tridecyl amine, tetradecyl amine, pentadecyl amine, hexadecyl amine, heptadecyl amine, octadecyl amine, nonadecyl amine, eicosyl amine, etc. Still another class comprises oil soluble alkylene polyamines and particularly N-alkyl alkylene polyamines including N-alkyl propylene diamines in which the alkyl group contains at least 6 and preferably at least 10 carbon atoms. N-alkyl propylene diamines in which the alkyl group is derived from tallow, lauric acid, coconut oil, soya oil, etc., are available commercially at relatively inexpensive prices because they are produced as by-product. For example, "Duomeen T" is an N-alkyl propylene diamine in which the alkyl group contains from about 12 to about 20 carbon atoms per group and mostly containing 16 to 18 carbon atoms per group. It is understood that a mixture of basic corrosion inhibitors may be employed.

As hereinbefore set forth, the basic corrosion inhibitor retards corrosion of the distillation and connecting cooling, condensing and collecting equipment. The distillate product may comprise the overhead fraction withdrawn from the upper portion of the distillation zone as would be the case, for example, when distilling to separate an overhead gasoline fraction from higher boiling material. At the same time or in a separate operation, a fuel oil or lubricating oil fraction may be separated as one or more side cuts. The distillate product, whether an overhead or side cut fraction, is subjected to treatment with an alkaline reagent in order to remove acidic components. For example, mercaptans and other acidic components are removed from gasoline by treatment with caustic (sodium hydroxide), potassium hydroxide, etc., or preferably with these in admixture with a solutizing agent including, for example, alcohols, and particularly methanol or ethanol, cresols, tannin, etc., potassium isobutyrate, and others. It is understood that any suitable alkaline treating process may be employed.

As a final step in the treating process, the treated distillate product is separated from the alkaline agent and the distillate product then sent to storage. In accordance with the present invention, an organic acid is commingled with the treated distillate product on its way to storage or is introduced directly into the storage tank. Any suitable organic acid may be employed and preferably comprises an inexpensive organic acid. A number of relatively inexpensive organic acids are available commercially, these being produced as by-products. One such acid is marketed commercially under the trade name of "VR–1 Acid." This acid is a liquid at 77° F., has an acid number of about 150, an iodine number of about 36 and is a mixture of polybasic acids, having a titration equivalent weight of about 350. Another inexpensive acid is available commercially under the name of "Dimer" acid. It is understood that any suitable organic acid may be employed and may be either monobasic or polybasic. It generally is preferred that the acid comprises a long chain carboxylic acid and may be selected from oleic acid, linoleic acid, palmitic acid, stearic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, phthalic acid, etc. As hereinbefore set forth, any suitable organic acid may be used and, when desired, a mixture of organic acids may be employed.

The basic corrosion inhibitor is introduced in the distillation zone in a sufficient concentration to retard corrosion thereof. The exact amount of inhibitor to be employed will depend upon the corrosive nature of the oil being distilled. In general, the concentration of basic corrosion inhibitor will be within the range of from about 1 to about 15 pounds per 1000 barrels of distillate product, although smaller or larger concentrations may be used. The corrosion inhibitor will be retained to a considerable extent in the distillate product and thereby will serve to retard corrosion of the connecting cooling, condensing and collecting equipment. The organic acid will be used in a concentration sufficient to form a salt and preferably an acid salt of the basic inhibitor. This will, in turn, depend upon the basic nitrogen content of the basic corrosion inhibitor. For example, in the substituted imidazoline there is one basic nitrogen per molecule. In "Duomeen-T" there are two basic nitrogens. When a monocarboxylic acid is used, it will be used in equal mol proportions with the substituted imidazoline to form the neutral salt and will be used in a larger concentration and preferably two mols to form the acid salt. On the other hand, when using a dicarboxylic acid with the substituted imidazoline, one mol of acid per two mols of imidazoline will be used to form the neutral salt or equal mols of acid and imidazoline will be used to form the acid salt. When using "Duomeen-T," two mols of a monocarboxylic acid salt or one mol of a dicarboxylic acid will be used to form the neutral salt and a larger concentration will be used to form the acid salt. As hereinbefore set forth, the salt will effectively retard corrosion of the storage tank, as well as being retained in part in the distillate product and thereby will provide protection against subsequent metallic equipment through or into which the distillate product is passed.

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

It has been established that the ASTM steam turbine oil corrosion test (ASTM Designation D665–52T) correlates with the results obtained in the storage of oil in storage tanks. In this test, a highly polished mild carbon steel rod is placed in 300 cc. of Nujol, to which 30 cc. of synthetic sea water was added, and then heated to and maintained at 140° F. with stirring for 48 hours in a beaker open to the atmosphere.

The basic corrosion inhibitor used in this example ws heptadecyl imidazoline and was utilized in a concentration of 0.01% by weight of the Nujol. After heating for 48 hours, corrosion of the steel rod was very heavy; that; is, the rod was completely covered with corrosion. On the other hand, the neutral salt of heptadecyl imidazoline and VR–1 acid (using one mol of acid per two

mols of imidazoline), when utilized in a concentration of 0.01% by weight of Nujol and tested in the same manner, resulted in only light corrosion (that is, one-tenth or less of the steel rod was covered with rust).

In still another run, the acid salt of heptadecyl imidazoline and VR–1 acid (using equal mols of acid and imidazoline), when tested in the same manner as heretofore described, resulted in only slight corrosion of the steel rod. (That is, one-tenth or less of the rod was covered with rust.)

