CORROSION INHIBITOR CONTAINING A WATER SOLUBLE EMULSION OF A FATTY AMINE WITH A CATIONIC EMULSIFIER

Inventors: Gerhard W. Scherf, Mineral Springs Road, RR-3, Dundas, Ancaster, Ontario; Gary C. Pfaff, 246 York Road, Dundas, Ontario, both of Canada

Filed: Aug. 27, 1970
Appl. No.: 67,570

U.S. Cl. ..................... 252/391, 21/2.7 R, 106/14, 210/59, 252/180, 252/312, 252/356, 252/390, 252/392, 260/564 F
Int. Cl. ...................... C23f 11/16, C23f 11/14
Field of Search ........... 252/391, 390, 392, 394, 395, 252/180, 312, 356; 21/2.7; 210/59; 106/14; 260/564 F

References Cited
UNITED STATES PATENTS
2,947,703 8/1960 Larsonneur .................... 252/391
3,088,796 5/1963 Kahler et al. .................. 252/392
3,203,904 8/1965 Brown .......................... 252/357
3,418,254 12/1968 Bishop et al. .............. 252/392

Abstract
A composition and method for inhibiting steam-corrosion, comprising adding to the water a stable, cationic, fatty amine emulsion which breaks down upon heating, thereby allowing the fatty amine to enter the vapor phase and coat the interior surfaces exposed to the steam. Optionally, an ethoxylated straight chain aliphatic acid may be added where the boiler water contains inorganic salt impurities, or is at a high temperature in order to maintain stability of the emulsion.

7 Claims, No Drawings
CORROSION INHIBITOR CONTAINING A WATER SOLUBLE EMULSION OF A FATTY AMINE WITH A CATIONIC EMULSIFIER

BACKGROUND OF THE INVENTION

1. Field of the Invention
   This invention relates to the inhibition of corrosion in boiler systems.

2. Description of the Prior Art

   The fatty amines noted above are useful in inhibiting corrosion in boiler systems and the like due to their unique balance of hydrophilic/hydrophobic properties and relatively high molecular weight. Fatty amines possess very desirable film forming properties, which enable them to escape the aqueous phase and deposit as nearly insoluble protective films on all surfaces inside a boiler system or the like. The insolubility of fatty amines in water, however, makes the initial application throughout the system unusually difficult. In order to be fed uniformly into the boiler water, these film forming fatty amines must first be thoroughly emulsified in water. Existing U. S. Pat. Nos. such as 2,712,531; 2,882,171; 2,956,889; 3,088,796; 3,239,470; 3,418,253; and 3,418,254, each of which are described above, suggest that primary non-ion emulsifiers can be used with film-forming fatty amines to inhibit boiler system corrosion. Other emulsifiers which can be used with fatty amines, but which have not previously been used in boiler system corrosion inhibition applications are cationics, such as amine salts, quaternary ammonium compounds, and other nitrogenous bases such as thiouionium salts. Thiouionium salts per se are well known. U. S. Pat. No. 2,051,943 discloses the use of S-alkyl and S-aryl thiouionium salts as emulsifying agents.

SUMMARY OF THE INVENTION

As is apparent from the above description of the prior art, the use of fatty amines to form a corrosion inhibiting film on metallic surfaces, such as encountered in boiler systems, is well known. The use of an emulsifier to allow feeding of the otherwise insoluble fatty amines at a fixed rate into the boiler water is also well known. However, the only emulsifiers that have been used successfully prior to this invention have been non-ionicics such as ethoxylate amines. The disadvantages of previous emulsifiers such as ethoxylate amines is that upon breakdown of the emulsion, the emulsifier remains in the boiler water and accumulates without degrading, thus reducing the efficiency of the boiler system. In sharp contrast, the novel composition claimed in this invention uses an emulsifier which degrades, upon continued heating, into volatile fractions, which thus do not accumulate within the boiler water. We have discovered novel cationic fatty amine...
emulsions which are stable until subjected to heating, at which time they break down to allow the fatty amine to enter the vapor phase and thus be carried throughout the boiler system, coating all exposed metallic surfaces thereof with a corrosion inhibiting film.

