United States Patent [19]

Go

[11] 3,819,328

[45] June 25, 1974

[54] **USE OF ALKYLENE POLYAMINES IN DISTILLATION COLUMNS TO CONTROL CORROSION**

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[73] Assignee: **Petrolite Corporation,** Wilmington, Del.

[22] Filed: **June 19, 1973**

[21] Appl. No.: **371,393**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 48,975, June 24, 1970, abandoned.

[52] **U.S. Cl.** ..... **21/2.5 R,** 21/2.5 B, 21/2.7 R, 203/7, 208/47

[51] **Int. Cl.** **C23f 14/02**

[58] **Field of Search** ..... 21/2.5 R, 2.5 B, 2.7 R; 203/7; 208/47; 252/390

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[57] **ABSTRACT**

Alkylene polyamines, such as ethylene diamine (EDA), are employed to control acid corrosion in distillation columns, such as occurs in petroleum distillation columns; preferably where the polyamine is employed in conjunction with a corrosion inhibitor, for example, a non-neutralizing corrosion inhibitor such as a film-forming corrosion inhibitor.

pH control is more accurately and easily achieved with polyamines, such as EDA, than with either ammonia or morpholine. By employing EDA one preferably regulates the pH between about 5.5 – 7 and preferably about 6 – 7 with minimal deviations therefrom, thus avoiding or minimizing corrosion on the acid side (< about pH 5.5) and fouling on the basic side (> about pH 7).

In addition, the addition of amines to the petroleum charge prior to distillation in place of caustic treatment reduces the amount of HCl in the distillation column without the disadvantages resulting from the conventional caustic treatment.

