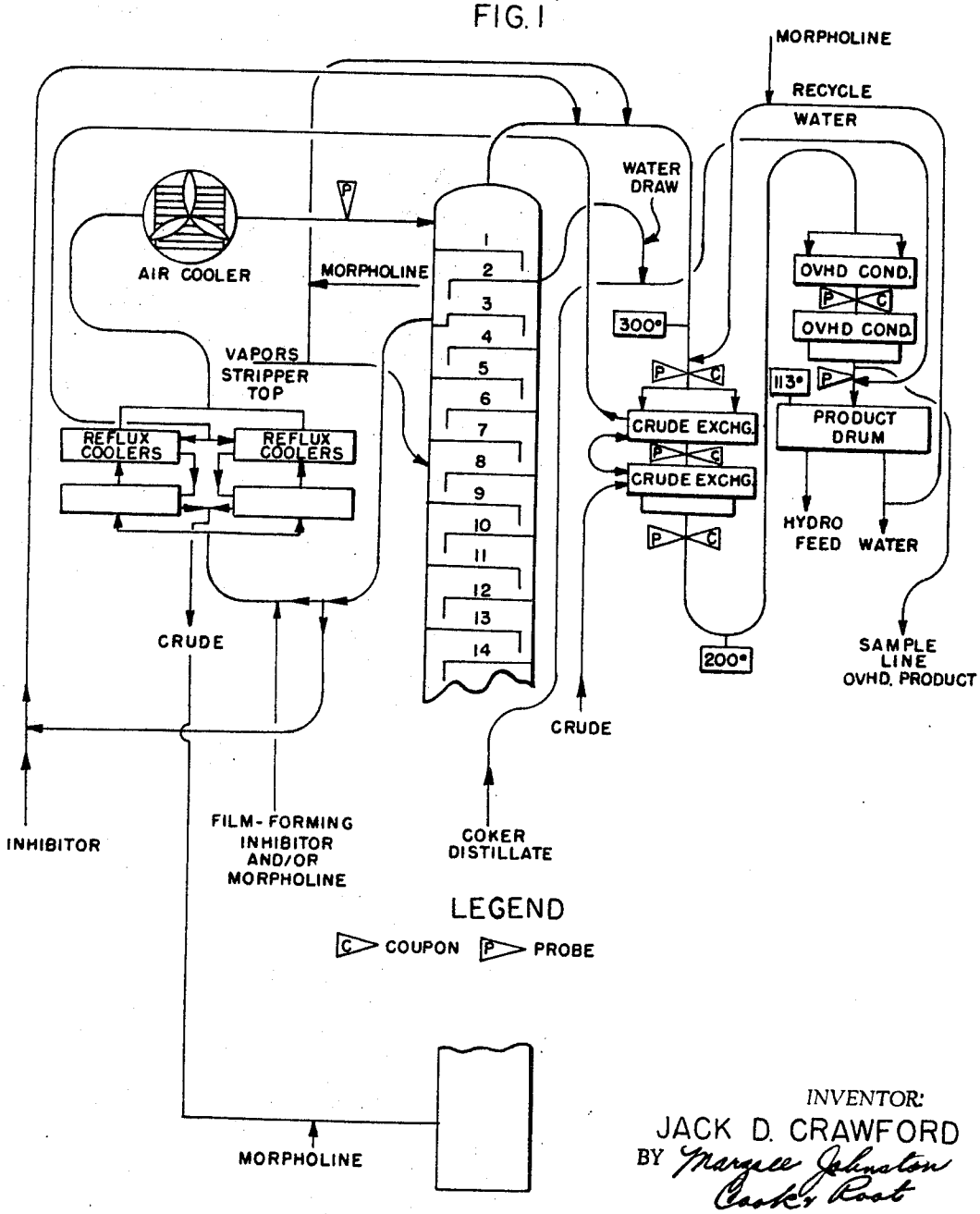
June 3, 1969 J. D. CRAWFORD 3,447,891

CORROSION INHIBITING PROCESS

Filed Sept. 3, 1964 Sheet 1 of 2

FIG. 1



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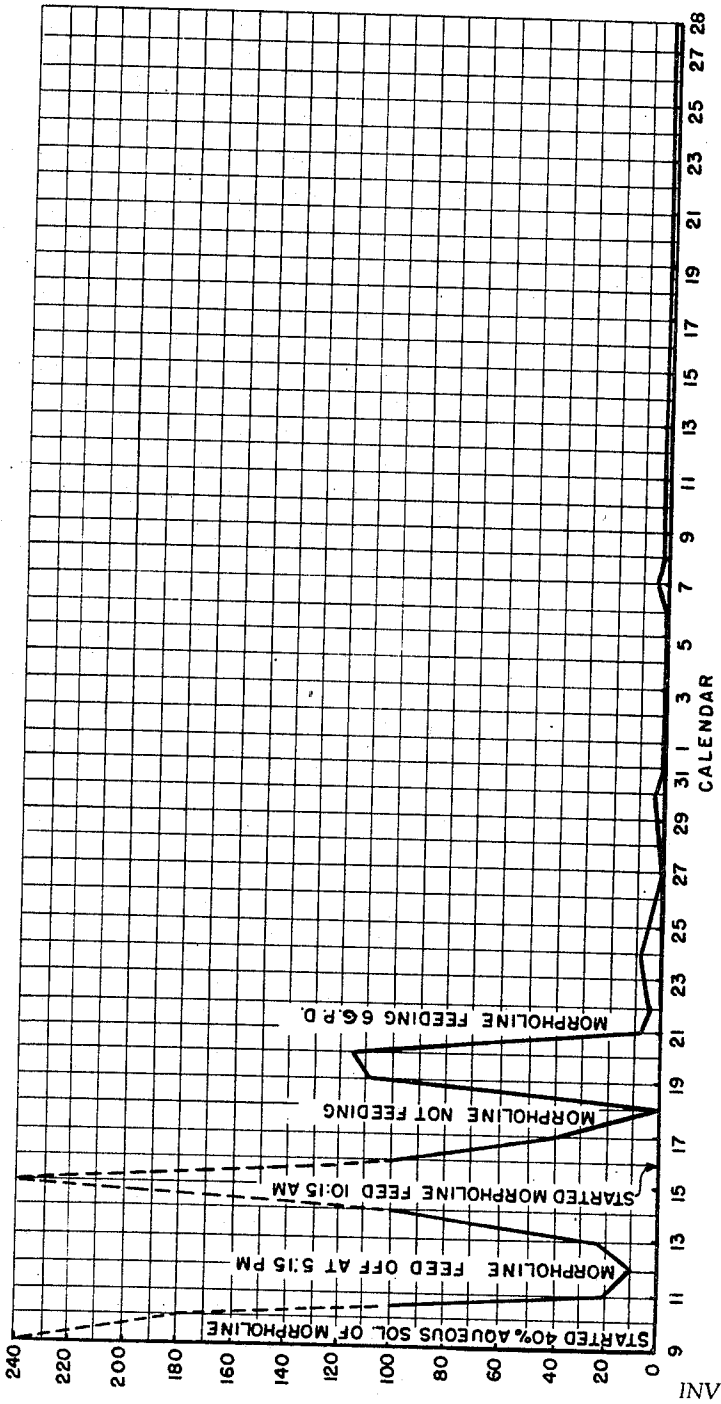
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Sheet 2 of 2

FIG. 2



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CORROSION INHIBITING PROCESS

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Int. Cl. C23f *14/02*
U.S. Cl. 21—2.5
10 Claims

ABSTRACT OF THE DISCLOSURE

A method of inhibiting corrosion in petroleum refining units in which distillation is taking place, which method comprises adding morpholine either alone or in combination with a film-forming amine to the petroleum product being distilled.

The present invention is directed to the prevention or control of corrosion of oil refining equipment. More particularly, the subject invention is directed to a process for eliminating acid corrosion which takes place at the point of initial water condensation in petroleum distillation units.

Petroleum crudes as well as gas oil, reduced crude, etc., are subjected to various processes in order to form lower boiling components such as gasoline. The product that is obtained from conversion is distilled to produce a gasoline fraction, a fuel oil fraction, lubricating oil fraction, etc. The lower boiling fractions and particularly gasoline are recovered as an overhead fraction from the distilling zones. The intermediate components are recovered as side cuts from the distillation zone. The fractions are cooled, condensed, and sent to collecting equipment. No matter what the source of the oil that is subject to distillation it has been found that corrosion of the equipment takes place. Acidic materials that are present in all crudes are carried along from the distillation zone with the distillate product and often cause extensive corrosion to take place on the metal surfaces of fractionating towers such as crude towers, trays within such towers, heat exchangers, receiving tanks, connecting pipes, etc. The most serious corrosion occurs in condensers and in the overhead line leading from the fractionating towers. The overhead line is used as a connection between the distillation tower and condensers. The distillate or stock which will be stored or used subsequently to charge other refining processes is condensed on the cooled surfaces of the condenser equipment and is then caught in an overhead accumulator drum. A portion of the distillate is recycled to the crude pot with the remainder being transferred to other refinery units.