It is an object of this invention to provide a novel composition for inhibiting the corrosion of metal surfaces exposed to water, and, in particular, boiler systems. The said composition comprises a water soluble emulsion of a fatty amine with one or more cationic emulsifiers. Optionally, an ethoxylated straight chain aliphatic acid may be added as an emulsifier stabilizer.

It is a further object of this invention to provide a novel method for inhibiting corrosion in boiler systems by adding to the boiler water a stable, water-soluble emulsion of fatty amines with one or more cationic emulsifiers so that said emulsion is fed uniformly into the boiler water, heating the boiler water so that the said emulsion is broken down and the fatty amines enter the vapor phase, and having the fatty amines carried throughout the system while in the vapor phase, so as to deposit a fatty amine film on all exposed metallic surfaces of the boiler system.

Other objects of this invention will become apparent from the further disclosures herein. It is intended, however, that the disclosures herein do not limit the invention but merely indicate preferred embodiments thereof, since various modifications within the scope of this invention will become apparent to those skilled in the art.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Useful fatty amines include saturated n-alkyl amines containing 12 to 22 carbon atoms; unsaturated n-alkyl amines having a saturated backbone containing 12 to 22 carbon atoms with 1 or 2 unsaturated moieties on the backbone; branched alkyl amines containing 12 to 22 carbon atoms; mixtures of any or all of the above; and hydrogenated mixtures of any of the above unsaturated amines. Examples of useful fatty amines include, but are not limited to: dodecylamine, tridecylamine; tetradecylamine; pentadecylamine; hexadecylamine; heptadecylamine; octadecylamine; nonadecylamine; eicosylamine; henecicosylamine; docosylamine; hexadecylamine; hydroxyethylhexadecylamine; hydroxyethylhexadecylamine; diethyhexadecylamine; dimethyltetradecylamine; triethyltridecylamine; tallow amines; hydrogenated tallow amines. The preferred fatty amines for utilization in this invention are octadecylamine and hydrogenated tallow amines. These fatty amines will be present in the composition of this invention in from about 8% to about 20% parts by weight, and preferably from about 8% to about 12 parts by weight.

Useful cationic emulsifiers are the salts of nitrogenous non-quaternary bases containing at least one sulfur atom, and in particular isothiouronium salts having the general formula:

\[ R - \text{SO}_{2} - C = \text{NH} \cdot \text{HR'} \]

where \( R \) is an alkyl hydrocarbon of \( C_{10-22} \) and \( R' \) is chloride, bromide, acetate or sulfate. Examples of useful cationic emulsifiers include, but are not limited to: dodecyl isothiouronium chloride, octadecyl isothiouronium chloride, eicosyl isothiouronium chloride, hydroxyethyl dodecyl isothiouronium acetate, triethyltridecyl isothiouronium bromide, hydrogenated tallow isothiouronium chloride. The preferred cationic emulsifiers for utilization in this invention are dodecyl isothiouronium chloride and paraffin wax isothiouronium chloride. The cationic emulsifier will be present in the composition of this invention in from about 1% to about 7 parts by weight, and preferably from 1% to about 4 parts by weight.

In order to maintain stability of the emulsion where the boiler water contains inorganic salts such as phosphates, and/or is at a high temperature, a straight chain aliphatic acid of \( C_{14-20} \) which has been ethoxylated with from 2 to 30 moles of ethylene oxide may be added to the emulsifier. The preferred stabilizer additive is octadecanoic acid ethoxylated with from about 5 to about 25 moles of ethylene oxide. The emulsion stabilizer will be present in the composition of this invention in from 0 to about 7 parts by weight and preferably from 0 to about 3 parts by weight. It should be noted that the preferred emulsion stabilizer is difficult to dissolve in water and therefore is not suitable for use as an emulsifier in the composition of this invention.

The foregoing components are combined with water to form a novel emulsion which is then diluted with water to form a steam-corrosion inhibiting composition containing from about 1 percent to about 25 percent by weight of solids.

