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INHIBITING CORROSION IN DISTILLATION PROCESSES

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Fig. 1

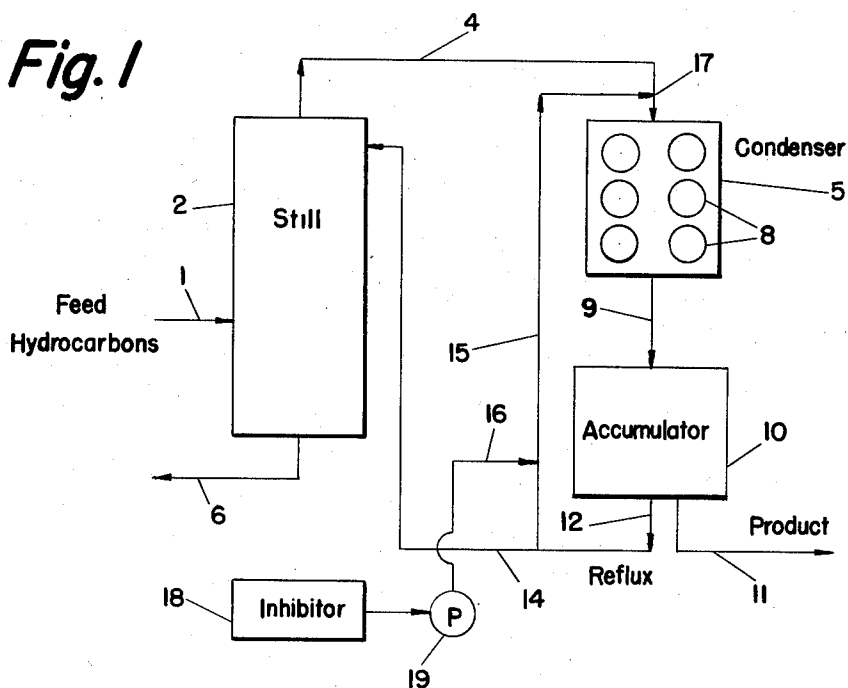
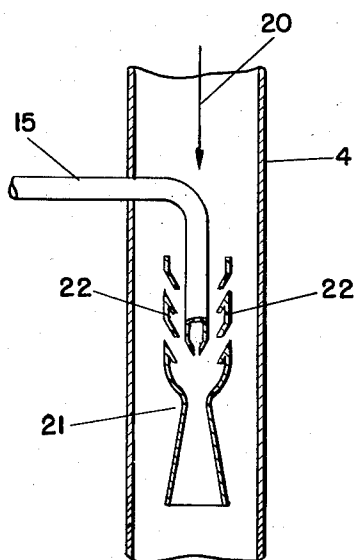


Fig. 2



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INHIBITING CORROSION IN DISTILLATION PROCESSES

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6 Claims. (Cl. 208—351)

This invention relates to a process for reducing corrosion in petroleum refining equipment, and more particularly relates to a process for inhibiting corrosion in condensers associated with distillation processes in petroleum refining operations.

In petroleum distillation processes, corrosion of metal apparatus caused by non-hydrocarbon impurities, such as acids, mercaptans, sulfides, and the like, is especially serious in condensers used for converting vaporized hydrocarbons to liquid phase. To combat this difficulty, corrosion inhibitors have been injected into the still usually at a location adjacent the upper end of the still. Such operation, however, is not effective for reducing the corrosion in the associated condenser, since effective inhibitors are generally relatively high boiling materials and are not removed in corrosion inhibiting quantities from the still, together with vaporized hydrocarbons, for subsequent introduction into the condenser. Relatively high boiling corrosion inhibitors have been injected into the overhead stream from the still which passes into the condenser, but such means are not effective since the inhibitor appears to contact only a portion of the condenser surface, i.e., the inhibitor appears to follow a defined path in flowing through the condenser and thus fails to prevent corrosion of the remaining surface. Many distillation processes operate with reflux, i.e., a portion of condensed material is returned to the upper portion of the still, since such operation increases the efficiency of the process and decreases the cost of equipment required to perform a given separation. In such operation, a corrosion inhibitor may be injected into the reflux passing to the still. This, however, does not overcome the difficulties as above set forth, i.e., where a relatively high boiling inhibitor is used, it is effective only in the still itself since it does not pass to the condenser with the still overhead, and since relatively low boiling inhibitors which would vaporize with the still overhead do not appear effective for preventing corrosion in the condenser.