One of the chief points of difficulty with respect to corrosion occurs in the area of the initial condensation of water that is carried over in the overhead line. The top temperature of the fractionating column is maintained above the boiling point of water. The initial condensate formed after the vapor leaves the column contains a high percentage of acidic materials such as hydrogen sulfide, hydrogen cyanide, CO_2, HCl, etc. Due to the high concentration of acids dissolved in the water, the pH of the first condensate is quite low. For this reason the water is highly corrosive. It is important, therefore, that the first condensate be rendered less corrosive.

In the past, ammonia has been added at various points in the distillation circuit in an attempt to control the corrosiveness of condensed acidic materials. Ammonia, however, has not proven to be effective with respect to eliminating corrosion caused by the initial condensate. It is believed that ammonia has been ineffective for this purpose because it does not condense quickly enough to neutralize the acidic components of the first condensate.

The ammonia tends to stay in the vapor phase until at least the point of the second condensation.

When using certain film-forming anticorrosive agents it has been found that a far more economical system is set up where the pH of the condensed liquids are maintained above about 4.5, and preferably at least about 5.0. This is true of virtually all amine film-forming inhibitors. A corrosion inhibitor of the film-forming type should be soluble in both aliphatics and aromatics in order to be dispersed throughout the stock. The inhibitors also should not tend to promote emulsification of the aqueous hydrocarbon phases.

It would be a valuable contribution to the art if a process could be devised which would overcome the corrosion problems found at the point of initial condensation in a distillation unit especially if the process is compatible with film-forming inhibitors. This would provide much improved overall protection of the refinery equipment. The subject invention is believed to represent such a contribution to the art.

It is an object of the present invention to provide a method of inhibiting corrosion in refining equipment and particularly in overhead lines and condensers, and more particularly at the point of initial condensation of the vapors occurring within the tower or in lines or condensers connected to the tower.

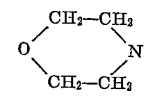
Another object of the invention is to provide a process for eliminating corrosion which process can be carried out economically and which does not tend to cause the formation of emulsions or create other problems.

Still another object of the invention is to provide a corrosion inhibiting process which can be used in conjunction with film-forming inhibitors and provide a highly desirable overall system for controlling corrosion of refinery equipment.

Other objects will become apparent to those skilled in the art from the following detailed description of the invention.

In general, the present invention comprises the discovery that the addition of a minor amount of morpholine to a crude oil charge or at various other points in the system effectively eliminates and/or controls corrosion that ordinarily occurs at and beyond the point of initial condensation of vapors within or leaving the distilling unit. The addition of morpholine to the crude substantially raises the pH of the initial condensate rendering the material noncorrosive or substantially less corrosive than was previously possible. The inhibitor can be added to the system either in pure form or as an aqueous solution. A sufficient amount of morpholine is added to raise the pH of the liquid at the point of initial condensation to above 4.0 and preferably to at least about 5.0.

Morpholine is a colorless liquid that is soluble in water, alcohol, or ether and has a boiling point of 128° C. Morpholine is a ring compound having the following formula



Morpholine is relatively inexpensive and is effective at concentrations that are sufficiently low to make the process economically feasible. It is believed that morpholine is capable of neutralizing the acidic materials found in the first condensate primarily because it is readily condensed. For this reason it goes into the first condensate rather than being carried over to subsequent condensing units.

The corrosion inhibitor of the present invention can be added to the unit in any one of several places. First of all, morpholine can be added to the crude oil charge.

This is a highly convenient method of carrying out the process since it will also neutralize condensate within the tower and in recirculating lines. The inhibitor can also be pumped directly into the gaseous overhead line. Morpholine can also be passed into the reflux line or can be added to recirculating H_2O at the top of the column. The particular point at which morpholine is added will depend largely on the design of the particular equipment, the personal preferences of the operator, and point where corrosion is most severe.