The steam-corrosion inhibiting composition may be utilized in the following novel manner. Said composition is added to the water in the boiler system by direct addition to the water storage tank, by feeding into water being added to the water storage tank, or by any other means, so that a ratio of from about 0.10 percent to about 2.0 percent by weight of said composition to the weight of the boiler water is maintained. The boiler water is then heated sufficiently to break down the emulsion into its component parts. Further heating of the boiler water will cause the fatty amine component to enter its vapor phase and become dispersed throughout the boiler system, whereupon it will become deposited as a film upon all exposed metallic interior surfaces of the system. Said film will then inhibit corrosion of the said surfaces caused by the steam passing across them. Although the film-coating process is independent of the steam generation, it is most frequently conducted simultaneously therewith.

The temperature at which the boiler system is functioning is not of importance as long as it is sufficient to break down the emulsion and vaporize the fatty amine. Thus, under pressure less than one atmosphere, the fatty amine will enter the vapor phase at a lower temperature and conversely, in a high pressure system, a higher temperature will be required to vaporize the fatty amine.

EXAMPLE 1

Preparation of an emulsifier within the scope of this invention.

A mixture of \( C_{12-14} \)-dodecyl chloride, this is a mixture of \( C_{12-14} \) chains which is predominantly \( C_{12} \) and sold as such, 61.6 g., thiourea, 57 g., and ethyl alcohol,
200 g., was refluxed until a clear colorless solution was obtained. The reaction was then allowed to proceed closer to completion by refluxing for an additional 6 hours. Upon cooling, a heavy precipitate formed. The solid 38.6 g., assumed to consist primarily of unreacted thiourea, was filtered off, and the alcoholic filtrate, containing 79.7 g. of solids, preserved for evaluation purposes. The filtrate solids were determined to be dodecyl isothiouronium chloride. The product was identified by its strong infrared absorption at 1645 cm⁻¹, believed to originate from a moiety containing the amidino-radical, —C(=NH)—NH₂.

Example II

Emulsification of Octadecylamine with dodecyl isothiouronium chloride.

Octadecylamine, 18 g., was blended with the product of Example I, 2 g., ("net," i.e. after evaporation of the alcoholic solvent) and subsequently ground in a porcelain mortar until the two components were thoroughly mixed. Distilled water, 80 g., was then added dropwise and the grinding procedure continued until a uniform "white" emulsion was obtained. Care was taken to avoid the generation of foam during the later stages of the emulsification process. The emulsion was then divided into 2 parts and diluted to 16.6 and 7 percent "solids," respectively, and the samples used for evaluation purposes. At 7 percent solids, the emulsion was very liquid, almost comparable to milk, and could be diluted infinitely with distilled water. No sign of phase separation occurred in 0.5 percent solutions of this emulsion in distilled water. The 16.6 percent emulsion had a cream-like appearance and showed the same characteristics as the 7 percent emulsion.

Example III

Emulsification of hydrogenated tallow amine with dodecyl isothiouronium chloride.

A mixture of fatty amine, (Armenian HTD, Armour Chem. Co.), 18 g., and the product of Example I, 3 g., was blended with water, 180 g., under continuous agitation. A small fraction of this quantity of water was added initially along with the fatty amine; the remainder was added slowly over a period of 1 hour. A viscous paste-like material formed under these conditions. An additional 3 g. of the emulsifier was then added, and the resulting product kept under slow agitation for 4 hours at 60°-70°C to yield a smoothly-flowing white emulsion.

Example IV(a)

Preparation of a modified version of dodecyl isothiouronium chloride.

Dodecyl chloride C₁₂₋₁₄. (This is a mixture of C₁₂₋₁₄ chains which is predominantly C₁₂ and sold as such.) 218.5 g., thiourea, 152.2 g., and ethyl alcohol, 400 g., were allowed to interact at 80°C under reflux conditions until the "water-solubility test" carried out with small samples of the reaction mixture according to the procedure described in Example IV(b) indicated that dodecyl chloride was converted nearly completely into soluble isothiouronium salts. The product was then isolated as described in Example I for C₁₁₋₁₈ dodecyl chloride.