12 Claims, 4 Drawing Figures

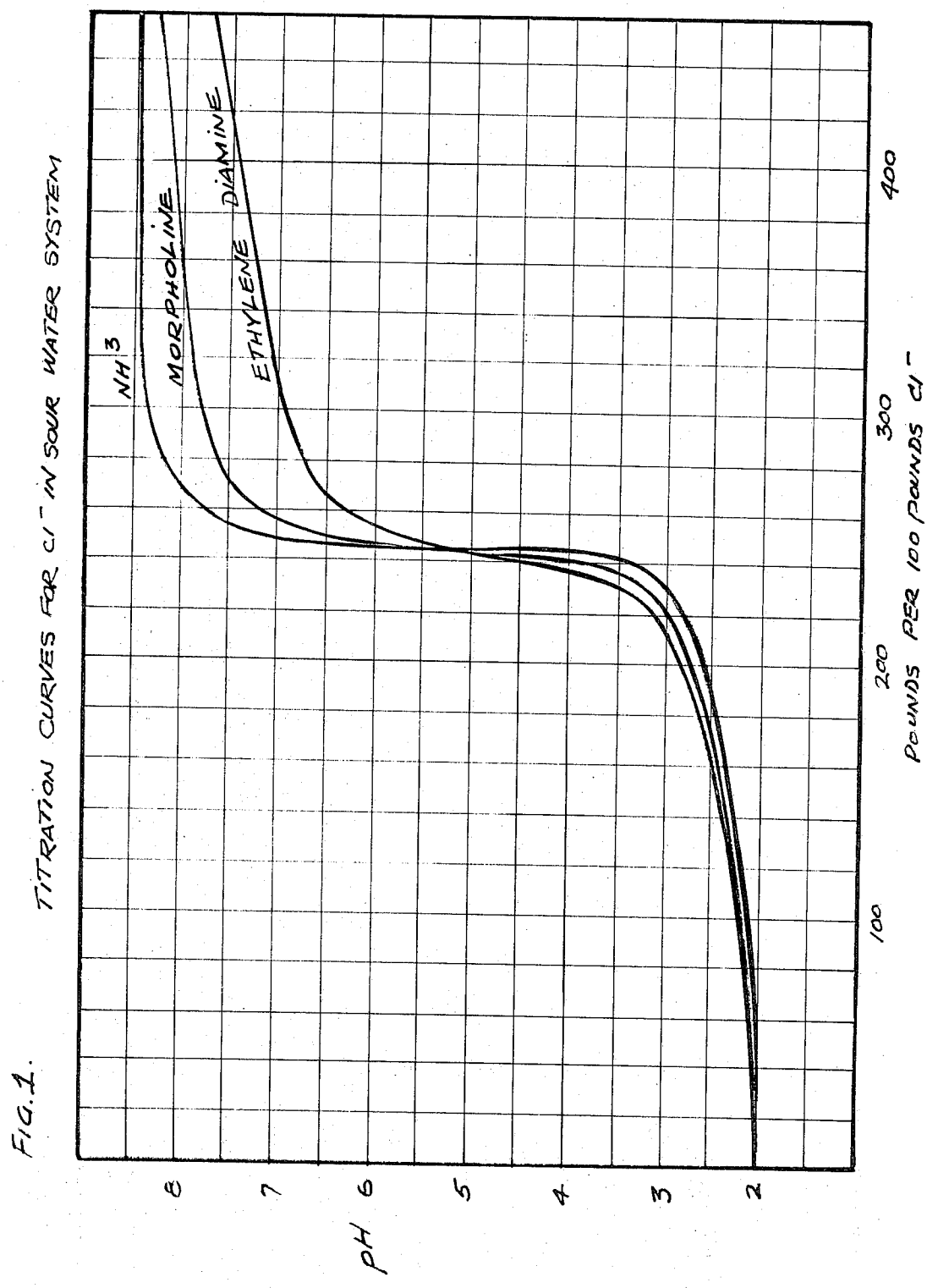


FIG. 1. TITRATION CURVES FOR Cl⁻ IN SOUR WATER SYSTEM

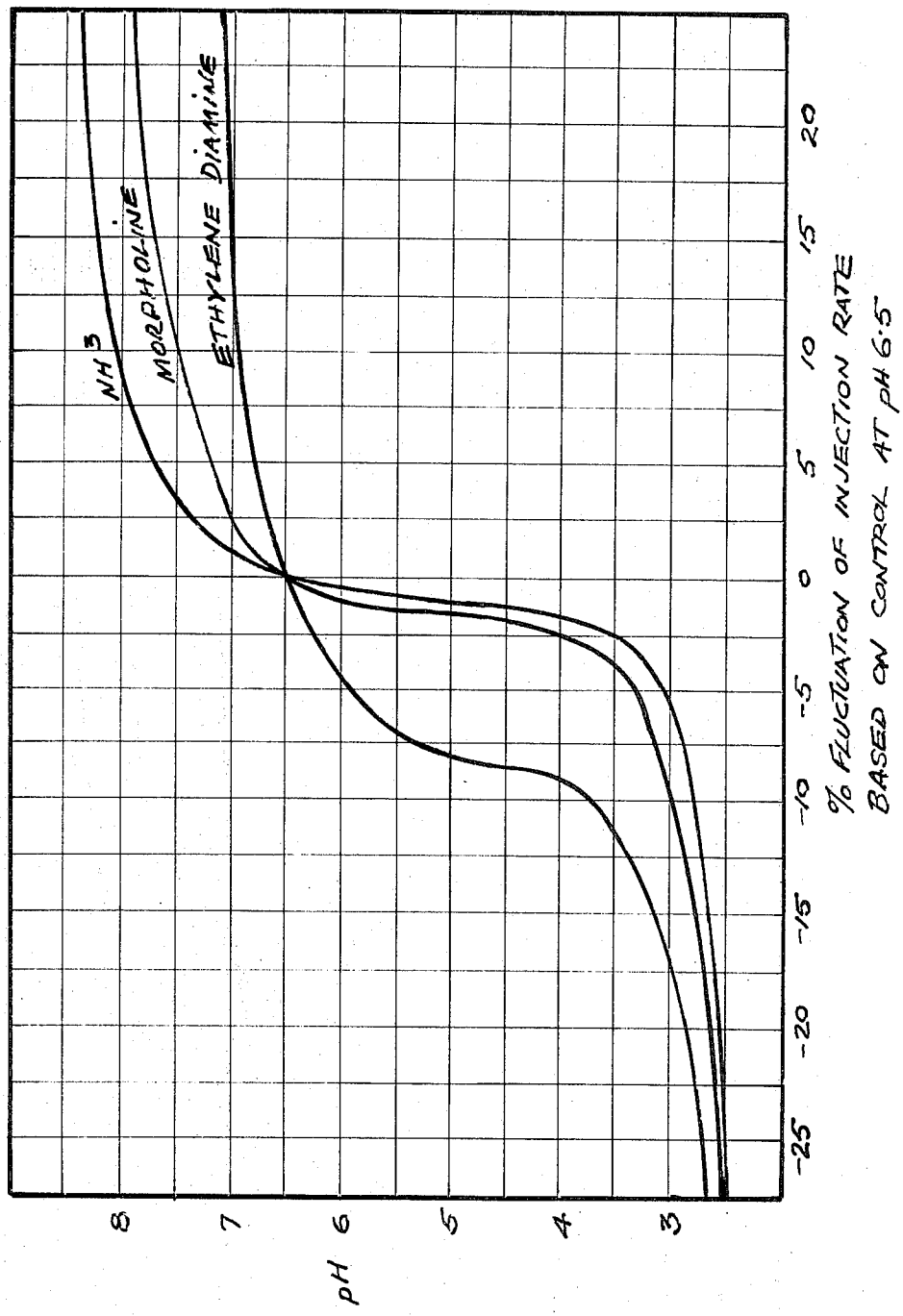

pH Vs. FLUCTUATION OF FEED RATE
NH3
MORPHOLINE
ETHYLENE DIAMINE
pH
8
7
6
5
4
3
% FLUCTUATION OF INJECTION RATE
BASED ON CONTROL AT pH 6·5
-25
-20
-15
-10
-5
0
5
10
15
20

Fig. 2.