In many systems it is feasible to recirculate the water that condenses in the overhead system. In this particular operation a much lower quantity of morpholine is required to provide a highly satisfactory process. It has been found, for example, that the addition of as little as 4 ppm of morpholine to crude oil stock based on the weight of the gross overhead provides a highly satisfactory system where the condensate water is recirculated. If the water is discarded rather than recirculated an increased amount of morpholine may be required to raise the pH of the first condensate above 4.5. The amount required can readily be determined by taking periodic pH readings or reading "Corrosometer" probes. The upper limit of the morpholine addition level depends largely on economic considerations. Unlike systems containing ammonia, it is not as essential that the pH be maintained below a given point. Morpholine as employed in the invention has no adverse effect on copper alloys and the like.

As was pointed out above, the use of morpholine to control the corrosiveness of the initial condensate lends itself well to the joint use of film-forming corrosion inhibitors. Such film-forming inhibitors operate most economically at a pH above 4.5. Due to the fact that morpholine is particularly effective in increasing the pH of the initial condensate the amount of film former that is required is substantially lessened.

Among the film-forming corrosion inhibitors which can be used in conjunction with morpholine to provide an overall system of protection are compounds formed by reacting certain aliphatic monoamines with polymerized fatty acids under salt-forming conditions.

The aliphatic monoamines used in preparing film-forming inhibitors are those amines having the general structural formula

$$R-\underset{\displaystyle R_2}{\underset{|}{N}}-R_3$$

where R is an aliphatic hydrocarbon radical of 8 to 22 carbon atoms in chain length and both R_2 and R_3 are selected from the group consisting of hydrogen and an aliphatic hydrocarbon radical of 1 to 22 carbon atoms in chain length.

The above structural formula includes both primary and secondary aliphatic monoamines as well as the tertiary aliphatic monoamines. Illustrative compounds coming within the above general formula include such primary amines as n-dodecyl amine, n-tetradecyl amine, n-hexadecylamine, lauryl amine, myristyl amine, palmityl amine, stearyl amine, and oleyl amine. Other commercially available primary amines include coconut oil amine, tallow amine, hydrogenated tallow amine and cottonseed oil amine. Useful secondary amines are dilauryl amine, dimyristyl amine, dipalmityl amines, distearyl amine, dicoconut amine and dihydrogenated tallow amine. In the case of many of the above amines, it will be noted that the source of alkyl substituent on the organic nitrogen is derived from a mixed vegetable oil or animal fat. For purposes of convenience, these compounds have been named from the derivative alkyl-containing components. This system of nomenclature, particularly in the case of alkyl substituents derived from naturally occurring products such as fats, oils and the like, is used for purposes of simplification. It is believed that those familiar with the art will readily understand that the alkyl substituent

varies in the case of a coconut substituent with the alkyl groups containing from 8 to 18 carbon atoms in chain length. Similarly, in the case of hydrogenated tallow, the alkyl substituent will vary from about 12 to 20 carbon atoms in chain length.

In addition to using primary or secondary amines as exemplified above, tertiary amines such as octyl dimethyl amine, octadecyl dimethyl amine, octadecyl methyl benzyl amine, hexyl diethyl amine, trilauryl amine, tricoconut amine, tricaprylyl amine, and similar type compounds also may be used.

Preferred aliphatic primary monoamines are amines having the general structural formula

$$R-NH_2$$

wherein R is an aliphatic hydrocarbon radical of from 8 to 22 carbon atoms in chain length. A preferred material of this type is the commercial product "Armeen SD" sold by the Armour Industrial Chemical Company which is known generically to the art as Soya amine. As applied to the above formula the R group is a mixed aliphatic radical which has the following components:

	Percent
Hexadecyl	10
Octadecyl	10
Octadecenyl	35
Octadecadienyl	45

Out of the group of tertiary amines listed above one of the most effective is dimethyl hydrogenated tallow amine. This preferred species may be considered as an ammonium molecule which has had its three hydrogen atoms replaced by three alkyl groups. Two of these alkyl groups are methyl and the third is a mixed alkyl substituent derived from hydrogenated tallow.

A representative analysis of the mixed radicals of the hydrogenated tallow group is as follows:

	Percent
Myristic	2
Palmitic	29
Stearic	68
Oleic	1

One of the preferred commercial sources of this tertiary amine is "Armeen M_2HT" sold by Armour Industrial Chemical Company.

The polymerized fatty acids are well known and have been described in numerous publications. Excellent descriptions of these materials may be found in Industrial and Engineering Chemistry, 32, page 802 et seq. (1940), and in the text "Fatty Acids" by Klare S. Markley, published by Interscience Publishers, Inc., New York City, 1947, pages 328 to 330. A specific example of such a polymer which has been found to be particularly useful is one which is prepared as a by-product of the caustic fusion of castor oil in the manufacture of sebacic acid. This material is composed primarily of dicarboxylic acids derived by bimolecular addition in an olefinic polymerization where linkage occurs through the opening of at least two unsaturated bonds. Typical properties of a material so obtained are as follows:

Acid value	150
Saponification value	172
Unsaponifiable matter, percent	3.7
Iodine No.	36
Moisture content, percent	0.86

The material is of course not pure but predominantly contains dicarboxylate polymers having about 34 to 36 atoms. A suitable commercial source of this dimer acid is Harchem Division of Wallace and Tiernan, Inc., and is known as "Century D–75 Acid."

A typical film-forming corrosion inhibitor useful in conjoint activity with morpholine may be prepared by combining 1 weight part of "Armeen SD" with 2.57 weight parts of a polymerized fatty acid obtained as the

residue of a dry distillation of castor oil with sodium hydroxide and reacting the mixture with stirring at a temperature of 60° C. for 20 minutes. The final reaction product is then dispersed in equal weight parts of a heavy aromatic solvent. This composition is identified hereinafter as Composition A.

Another useful film-forming corosion inhibitor composition is prepared by heating 14 parts of "Armeen M_2HT" to the melting point and adding thereto 36 parts of "Century D–75 Acid." The mixture was reacted for 10 minutes at 130–150° F. and the resultant product added to a heavy aromatic solvent in equal proportions by weight of product to solvent. This composition is hereinafter referred to as Composition B.

Distillation range	mm.	760
Initial boiling point	° C.	171
Percent:		
10	° C.	184
50	° C.	230
90	° C.	260
End point	° C.	278

In reacting the above recited amines with polymerized fatty acids to obtain the film-forming compositions, care should be taken to maintain salt-forming conditions. This is done primarily by using reaction temperatures of from 25 to 100° C., and by avoiding the presence of materials which cause the splitting out of water. This environment is sometimes referred to as "neutralizing conditions". It is the salt producible from the above listed reactants which is of primary interest in the instant invention. Further care must be taken in conducting the reaction, to eliminate the possibility of presence of free amines in the final reaction product. Reaction proportions conductive to accomplishing this, typically include the above recited use of a weight ratio of typical polymer to typical monoamine of 2.57:1.

Additional film-forming compositions that can be used in conjunction with the subject inhibitor include those disclosed in U.S. Patent 3,003,955 among others.

The subject invention can be understood more fully by reference to the attached drawing in which:

FIGURE 1 is a diagrammatic sketch of a typical refinery unit; and

FIGURE 2 is a graph which illustrates the reduction of corrosion due to the use of morpholine in a distillation unit.

As was pointed out above, the inhibitor (morpholine) can be added to the system at a variety of points. In the schematic drawing the inhibitor is shown as being added to recycled water at the top of the column as well as to the crude oil charge and the reflux line. The drawing also shows the inhibitor being added directly to the gaseous overhead line. As shown in FIG. 1, probes and coupons have been placed at critical points in the system. These are the points most often affected by initial condensate corrosion. Such corrosion occurs whenever the temperature falls below the boiling point of water, whereby the water vapor condenses providing an aqueous solution of acidic components.

The graph of FIG. 2 shows the effect of the addition of morpholine to the refining unit. On Dec. 9th the addition of a 40% aqueous solution of morpholine to the system was begun. At this point approximately 8 gallons per day of morpholine were added to the recycled pump discharge. At the beginning of the program a mild steel electrical resistance probe located between the overhead crude exchangers showed a corrosion rate of 240 m.p.y. The following day the rate had been lowered at 174 m.p.y. By Dec. 11 the rate had been reduced to 20 m.p.y. On Dec. 12 the rate had reached 10 m.py at which point the addition of morpholine to the system was stopped In the ensuing three days the rate of corrosion rose to its previous peak of 240 m.p.y. whereupon the addition of morpholine was again commenced. By Dec. 18 the corrosion rate had reached 0 m.p.y. At this point the feed of morpholine was again interrupted for slightly over 1½ days, at which time the corrosion rate had reached 113 m.p.y. The subsequent feeding of morpholine at a rate of 6 gallons per day returned the corrosion rate to 7.5 m.p.y. and then to from 2.4 to 0 m.p.y. which was the approximate rate at the completion of the test. Subsequently, the dosage was reduced to 4 gallons per day and the corrosion rate was held at about 0.9 m.p.y. for a period of 9 months. The dosage of the film-forming corrosion inhibitor was also reduced to one-half the amount previously used in combination with ammonia.

As is apparent from the above tests, the addition of morpholine to the refining unit substantially eliminates corrosion. Likewise, the pH of the initial condensate is raised to above 4.0, and preferably at least 5.0 and is retained at a relatively constant level. It was found, for example, that at a 6 gallon per day feed the pH varied only between 6.2 and 7.6 and that most of the readings were between 6.8 and 7.2 for any given day. Without morpholine addition the pH would drop to about 4.0 causing serious corrosion problems.

The process of the invention may be carried out without creation of various problems that arise through the use of ammonia. For example, the employment of morpholine obviates such serious consequences of ammonia use as ammonium chloride deposition, corrosion of copper alloys due to uncontrolled high pH, etc. The term "initial condensate" as it is used herein signifies a phase formed when the temperature of the surrounding environment reaches the dew point of water. At this point a mixed phase of liquid water, hydrocarbon and vapor may be present. As is evident from the above discussion such initial condensate may occur within the distilling unit itself or in subsequent conductors.

Obviously many modifications and variations of the invention as hereinbefore set forth may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

I claim:

1. A process for controlling corrosion caused by acidic components in the initial condensate of a distilling petroleum product in a refining unit which comprises: adding a corrosion inhibiting amount of morpholine to said petroleum product as it passes through the refining unit.

2. A process for controlling corrosion caused by acidic components in the initial condensate of a distilling petroleum product in a refining unit which comprises: adding a corrosion inhibiting amount of morpholine to said petroleum product as it passes through the refining unit, the amount of morpholine added to said product being sufficient to raise the pH of the water of the initial condensate to above 4.0.

3. A process for controlling corrosion caused by acidic components in the initial condensate of a distilling petroleum product in a refining unit which comprises: adding a corrosion inhibiting amount of morpholine to said petroleum product as it passes through the refining unit, the amount of morpholine added to said product being sufficient to raise the pH of the water of the initial condensate to at least about 5.0.

4. A process as in claim 1 wherein morpholine is added to the overhead line of the distilling unit.

5. A process as in claim 1 wherein morpholine is added to the petroleum product before said product is passed through the fractionating column of the distilling unit.

6. A continuous process for inhibiting corrosion during the distillation of a petroleum product in a distilling unit containing a fractionating tower and an overhead line caused by acidic components dissolved in the water of the initial condensate of a distilling petroleum product which comprises: continuously adding to the product being distilled a corrosion inhibiting amount of morpholine, and

continuously recycling the water condensed to the overhead line of the fractionating tower of the distilling unit.

7. A process as in claim 6 wherein the amount of morpholine added to said product is sufficient to raise the pH pH of the water of the initial condensate to above 4.0.

8. A process as in claim 6 wherein the amount of morpholine added to said product is sufficient to raise the pH of the water of the initial condensate to at least 5.0.

9. A method of inhibiting corrosion taking place on the metal surfaces of a petroleum distilling unit which comprises: adding to the product being distilled a corrosion inhibiting amount of a film-forming amine along with morpholine in an amount sufficient to raise the pH of the water of the initial condensate to above 4.0.

10. A method of inhibiting corrosion taking place on the metal surfaces of a petroleum distilling unit which comprises: adding to the product being distilled a corrosion inhibiting amount of a film-forming amine along with morpholine in an amount sufficient to raise the pH of the water of the initial condensate to at least about 5.0.

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BARRY S. RICHMAN, *Primary Examiner.*

U.S. Cl. X.R

21—2.7, 58; 106—14; 203—7; 208—47; 252—390, 396