Example IV(b)

"Water-solubility test"

This test was developed as a control method for the production of dodecyl isothiouronium chloride from dodecyl chloride and thiourea, and is based on the water-insolubility of dodecyl chloride.

Equipment: Graduated test tube, centrifuge tube or cylinder (50 ml. size used on lab. scale reaction).

Procedure: 30 ml. of a 10 % NaCl solution was placed in the graduated tube; 10 ml. of the alcoholic reaction mixture (after settling of the undissolved thiourea) are then mixed with the salt solution. (Because of the high content of unreacted thiourea which was dissolved in hot alcohol, but precipitates at room temperature, the sample may solidify in the sampling pipet. If this occurs, the sample can be recovered by warming the salt solution and drawing it up into the pipet several times, and by keeping the pipet in a hot water bath at 80°-100°C). The product/salt mixture yields a cloudy white solution at room temperature; as product concentration increases however, a precipitate will form in larger quantities.

The graduated tube containing the product/salt mixture is then heated in a water bath until a clear solution is obtained. If any unreacted dodecyl chloride is present in the reaction mixture, it will reveal itself by forming a separate layer on the surface of the water/salt solution. Measuring the volume of unreacted dodecyl chloride thus affords a semi-quantitative estimate of the progress of the reaction. In the final stage, no dodecyl chloride will separate out at 50°-60°C. The mixture can then be centrifuged in order to facilitate the detection of any residual amounts of dodecyl chloride, which may have escaped the natural gravimetric separation. All samples are compared to a "blank" obtained by mere physical blending of the reagents mentioned above.

Example V

Emulsification of octadecylamine with a modified version of dodecyl isothiouronium chloride.

Octadecylamine, 9 g., was blended with the product of Example IV(a), 1 g. ("net," i.e. after evaporation of the alcoholic solvent), and subsequently ground in a porcelain mortar until the two components were thoroughly mixed. Distilled water, 90 g., was then added dropwise and the grinding procedure continued until a uniform "white-creamy" emulsion was obtained. Care was taken to avoid the generation of foam during the later stages of the emulsification process. No sign of phase separation occurred in 0.5 percent solution of this emulsion in distilled water.

Example VI

Preparation of an emulsifier within the scope of this invention.

A mixture of chlorinated paraffin wax containing 40-42 percent chlorine by weight, 89 g., thiourea, 34 g., and acetic acid, 200 g., was refluxed for 8 hours at 122°C. Ether was then added to the reaction mixture at room temperature in order to extract the acetic acid and unreacted thiourea. Filtration of the ether/product mixture yielded a light-brown semi-solid material (78
Emulsification of octadecylamine with paraffin wax isothiouanium. Octadecylamine, 10 g., was blended with the product of Example VI, 2.5 g., and subsequently ground in a porcelain mortar until the two components were thoroughly mixed. Distilled water, 90 g., was then added dropwise and the grinding procedure continued until a uniform “creamy-white” emulsion was obtained. Great care was taken to avoid the generation of foam during the later stages of the emulsification process. No sign of phase separation occurred in 0.5 percent solution of this emulsion in distilled water.

In the following examples emulsions of the fatty amine and emulsifier were prepared. These examples are summarized in the following two tables where there is recorded for each example the amine, the emulsifier, the stabilizer where used, the method of mixing and the stability of the resulting emulsion.

The stability tests were carried out by placing between one to ten parts of weight of the emulsion into approximately 100 grams of the test medium which was distilled water, tap water, cold and hot (80°C) salt solution and observing the effects of this dilution upon the emulsion. Then the consistency of the final mixture was observed. Where stability upon dilution with distilled water was not obtained, it was concluded that the initial emulsification of the amine was incomplete.