An object of the present invention is to provide a process for separating hydrocarbons by distillation wherein corrosion to the cooled metal surfaces of condensers associated with distillation operations is eliminated or substantially reduced. Another object is to provide a process for inhibiting corrosion in condensers associated with petroleum distillation processes wherein relatively high boiling, effective corrosion inhibitors are employed. Other objects and their achievements in accordance with the process of the invention will be apparent hereinafter.

It has now been found that, in a distillation process using reflux, by diverting a small portion of the reflux stream, incorporating a relatively high boiling corrosion inhibitor in the diverted portion, and injecting the resulting composition containing the corrosion inhibitor into the still overhead passing to the condenser, the above and other objects are achieved.

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Accompanying Figure I is a flow diagram showing an embodiment of the process of the invention. Figure II shows, in schematic form, a preferred means of injecting the inhibitor-hydrocarbon composition into the still overhead. Both figures are described in detail hereinafter.

In an embodiment of the process, hydrocarbon vapors from a still are passed to a condenser and therein converted to liquid phase. A portion of the condensed liquid is taken as product and the remaining portion divided into two streams. One stream, which constitutes a major proportion of the divided material, is injected as reflux into the upper portion of the still. The remaining portion of the divided stream, conveniently designated as a "drag stream," is admixed with a relatively high boiling, effective corrosion inhibitor and injected into the still overhead passing to the condenser, preferably at a location immediately adjacent the condenser so that the hydrocarbons of the drag stream enter the condenser while in liquid phase. As has been found, by such operation corrosion otherwise encountered in the condenser, e.g., to the cooled metal surfaces of the condenser, is greatly reduced and other advantages are obtained.

The process of the invention is especially applicable for separating hydrocarbons by distillation, such as processes for depropanizing and/or debutanizing mixtures of hydrocarbons boiling in the gasoline range, or separating relatively low boiling from relatively high boiling gasoline hydrocarbons, or separating hydrocarbons boiling in the gasoline range from still higher boiling hydrocarbons, e.g. hydrocarbons boiling in the kerosene or gasoline boiling range, in topping crude oil, and the like. In general, however, the process of the invention can be used in any process wherein hydrocarbons are separated by distillation and the separated lower boiling hydrocarbons condensed from vapor to liquid phase in contact with corrodible metal surfaces.

Attention is now directed to the accompanying flow diagram which illustrates an embodiment of the processes of the invention. A mixture of hydrocarbons, such as hydrocarbons having from 3 to 12 carbon atoms per molecule, is introduced as feed to the process through line 1 to still 2. The low boiling hydrocarbons, i.e., hydrocarbons having 3 or 4 carbon atoms per molecule are removed as overhead from still 2 through line 4 and passed to condenser 5. Higher boiling hydrocarbons are removed from the still through line 6. Condenser 5 has cooling coils 8 which remove heat from the entering hydrocarbons. Liquefied hydrocarbons pass through line 9 and enter accumulator 10. A portion of the accumulated hydrocarbons are removed through line 11 as a product of the process. The remaining hydrocarbons in accumulator 10 are passed through line 12. This hydrocarbon stream is divided so that a major portion thereof passes through line 14 and a minor portion, i.e., a drag stream, passes through line 15. The major portion passing through line 14 is injected into the upper portion of still 2 as reflux. Into the drag stream passing through line 15 is injected, through line 16, a relatively high boiling corrosion inhibitor. The inhibitor is stored in 18 and injected by means of pump 19. The resulting admixture of hydrocarbons and inhibitor passes through line 15 and is injected into line 4 at 17, which is a location in line 4 close to condenser 5. Injection at 17 should be close enough to condenser 5 so that the injected liquid is not substantially vaporized prior to its introduction into condenser 5.

Figure II illustrates a preferred means of injecting the admixture of reflux drag stream and corrosion inhibitor into the still overhead as indicated generally by 17 in

Figure I. In Figure II, numerals 4 and 15 represent the same portions of the process as the same numerals in Figure I, namely, the still overhead to the condenser and the admixture of reflux and inhibitor, respectively. The arrow indicated by numeral 20 shows the direction of flow of the still overhead through conduit 4. Numeral 21 indicates an aspirator, preferably of conventional design, which provides for mixing of the liquid from 15 with the gases in 4. In operation, a portion of the vaporized hydrocarbons flowing through conduit 4 is drawn through openings 22 of aspirator 21 by the liquid injection through the aspirator, and the aspirator provides excellent mixing of the liquid and vapor. The use of aspirator 21 apparently results in a substantially uniform distribution of the corrosion inhibitor throughout the condenser so that all of the metal surfaces therein are protected against corrosion.

Valves, pumps, meters, and the like, the location and operation of which will be apparent to those skilled in the art, have been largely omitted in the interest of simplicity.

By operating in accordance with the process of the invention, it has been found that corrosion of the metal surfaces in the condenser is substantially completely eliminated. It has been further found that the relatively small portion from the reflux stream which is injected, together with the inhibitor into the still overhead passing to the condenser enhances the efficiency of the condenser by providing a liquid film on the upper cooling tubes of the condenser, thereby providing for more efficient operation.

In operating the process of the invention, only a relatively small proportion of the reflux need be injected together with the inhibitor into the still overhead. The ratio of such material to total reflux can be within the range of from 1:200 to 1:2000, and preferably is in the range of from 1:400 to 1:800, the ratios being expressed on a volume basis.

Materials heretofore described as corrosion inhibitors and which may be commercially available give good results in the present process. For example, the ethylene oxide adduct of a primary rosin amine, the polyoxyethylated glycol ether derivative of dehydroabiethylamine, and semi-polar high-molecular weight compounds of the imidazoline type give good results. It is preferred, however, to use an inhibitor which boils at a temperature above the temperature of the still overhead into which it is injected. The inhibitor can be injected into the reflux hydrocarbons as a solution which may be miscible or immiscible with the reflux hydrocarbons, and good results obtained. Other materials can be injected into the still overhead, in addition to the inhibitor-reflux hydrocarbons, in some instances with good results. For example, an aqueous solution of sodium hydroxide or ammonium hydroxide can be used with good results in some instances, especially in applications where the still overhead contains an appreciable quantity of water.

The quantity of the inhibitor injected does not appear critical in most instances, a corrosion inhibiting quantity being employed. Usually a quantity such that the concentration thereof in the still overhead is from 1 to 20 p.p.m. (parts per million) gives good results and is preferred. Larger quantities up to about 500 p.p.m. do not appear deleterious but generally no appreciable advantage is obtained for using such relatively large quantities.

In order to illustrate the advantages of the process of the invention, a mixture of hydrocarbons consisting of hydrocarbons boiling in the gasoline range, propane and butane were injected into a still at a rate of about 500 bbl./hr. (barrels per hour). The temperature and pressure of the still was maintained so that a mixture consisting principally of propane and butane was taken as overhead, the temperature at the still top being maintained at about 154° F. and the pressure in the still being main-

tained at about 100 p.s.i. Hydrocarbons boiling in the gasoline range were removed from the still bottom as liquid product. The vaporized mixture, consisting principally of propane and butane but containing some corrosive non-hydrocarbons such as hydrogen sulfide, was continuously passed into a condenser wherein the hydrocarbons were converted to liquid phase by contact with cooled metal surfaces in the condenser. The liquefied hydrocarbons then passed to an accumulator from which a mixture of propane and butane as a product was removed at a rate of about 100 bbl./hr. and from which reflux, at the rate of about 200 bbl./hr., was introduced into the upper portion of the still. The temperature of the reflux as introduced into the still was about 104° F. In this operation, severe corrosion of the metal surfaces within the condenser, especially the cooling coils, was observed so that replacement thereof at relatively short intervals of about 2 to 4 years was necessary. A corrosion inhibitor was then injected into the still overhead passing into the condenser. About 2.5 cc. per minute (amounting to about 6 parts per million based on the quantity of hydrocarbons in the still overhead) of inhibitor dissolved in about 122.5 cc. of water was injected into the overhead. The inhibitor was a commercially available ethylene oxide adduct of primary rosin amine. Corrosion in the condensers was somewhat decreased, but a major portion of the surface area of the cooling coils was severely corroded, making a replacement thereof necessary at intervals of from about 3 to 5 years.

The foregoing operation was changed by dividing the reflux hydrocarbon stream into two portions, a major portion which passed to the still as before and a drag stream which flowed at a rate of about 10 to 20 gallons per minute. The same quantity, namely about 2.5 cc. per minute, of the same corrosion inhibitor dissolved in the same quantity of water, about 122.5 cc., was injected into the drag stream and the resulting mixture injected into the overhead from the still at the same location used before. This operation substantially completely eliminated corrosion within the condenser. After operation for several months, observation of the rate of corrosion showed that replacement of the cooling coils would not be necessary for at least about 10 years. It was also observed that the cooling efficiency of the condenser was substantially increased so that the cooling coils in the condensers could be operated at somewhat higher temperatures while maintaining the same efficiency.

The foregoing example illustrates a preferred embodiment of the process of the invention. Other embodiments will be apparent to those skilled in the art. Thus, while the process is especially applicable to distillation operations involving reflux, the process is operable without reflux by admixing the inhibitor with a portion of condensed product and injecting the resulting composition into the still overhead passing to the condenser.

The invention claimed is:

1. In a process for separating hydrocarbons by distillation wherein a portion of the hydrocarbons is converted to vapor phase, the vaporized hydrocarbons continuously passed to a condenser having cooled metal surfaces wherein the vaporized hydrocarbons are converted to liquid phase, and wherein a portion of the condensed hydrocarbons is returned as reflux to the distillation, the improvement which comprises continuously separating a minor proportion of hydrocarbons from the reflux, admixing a corrosion inhibitor with the separated portion of the reflux hydrocarbons, and injecting the resulting mixture into the vaporized hydrocarbons passing to the condenser.

2. In a process for separating hydrocarbons by distillation wherein relatively low boiling hydrocarbons and corrosive non-hydrocarbons are converted to vapor phase and continuously passed to a condenser having cooled, corrodible metal surfaces wherein the vaporized hydrocarbons are converted to liquid phase, and wherein a por-

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tion of the condensed hydrocarbons is returned as reflux to the distillation, the improvement which comprises continuously separating a drag stream from the reflux, the volume ratio of the drag stream to the total reflux being in the range of from 1:200 to 1:2000, admixing a corrosion inhibiting quantity of a corrosion inhibitor with said drag stream, and continuously injecting the resulting mixture into vaporized hydrocarbons passing to the condenser.

3. Process according to claim 2 wherein the reflux drag stream corrosion inhibitor mixture is introduced into the vaporized hydrocarbons at a location adjacent the condenser whereby the introduced mixture enters the condenser in liquid phase.

4. Process according to claim 3 wherein a mixture of propane and butane is separated from higher boiling hydrocarbons.

5. Process according to claim 2 wherein said corrosion inhibitor has a boiling point above the temperature

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of the vaporized hydrocarbons passing through the condenser.

6. Process according to claim 2 wherein said corrosion inhibitor is an ethylene oxide adduct of primary rosin amine.

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