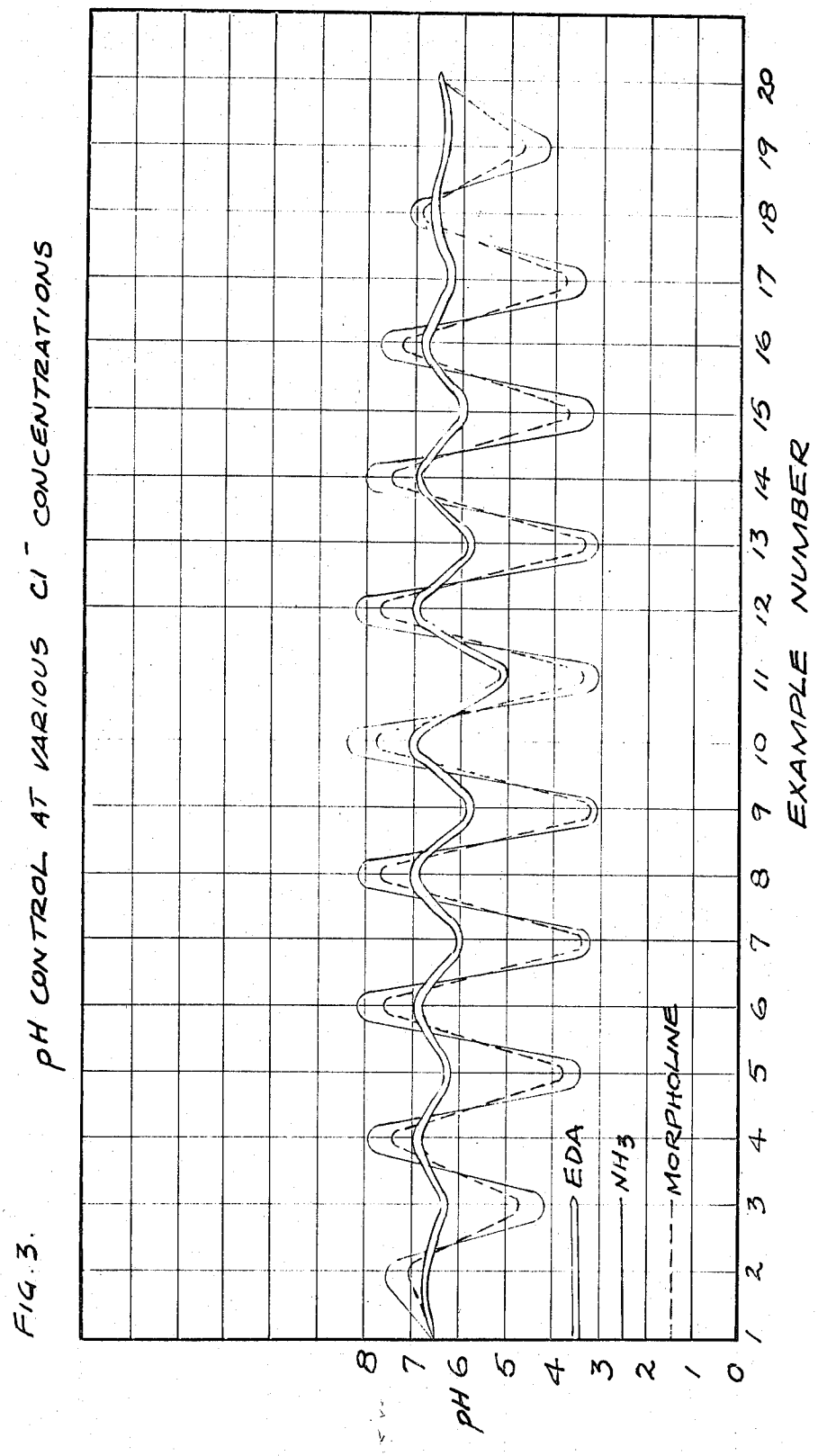
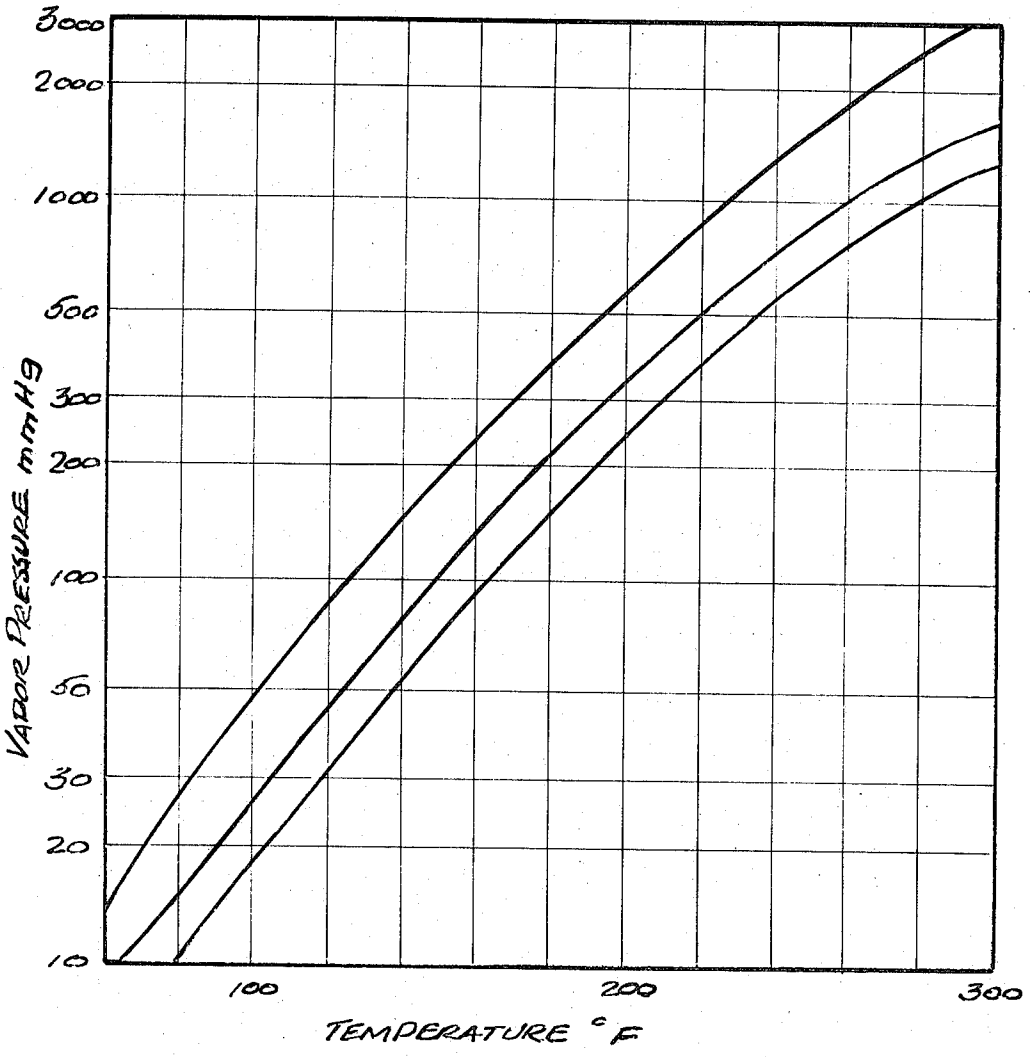

pH CONTROL AT VARIOUS Cl⁻ CONCENTRATIONS
pH
8
7
6
5
4
3
2
1
0
EDA
NH3
MORPHOLINE
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20
EXAMPLE NUMBER

FIG. 3.