As the use of these compositions on occasion requires stability under more severe conditions, such as in the presence of salts, selected compositions of the emulsified amines were also tested for their stability towards inorganic salts and towards hot salt solutions. In the tables, the following symbols or abbreviations are used:

- T = tap water
- D = distilled water
- ODAM = octadecylamine
- B = mechanical blender
- M = mortar and pestle
- EDTA = Ethylenediamine tetra-acetic acid
- SP = tribasic sodium phosphate
- TEA = triethanolamine
- TPP = triphenyl phosphate
- HX = 1,2-hexamidine
- SA = salicylic acid
- OA = oxalic acid
- PHA = phthalic acid
- E-T13 = Ethodoumeen T-13 (Armour) (modified polyacrylamide)
- H = Homogenizer
- CP35 = Cyanamer P-35 (polyethoxylated aliphatic diamine)
- HT = Heat and agitate
- LTM-N = laurel trimethylene ammonium chloride
- CPA = Nonionic polyacrylamide cationized with N-methyl dimethylamine
- STO = ethoxylated steary acid of 39 percent by weight ethylene oxide
- IMD = imidazoline which is the reaction product of equimolar amounts of hydroxyethyl ethylenediamine and oleic acid.
- LAO = lauryl alcohol ethoxylated with 12 moles of ethylene oxide.
- HTAA = Hydrogenated tallow amine acetate
- HTA = Hydrogenated tallow amine

Salt Solution = an aqueous solution of:
- 0.75 percent by weight of mono and di-sodium phosphate
- 0.25 percent by weight of sodium hydroxide
- 0.50 percent by weight of sodium sulfite
- 0.50 percent by weight of ethylene diamine tetra-acetic acid

### Table 1

<table>
<thead>
<tr>
<th>Example No.</th>
<th>Water used</th>
<th>Gms. water</th>
<th>Amino used</th>
<th>Emulsifier used</th>
<th>Gms. stabilizer used</th>
<th>Gms. stabilizer used</th>
<th>Method of mixing</th>
<th>Stability to</th>
</tr>
</thead>
<tbody>
<tr>
<td>VIII...</td>
<td>D</td>
<td>90 ODAM</td>
<td>9 Same as in Ex. VI...</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IX...</td>
<td>D</td>
<td>90 ODAM</td>
<td>9 Same as in Ex. I...</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>X...</td>
<td>D</td>
<td>90 ODAM</td>
<td>15</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>XI...</td>
<td>D</td>
<td>90 ODAM</td>
<td>15</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>XII...</td>
<td>D</td>
<td>90 ODAM</td>
<td>15</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>XIII...</td>
<td>D</td>
<td>90 ODAM</td>
<td>15</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>XIV...</td>
<td>D</td>
<td>90 ODAM</td>
<td>9</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>XV...</td>
<td>D</td>
<td>90 ODAM</td>
<td>9</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>XVI...</td>
<td>D</td>
<td>90 ODAM</td>
<td>9</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>XVII...</td>
<td>D</td>
<td>90 ODAM</td>
<td>9</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>XVIII...</td>
<td>D</td>
<td>90 ODAM</td>
<td>9</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Table 2

<table>
<thead>
<tr>
<th>Example No.</th>
<th>Water used</th>
<th>Gms. water</th>
<th>Amino used</th>
<th>Emulsifier used</th>
<th>Gms. stabilizer used</th>
<th>Gms. stabilizer used</th>
<th>Method of mixing</th>
<th>Stability to</th>
</tr>
</thead>
<tbody>
<tr>
<td>XX...</td>
<td>D</td>
<td>90 ODAM</td>
<td>9 TPA...</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>XXI...</td>
<td>D</td>
<td>87.78 ODAM</td>
<td>10 Same as in Ex. IVA...</td>
<td></td>
<td>2.22</td>
<td>STO...</td>
<td>1.5</td>
<td>M</td>
</tr>
<tr>
<td>XXII...</td>
<td>D</td>
<td>87.78 ODAM</td>
<td>10</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>XXIII...</td>
<td>D</td>
<td>87.78 ODAM</td>
<td>10</td>
<td></td>
<td>2.72</td>
<td>STO...</td>
<td>2</td>
<td>M</td>
</tr>
<tr>
<td>XXIV...</td>
<td>D</td>
<td>90 ODAM</td>
<td>10</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>XXV...</td>
<td>D</td>
<td>90 ODAM</td>
<td>10 Same as in Ex. Iva...</td>
<td></td>
<td>2.5</td>
<td>STO...</td>
<td>1</td>
<td>M</td>
</tr>
<tr>
<td>XXVI...</td>
<td>D</td>
<td>88.5 D plus</td>
<td>8</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Stability to