From the above data, it will be noted that the heptadecyl imidazoline is ineffective to retard corrosion of oil in storage tanks. On the other hand, both the neutral salt and the acid salt of heptadecyl imidazoline with VR–1 acid were effective in retarding corrosion.

Example II

In another series of runs similar to those described in Example I, the basic corrosion inhibitor is "Duomeen-T." While this compound is effective in retarding corrosion during distillation of the effluent products of thermal cracking, it is not effective in retarding corrosion in the final storage tanks. The "Duomeen-T" is introduced into the upper portion of the fractionator in a concentration of 7 pounds per 1000 barrels of the overhead fraction withdrawn from the upper portion of the fractionator. The overhead fraction is sent through heat exchangers into a receiver. The "Duomeen-T" serves to retard corrosion of this equipment. The cracked gasoline then is subjected to treatment with caustic methanol, and the treated gasoline is sent to storage. VR–1 acid is commingled with the treated gasoline on its way to storage in a concentration sufficient to form the acid salt of the "Duomeen-T."

I claim as my invention:

1. A method of preventing corrosion of distillation and connecting collecting equipment and of subsequent storage equipment used in the refining of hydrocarbon oil, wherein said oil is subjected to treatment with an alkaline agent between the collecting and storage thereof, which comprises distilling the oil in the presence of a basic corrosion inhibitor which is in part retained in a distillate product of said distillation and selected from the group consisting of an imidazoline, an oil-soluble alkyl amine and an oil-soluble alkylene polyamine, whereby the corrosion of said distillation and of said collecting equipment is retarded, thereafter subjecting said distillate product to treatment with an alkaline agent selected from the group consisting of sodium hydroxide and potassium hydroxide and retaining at least a portion of said basic corrosion inhibitor in said distillate product, thereafter commingling a long chain carboxylic acid with the treated distillate product containing basic corrosion inhibitor in a concentration sufficient to form a salt of the basic corrosion inhibitor, and passing the resultant mixture into storage equipment, said salt serving as an inhibitor to retard corrosion of said storage equipment.

2. A method of preventing corrosion of distillation and connecting cooling and collecting equipment of a hydrocarbon oil cracking unit and of subsequent storage equipment, which comprises distilling the oil in the presence of a basic corrosion inhibitor which is in part retained in a distillate product of said distillation and selected from the group consisting of an imidazoline, an oil-soluble alkyl amine and an oil-soluble alkylene polyamine, whereby the corrosion of said distillation and of said cooling and collecting equipment is retarded, thereafter subjecting said distillate product to treatment with caustic solution and retaining at least a portion of said basic corrosion inhibitor in said distillate product, thereafter commingling a long chain carboxylic acid with the treated distillate product containing basic corrosion inhibitor in a concentration sufficient to form a salt of the basic corrosion inhibitor, and passing the resultant mixture into storage equipment, said salt serving as an inhibitor to retard corrosion of said storage equipment.

3. The process of claim 2 further characterized in that said distillate product is removed as an overhead fraction and comprises gasoline components.

4. The process of claim 2 further characterized in that said distillate product is removed as a side cut and comprises components heavier than gasoline.

5. A method of preventing corrosion of distillation and connecting cooling and collecting equipment of a gasoline reforming unit and of subsequent storage equipment, which comprises distilling the gasoline in the presence of a basic corrosion inhibitor which is in part retained in a distillate product of said distillation and selected from the group consisting of an imidazoline, an oil-soluble alkyl amine and an oil-soluble alkylene polyamine, whereby the corrosion of said distillation and of said cooling and collecting equipment is retarded, thereafter subjecting said distillate product to treatment with caustic solution and retaining at least a portion of said basic corrosion inhibitor in said distillate product, thereafter commingling a long chain carboxylic acid with the treated distillate product containing basic corrosion inhibitor in a concentration sufficient to form a salt of the basic corrosion inhibitor, and passing the resultant mixture into storage equipment, said salt serving as an inhibitor to retard corrosion of said storage equipment.

6. A method of preventing corrosion of distillation and connecting cooling and collecting equipment of a crude oil distillation unit and of subsequent storage equipment, which comprises distilling the oil in the presence of a basic corrosion inhibitor which is in part retained in a distillate product of said distillation and selected from the group consisting of an imidazoline, an oil-soluble alkyl amine and an oil-soluble alkylene polyamine, whereby the corrosion of said distillation and of said cooling and collecting equipment is retarded, thereafter subjecting said distillate product to treatment with caustic solution and retaining at least a portion of said basic corrosion inhibitor in said distillate product, thereafter commingling a long chain carboxylic acid with the treated distillate product containing basic corrosion inhibitor in a concentration sufficient to form a salt of the basic corrosion inhibitor, and passing the resultant mixture into storage equipment, said salt serving as an inhibitor to retard corrosion of said storage equipment.

7. The process of claim 6 further characterized in that said distillate product is removed as an overhead fraction and comprises gasoline components.

8. The process of claim 6 further characterized in that said distillate product is removed as a side cut and comprises components heavier than gasoline.

9. The method of claim 1 further characterized in that the said basic corrosion inhibitor is an imidazoline.

10. The method of claim 1 further characterized in that the said basic corrosion inhibitor is an N-alkyl propylene diamine in which the alkyl group contains at least 6 carbon atoms.

11. The method of claim 1 further characterized in that the said basic corrosion inhibitor is heptadecyl imidazoline.

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