FIG. 4.

VAPOR PRESSURES OF WATER, ETHYLENE DIAMINE AND MORPHOLINE AT VARIOUS TEMPERATURES.



USE OF ALKYLENE POLYAMINES IN DISTILLATION COLUMNS TO CONTROL CORROSION

This application is a continuation-in-part of S.N. 48,975 filed June 24, 1970, which application only has become abandoned.

This invention relates to the control of acid corrosion in distillation columns such as occurs in petroleum distillation columns.

Petroleum crudes as well as gas oils, reduced crudes, etc., are subjected to various processes in order to form lower boiling components such as gasoline, etc. The products obtained are distilled to produce a gasoline fraction, a fuel oil fraction, or lubricating oil fraction, etc. The lower boiling fractions and particularly gasoline are recovered as an overhead fraction from distillation zones. The intermediate components are recovered as side cuts from the distillation zone.

The fractions are coolec, 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 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 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 condensate is quite low. For this reason the water is highly corrosive. It is important, therefore, that the condensate be rendered less corrosive.

One approach to the solution of overhead distillation acid corrosion is the use of ammonia. However, ammonia being more volatile than water is often carried beyond the point of condensation so that its effectiveness is diminished. In addition ammonia tends to form NH_4Cl which is trapped in stagnant locations causing fouling. Since NH_4 Cl contains the chloride ion, it creates a high level of corrosion in a localized area unreachable by corrosion inhibitor treatment, thus rendering the system virtually unprotected at that point.

Another approach to overhead corrosion comprises the use of certain amines such as morpholine. These amines are more expensive than ammonia but they still cause salt deposition of their HCl salts and subsequent local corrosion. In addition since certain of these amines and their derivatives are excellent emulsifiers, they often cause process difficulties down stream.

In the overhead distillation column it is highly desirable to maintain a pH with minimal deviations of between about 6 and 7, (since an acidic pH tends to cause acid corrosion) whereas a pH higher than 7 tends to cause fouling with the attendant deposition of HCl salts which cause localized corrosion in the unprotected areas of deposition.

In adding ammonia or morpholine to the column a variation in the rate of addition causes problems. For example, where 6.5 is the target pH, a variation of ± 10 percent in the addition would yield a pH of about 2.8 or 8.8 with NH_3 and 3.2 or 7.5 with morpholine, thus causing acid corrosion in the lower pH ranges and fouling in the higher pH ranges.

I have now discovered that in contrast to NH_3 or morpholine, when ethylene diamine (EDA) is employed to control pH, an addition rate fluctuation of ± 10 percent would still give a pH between about 6 – 7 with minimal deviation. When a pH of 6.8 is used as the target point, such control is easily obtained. In this way corrosion at the lower pH's and fouling at the higher pH's are avoided.

The advantages of this invention are illustrated in the following Figures:

FIG. 1 presents titration curves obtained by neutralizing the Cl^- ion in sour water systems by employing NH_3, morpholine and ethylene diamine as neutralizing agents. It is to be noted that because of its greater buffering action, the curve for ethylene diamine is not as steep as that obtained with either ammonia or morpholine.

FIG. 2 presents a graph of pH as a percent fluctuation of the injection or feed rate based on desired control at pH 6.5. It is noted from this curve that, in contrast to the steep curve with both NH_3 and morpholine, EDA gives a flat curve indicating that variation in the feed rate has less affect on pH as compared to NH_3 or morpholine.

By moving the control point to pH 6.8 in the case of EDA, a variation ± 10 percent in feed will still maintain a pH of about 6 to 7 in contrast to the wide fluctuations with either NH_3 or morpholine. Stated another way, with EDA deviations from a pH of 6 to 7 are minimized.

The purpose of neutralizing corrosive systems is to maintain the pH as close as possible to a pH of 7 with minimum temporary deviations. However, during actual neutralization the deviation from 7 can vary widely. This is clearly shown in FIG. 3 and Table I which compares the use of ethylene diamine with ammonia and morpholine as neutralizers. Even though the average pH may be close to 7, temporary deviations cause corrosion.

In refinery practice, pH control is maintained indirectly by measuring chloride concentration. Thus, chloride concentration is maintained at 60 ppm ± 10, i.e., from 50 – 70 ppm chloride, the ± standard deviation (σ) being ± 10. Theoreticaly the following pH's are the ranges for the neutralizer shown in the attached tables

Neutralizer	pH Range
NH_3	2.8 to 8.2 pH
Morpholine	3.0 to 7.6 pH
E.D.A.	3.9 to 7.0 pH

Note that EDA has the narrowest theoretical pH range.

In practice close pH control is desired. This is shown in FIG. 3 and in Table I where it is demonstrated that EDA maintains the pH within the desirable pH range of 5.5 to 7.0 and most preferably 6 – 7, more effectively than either ammonia or morpholine. Although some deviations from this range may occur, they are minimal as compared to NH_3 or morpholine.

Refinery Example 1

Table I

Crude charge		100,000 B/D	
Overhead water condensate		30 gpm	
Average chloride concentration		60 ppm	
Range of chloride concentration		50–65 ppm	
	NH_3	EDA	Morpholine
Injection Rate	11 lb/day	5 gal/day	12 gal/day

pH at different chloride levels

Example Number	Cl ppm	NH_3	EDA	Morpholine
1	60	6.5 *	6.5 *	6.5 *
2	58	7.5	6.7 *	7.0 *
3	61	4.1	6.3 *	4.7
4	56	7.9	6.9 *	7.3
5	62	3.3	6.2 *	3.7
6	54	8.1	6.9 *	7.5
7	63	3.1	5.9 *	3.3
8	52	8.1	7.0 *	7.6
9	64	3.0	5.7 *	3.3
10	50	8.3	7.0 *	7.7
11	65	2.9	5.0	3.1
12	53	8.2	7.0 *	7.6
13	64	3.0	5.7 *	3.3
14	55	8.0	6.9 *	7.4
15	63	3.1	5.9 *	3.3
16	57	7.7	6.8 *	7.2
17	62	3.3	6.2 *	3.7
18	59	7.1	6.6 *	6.8 *
19	61	4.1	6.3 *	4.7
20	60	6.5 *	6.5 *	6.5 *

* Within desirable pH range

FIG. 3 is a graph of the pH at different chloride (Cl^-) concentrations of the particular examples in Table I when treated with EDA, NH_3, and morpholine, demonstrating that a more narrow pH range is obtained with EDA than with either NH_3 or morpholine.

From the above data it is evident that the present invention employing EDA is more effective than either NH_3 or morpholine in keeping the pH range within about 5.5 and 7.0 and preferably 6 – 7 with minor deviations where corrosion is minimal. Since corrosion is a great problem in refining, this improvement is of high commercial significance.

Although there are temporary deviations from the above desired and preferred ranges, these deviations are minimal as compared to NH_3 and morpholine. This is clearly shown in FIG. 3.

I have also discovered that polyamines such as ethylene diamines have the following additional advantages.

A. Ethylene Diamine is a volatile amine which has a vapor pressure range very similar to water. In the overhead vapor system of the column it will condense somewhat at the same time as the acidic water to give instantaneous neutralization, without premature condensation.

FIG. 4 presents the vapor pressures of water, EDA and morpholine at various temperatures from which it is evident that EDA has a vapor pressure closer to water than morpholine and thus in an overhead vapor system it will condense somewhat at the same time as acidic water to give instantaneous neutralization without premature condensation. The vapor pressure of NH_3 on the other hand is very high and its condensate is difficult to control and condense at the proper location.

B. Although ethylene diamine is more expensive than NH_3, it is less expensive than morpholine. Comparative properties of ammonia, ethylene diamine and morpholine are shown in Table II.

Table II

PROPERTIES OF AMMONIA, ETHYLENE DIAMINE AND MORPHOLINE

	Ammonia	Ethylene Diamine	Morpholine
Molecular Weight	17	60	87
Equivalent Weight	17	30	87
Specific Gravity	0.82	0.91	1.00
Boiling Point, °C.	−33	117	128
Flash Point, °F.	—	99	102
Pounds to Neutralize 100 Pounds of Cl^- to pH 6.5	48	97	250

Because of the neutralization stoichiometry, a little EDA goes a long way in neutralization with low cost performance. It has one-fourth the cost of morpholine in neutralization.

C. Unlike NH_3, ethylene diamine can be formulated with a corrosion inhibitor in any proportion with the aid of a common solvent. The ability of EDA to do so offers the versatility to vary the dosage according to the need of corrosion protection. When the overhead condensing system has a high level of acidic conditions, more neutralizers will be used to control the desired pH and thereby an automatically higher dosage of inhibitor is also present to combat high corrosion condition. On the other hand, at low acidic level, the inhibitor is automatically reduced.

D. The corrosion inhibitors employed are surface active and thereby offer detergent action to combat fouling; and the detergency requirement of the system will be automatically satisfied according to thhe need of the system, by controlling the rate of addition of the EDA corrosion inhibitor mixture.

E. EDA has excellent water tolerance.

Corrosion inhibitors are also employed in addition to EDA. The corrosion inhibitor is generally a nitrogen compound of high molecular weight such as amines, amides, aminoamides, imidazolines, etc., which may be dissolved in a solvent. Since they are believed to form a protective film on the metal surface to inhibit corrosion, they are called film-forming corrosion inhibitors.

Since corrosion inhibitors are surface active and tend to stabilize oil/water emulsions, when water is entrained in the oil, they can cause difficulties in product finishing processes and pollution. Since corrosion inhibitors vary widely in their tendency to stabilize emulsions, the inhibitor dosage should be less than that concentration which will create a emulsion problem.

Although the inhibitor and EDA may be added separately, it is convenient to formulate a common solution of EDA and the corrosion inhibitor so that a fixed ratio of corrosion inhibitor is present per unit EDA. This solution offers the versatility of varying dosage according to the need of corrosion protection. Thus, when the overhead condensate system has a high level of acid, more neutralizers will be used to control the desired pH and a higher dosage of inhibitor will automatically be

present to combat a high corrosion condition. Conversely, at a low acidic level, the inhibitor will also be automatically reduced.

In addition to acting as a corrosion inhibitor, the detergency of the corrosion inhibitor is very effective in breaking up fouling deposits which may form, thus preventing localized corrosion.

In general, the film-forming organic corrosion inhibitors which are employed in this invention are generally heteropolar, for example, cationic in nature. The most widely used type of film-forming corrosion inhibitor is the cationic type, which is generally a comparatively high molecular weight organic compound containing one or more basic nitrogen atoms.

In general, assuming a monomolecular layer, the more effective film-forming corrosion inhibitors are those which cover the largest area per molecule and form the most coherent and oriented film.

Typical but non-limiting examples, of film-forming corrosion inhibitors are presented below.

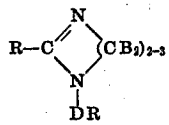
A wide variety of nitrogen bases are known to be film-forming corrosion inhibitors. The following are a few non-limiting examples:

1. Oxazolines (U.S. Pat. No. 2,587,955)
2. Tetrahydropyrimides (U.S. Pat. No. 2,640,029)
3. Imidazolines (Re. 23,227)
4. Pyrrolinediones (U.S. Pat. No. 2,466,530)
5. Amino amides (U.S. Pats. No. 2,550,682 and 2,598,213)
6. Quaternary amines (U.S. Pat. No. 2,659,693)
7. Monoamines, such as Rosin Amine
   (OIL GAS JOURNAL 46, No. 31, 91-6 (1946)
   Oxyalkylated Rosin Amine (U.S. Pat. No. 2,564,749)
   Rosin Amine + solubilizing agent (U.S. Pat. Nos. 2,564,757 and 2,564,753)

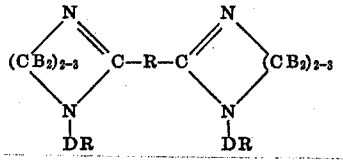
The imidazolines employed in the specific examples are a member of the cyclic amidine family of compounds and are prepared in the manner described in Reissue 23,227, U.S. Pat. No. 2,468,163, and elsewhere.

They may be described, for example, as follows:

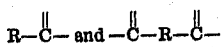
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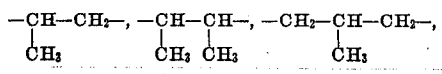
(2)



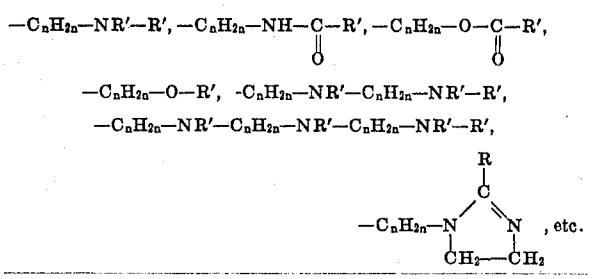
where



are residues derived from the carboxylic acid employed in preparing the compound wherein R is, for example, a hydrocarbon radical, having, for example, up to about 30 carbon atoms, such as 1 – 30 carbon atoms, B is hydrogen or a hydrocarbon radical, for example, a lower alkyl, such as methyl - for example, where CB_2

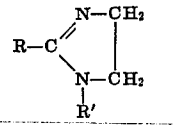


but preferably $-CH_2-CH_2-$ or $-CH_2-CH_2-_{CH2}-$, and R is the residue derived from the cyclic amidine-forming polyamine, for example where DR is



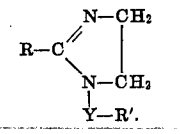
and wherein *n* is, for example, the numeral 1 to 6 and R′ is hydrogen or an aliphatic, cycloaliphatic hydrocarbon, etc., radical.

In the simplest case, the group R′ may be directly attached to the 1-nitrogen atom of the ring, as follows:

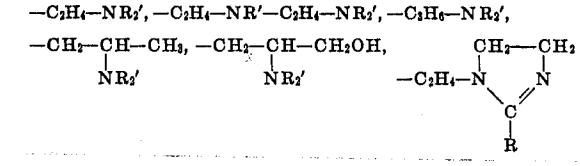


The particularly outstanding corrosion-preventative reagents result when the cyclic amidine contains basic nitrogen groups in addition to those inherently present in the imidazoline ring. In general, compounds of this type which are effective are those in which the basic nitrogen group is contained in the radical D in the above formula.

In this case the products may be represented by the formula

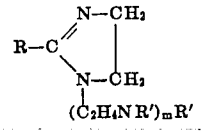


where R and R′ are hydrogen or a hydrocarbon radical, and in which at least one of the groups R and R′ is an aliphatic or cycloaliphatic hydrocarbon group containing from 8 to 32 carbon atoms; and Y is a divalent organic radical containing amino groups. The group R′ may be, and usually is, an amino nitrogen substituent. Examples of organic radicals which Y - R′ may represent are



$-C_2H_4-NR'-C_2H_4-NR'-C_2H_4-NR_2$, where R' and R have their previous significance.

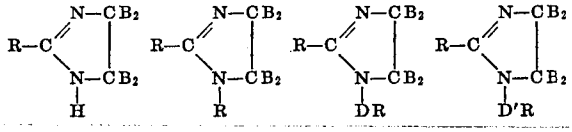
Of this class of corrosion inhibitors in which an amino group occurs as a portion of the 1-nitrogen substituent, those which are derived from the polyethylene polyamines appear to be particularly effective as corrosion inhibitors. These have the general formula



where R and R' have their previous meanings, and *m* is a small number, usually less than 6. Amides of these imidazolines are also effective.

Imidazolines have been described in Re. 23,227. A typical claim is as follows:

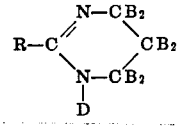
"A process for preventing corrosion of metals, comprising the step of applying to such metals a substituted imidazoline selected from the class consisting of



in which D represents a divalent, non-amino organic radical containing less than 25 carbon atoms, composed of elements from the group consisting of C, H, O, and N; D' represents a divalent, organic radical containing less than 25 carbon atoms, composed of elements from the group consisting of C, H, O and N'; D' represents a divalent organic radical containing less than 25 carbon atoms, composed of elements from the group consisting of C, H, O and N, and containing at least one amino group; R is a member of the class consisting of hydrogen and aliphatic and cycloaliphatic hydrocarbon radicals; with the proviso that at least one occurrence of R contains 8 to 32 carbon atoms; and B is a member of the class consisting of hydrogen and alkyl radicals having not over 2 carbon atoms, with the proviso that at least three occurrences of B be hydrogen."

Tetrahydropyrimidines have been described in U.S. Pat. No. 2,640,028 where a typical claim is as follows:

"A process for preventing corrosion of metals including the step of applying to such metals a substituted tetrahydropyrimidine of the formula type:



where D is a member of the class consisting of D' -R and R' D' represents a divalent organic radical containing less than 25 carbon atoms, composed of elements from the group consisting of C, H, O and N; R is a member of the class consisting of hydrogen and hydrocarbon radicals, with the proviso that at least one occurrence of R contains from 8 to 32 carbon atoms; B is a member of the class consisting of hydrogen and hydrocarbon radicals containing less than 7 carbon atoms, with the proviso that at least three occurrences of B be hydrogen."

In general, the preferred embodiments of film-forming corrosion inhibitors are of the type of cyclic amidines described above and acylated alkylene polyamines of the type described in U.S. Pat. No. 2,598,213 which are by reference incorporated in the present invention.

As is quite evident, other film-forming corrosion inhibitors are known and new film-forming inhibitors will be constantly developed which are useful in this invention. It is therefore not only impossible to attempt a comprehensive catalogue of such inhibitors, but to attempt to describe the invention in its broadest aspects in terms of specific chemical names of film-forming corrosion inhibitors used would be too voluminous and unnecessary, since one skilled in the art could by following known testing procedures select the proper film-forming inhibitor. This invention lies in the use of suitable film-forming corrosion inhibitors in the process and compositions of this invention and their individual composition is important only in the sense that their properties can effect the process.

For optimum results EDA is generally formulated with the corrosion inhibitors in a solution suitable for controlled addition to the system. Depending on the particular corrosion inhibitor the ratio of EDA to corrosion inhibitor can vary widely such as from about 0.75'–0.99 or more, for example from about 0.85–0.98, such as from about 0.90–0.97, but preferably from 0.92–0.95 exclusive of solvent. The concentration of EDA + corrosion inhibitor in the solvent can vary widely such as from about 5–85 percent for example from about 10–60 percent, such as from 20–50 percent, but preferably from 30–45 percent.

A typical formulation by weight is as follows:

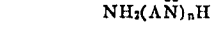
Formulation A

EDA	40%
Film Forming Corrosion Inhibitor	2%
Alcohol	5%
Hydrocarbon	53%
	100%

The corrosion inhibitor is the reaction product formed by acylating diethylenetriamine with naphthenic acid to yield imidazolines and amides.

The rate of addition can vary widely and will depend on the particular formulation employed and the acidity of the system. In general it should be sufficient to maintain the overhead pH at a goal of about 6 to 7.

Although EDA is the preferred polyamine, other polyalkylene-polyamines can also be employed such as those of the formula



where *n* is an integer such as from 1 – 10 and A is alkylene preferably lower alkylene and most preferably eth-

ylene and/or propylene. Preferably the polyethylene polyamine are preferred when n=1–5, i.e.

$$NH_2(CH_2CH_2N)_{1-5}H.$$

The polyamine can be added to the distillation unit at any suitable place. For example, the polyamine can be added to the petroleum charge. This is a highly convenient method of carrying out the process since it will also neutralize condensation within the tower and recirculation lines. The polyamine can also be pumped directly into the gaseous overhead line. The polyamine can also be passed into the reflux line or can be added to recirculating water at the top of the column. The particular point at which the polyamine is added will depend largely on the design of the particular equipment, the personal preference of the operator, the point where corrosion is more severe, etc.

In addition to the use of polyamines in controlling acid corrosion in the distillation column by regulation of the pH within the general range of about pH 6–7 with minimum variations on the acid or the basic side, the addition of amines to the petroleum charge prior to distillation in place of a conventional caustic treatment reduces the amount of HCl in the overhead condensate without the disadvantages resulting from the conventional caustic treatment.

Crude petroleum as received by the refinery generally contains brine (0.2 to 2.0 percent) which cannot be removed in the field. The brine solution consists primarily of sodium, calcium and magnesium chlorides. Although the desalting process is designed to remove these impurities, a small amount of salt solutions is retained in the desalted crude as it is charged into the crude unit. When the crude oil is subjected to a distillation temperature of as high as 700°F., chloride salts are hydrolyzed and decomposed to liberate hydrogen chloride that is then carried overhead in the fractionation towers. Caustic soda has been employed for many years to reduce the hydrogen chloride evolution in the distillation process. This is normally done by injecting an aqueous solution of caustic into the desalted crude oil charge line. It is theorized that sodium hydroxide reacts with the readily hydrolyzable salts such as magnesium chloride to form more stable sodium chloride and the corresponding hydroxide. However, the introduction of caustic causes fouling in the preheat exchangers and causes excessive coking in furnace tubes in addition to causing an increase in sodium content of residual fuel oil.

I have discovered that when amines such as alkylene polyamines are added to the crude instead of using the conventional caustic treatment, one achieves a reduction of HCl in the distillation column without the disadvantages caused by caustic injection. Thus by adding such amines in place of caustic into the desalted crude, I have achieved HCl reduction without the disadvantages caused by the use of caustic.

This result is unexpected since it cannot be explained by the general theory that NaCl is less readily hydrolyzed than MgCl since the amines employed herein are less basic than caustic. Therefore, the reason for this unexpected action is not understood.

Thus in addition to the injection of amines into the crude with the resulting reduction of overhead HCl without caustic disadvantages, the polyamine can also be injected into the distillation column as described herein.

The following examples are presented for purposes of illustration and not of limitation.

A two-liter pot was filled with 700 ml of crude oil or gas oil for each distillation; 4 ml of a water solution of 3.75 g Mg Cl_2/6 H_2O/100 ml or 0.15 g of $MgCl_2 \cdot 6H_2O$ also was charged to each distillation. The laboratory still pot was equipped with a 2½ ft. stainless steel saddle packed heated column of approximately six to eight plates.

Example A

Crude Oil Distillation.

The crude oil used for these distillations contained 2.5 ppm chloride in addition to the chloride that was added. The density of the crude was 0.825, therefore, the weight of crude charged was 577 g. The crude oil and the 4 ml of salt solution were heated to 130° C. removing water during this period. In order to simulate the steaming effect of a crude unit 2–5 drops of water was added above 155° because of excess foaming and for the same reason could not be heated above 175° C. which was the final pot temperature. The condensate from the still was removed by means of a glass tube submersed in 20 ml of water in order to collect the chloride that distilled over. The total grams of chloride ion contained in the crude oil distillations was as follows:

0.00175 g (from 2.5 ppm in crude)
0.02616 g from salt solution charge
0.02791 g Total Cl^- in crude runs

Tabulation of crude oil distillations is as follows:

	Total Ml H_2O in receiver	pH of condensate water	PPM * chloride in condensate H_2O	% Chloride obtained in condensate
Blank	23.36	4.0	17.7	1.5%
NaOH (1)	31.56	4.3	3.6	0.41%
EDA (2)	28.45	5.1	3.2	0.33%

* Chloride content is adjusted as if 23.36 ml of water
(1) NaOH charged = .065 g (1 ml at 6.5 g/100 ml)
(2) EDA charged = 0.139 g (1 mol at 13.9 g/100 ml)

Example B

Gas Oil Distillations

The only chloride present was from the 4 ml of $MgCl_2$ solution added to the pot (0.02616 g of Cl^-). The Gas oil water mixture was heated to 150° C. before adding the additional water. Water was added from 150° to 215° C. at 2–5 drops per every 5° C. The batch was then reheated to 215° C. (419° F.) where gas oil started refluxing such that no further increase in pot temperature could be obtained. Receiver water charge for chloride absorbing in the gas oil runs was 15 ml.

Tabulation of gas oil distillations is as follows:

	Total Ml H_2O in receiver	pH of condensate water	PPM * chloride in condensate H_2O	% Chloride obtained in condensate
Blank	25.40	7.7	3 (1)	0.35%
NaOH	32.38	8.5	1.4 (2)	0.17%
EDA	31.05	7.7	1.7	0.2%

(1) diluted to 31.05 ml for chloride + pH determinations.
(2) ppm chloride corrected for 31.05 ml water in summary section.

The NaOH and EDA charges for the gas oil runs were the same as reported in details for the crude oil distillations. The chloride content of the water distillate layers from the laboratory still were as follows: On (A) a crude oil, (B) gas oil using a 10 percent excess of EDA or NaOH over the amount of chloride charged.

A. Crude oil runs - pot temperature to 347° F.
1. Blank run Cl^- = 17.7 ppm
2. NaOH run Cl^-= 4.8 ppm (73 percent reduction)
3. EDA run Cl^- = 3.9 ppm (78 percent reduction)

B. Gas oil runs - pot temperature to 419° F.
1. Blank run Cl^- = 3 ppm
2. NaOH run cl^- = 1.4 ppm (53 percent reduction)
3. EDA run Cl^- = 1.7 ppm (43 percent reduction)

The above data shows a definite effect of the ability of EDA to reduce the amount of chloride in distillate condensates.

Refinery Example A

Formulation A is injected into the overhead system of a refinery distillation unit so that neutralization takes place in the vapor-condensate system as soon as water condensation occurs to form an acid solution. The dosage is adjusted so as to maintain the pH goal of about 6 – 7 with sufficient control so that there are minimal deviations below about 5. In this way corrosion is minimized.

Refinery Example B

The above example is repeated except that the petroleum feed is pretreated with EDA instead of caustic as was done in Example A. Formulation A is then injected into the overhead system in the manner of Refinery Example A.

The petroleum feed in Refinery Examples A and B are crudes.

Refinery Examples C and D

Examples A and B are repeated except that the feeds are gas oils.

From the foregoing description various modifications in this invention will be apparent to those skilled in the art which do not depart from the spirit of the invention.

I claim:

1. A process of controlling corrosion caused by acidic components in a petroleum system containing a petroleum medium which comprises regulating the pH of said petroleum medium in said petroleum system to between about 5.5 to about 7 by adding an alkylene polyamine to said petroleum system.

2. The process of claim **1** where the alkylene polyamine is ethylene diamine.

3. The process of claim **1** where a film-forming corrosion inhibitor is also added to said petroleum system.

4. The process of claim **3** where the alkylene polyamine is ethylene diamine.

5. The process of claim **1** which comprises regulating the pH of said petroleum medium in said petroleum system to between about 5.5 to about 7 by adding said alkylene polyamine to said petroleum system, said petroleum system including a distillation unit through which said petroleum medium passes.

6. The process of claim **5** where the alkylene polyamine is ethylene diamine.

7. The process of claim **5** where a film-forming corrosion inhibitor is also added to said petroleum system.

8. The process of claim **7** where the alkylene polyamine is ethylene diamine.

9. The process of claim **5** wherein said petroleum system includes an overhead vapor-condensation means and where the pH of said petroleum medium in said petroleum system is regulated to between about 5.5 to about 7 by adding the alkylene polyamine to the overhead vapor-condensation means.

10. The process of claim **9** where the alkylene polyamine is ethylene diamine.

11. The process of claim **9** where a film-forming corrosion inhibitor is also added to said petroleum system.

12. The process of claim **11** where the alkylene polyamine is ethylene diamine.

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