- Salt solution
- Hot salt solution (80°C)
It is apparent from the results shown in the tables above that complete emulsification of the octadecylamine as judged by the above-mentioned solution test was only achieved when at least one of the emulsifiers cited in the relevant claims of this application were applied. Stability of the emulsion towards salt solution could be achieved by means of selected stabilizers such as ethoxylated stearic acid. It should be noted also that the presence solely of the compounds classed as stabilizers in this application was not sufficient to bring about emulsification of the fatty amine.

What we claim is:

1. A steam-corrosion inhibiting composition comprising an aqueous emulsion containing from about 1 percent to about 25 percent by weight of solids consisting of:
   A. from about 8 to about 20 parts by weight of a fatty amine selected from the group consisting of
      1. one or more saturated n-alkylamines containing from about 12 to about 22 carbon atoms,
      2. tallow amine
      3. hydrogenated tallow amine
      4. branched alkyl amines containing from about 12 to about 22 carbon atoms,
      5. a mixture of any of the above said amines, and
   B. from about 1 to about 7 parts by weight of a cationic emulsifier having the general formula

\[
\begin{align*}
R & \equiv \text{alkyl hydrocarbon having from about 10 to about 22 carbon atoms and } R' \text{ is one of a group consisting of an acetate, a bromide, a chloride, and a sulfate; and} \\
& \text{C. from 0 to about 7 parts by weight of an emulsion stabilizer consisting of an ethoxylated straight chain unsubstituted acid containing from about 14 to about 20 carbon atoms in the chain.}
\end{align*}
\]

2. A composition according to claim 1 in which said fatty amine is octadecylamine.

3. A composition according to claim 1 in which said fatty amine is hydrogenated tallow amine.

4. A composition according to claim 1 in which said cationic emulsifier is dodecyl isothiouronium chloride.

5. A composition according to claim 1 in which said cationic emulsifier is paraffin wax isothiouronium chloride.

6. A composition according to claim 1 in which the emulsion stabilizer is present in up to 7 parts by weight.

7. A composition according to claim 6 in which said emulsion stabilizer is octadecanoic acid ethoxylated with from about 5 to about 25 moles of ethylene oxide.

\[
\begin{align*}
R = & \equiv \text{alkyl hydrocarbon having from about 10 to about 22 carbon atoms and } R' \equiv \text{one of a group consisting of an acetate, a bromide, a chloride, and a sulfate; and} \\
& \text{C. from 0 to about 7 parts by weight of an emulsion stabilizer consisting of an ethoxylated straight chain unsubstituted acid containing from about 14 to about 20 carbon atoms in the chain.}
\end{align*}
\]
UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 3,718,604
DATED : February 27, 1973
INVENTOR(S) : Gerhard W. Scherf and Gary C. Pfaff

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Below the names and addresses of the inventors, insert --[73] Assignee: Diamond Shamrock Corporation, Cleveland, Ohio--. Under Abstract, line 8, "containers" should be --contains--. Column I, line 39, after "lated" delete the word "guide" and substitute therefor --amide--; Column I, line 58, "primary" should be --primarily--. Table II, Example XXIX, under the heading "Gms. water", "87.87" should be --87.78--.

Signed and Sealed this
Tenth Day of May 1977

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks
UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 3,718,604
DATED : February 27, 1973
INVENTOR(S) : Gerhard W. Scherf and Gary C. Pfaff

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Below the names and addresses of the inventors, insert --[73] Assignee: Diamond Shamrock Corporation, Cleveland, Ohio--. Under Abstract, line 8, "containers" should be --contains--. Column 1, line 39, after "lated" delete the word "guide" and substitute therefor --amide--; Column 1, line 58, "primary" should be --primarily--. Table II, Example XXIX, under the heading "Gms. water", "87.87" should be --87.78--.

Signed and Sealed this
Tenth Day of May 1977

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks