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3,294,695 CORROSION INHIBITING COMPOSITIONS AND PROCESSES

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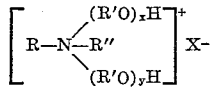
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This invention relates to corrosion inhibiting compositions and processes, and more particularly to compositions and methods for inhibiting corrosion and pitting caused by aqueous solutions of pickling and cleaning acids, such as sulfuric, sulfamic, phosphoric, citric, etc. acids.

In formulating a corrosion inhibiting compound for use in aqueous solutions of metal corroding acids, major problems have existed with respect to the safety hazard, necessity for solvents, unpleasant odors developed, as well as effectiveness in reducing corrosion. I have discovered that by employing quaternaries of alkoxylated amines in combination with dibutylthiourea, a formulation is provided having sufficient solubility at use concentrations as to eliminate the requirements of a solvent, while at the same time the product has a high flash point which meets all safety hazard requirements, and the composition further gives extremely high protection against corrosion.

A primary object, therefore, is to provide a composition and process meeting safety hazard requirements and providing effective protection against corrosion by aqueous acid solutions. A further object is to provide a composition which eliminates the need for solvents while at the same time having a high flash point providing for the utmost of safety in use. A further object is to provide a composition in which the active materials are effectively dispersed for yielding high efficiency in use. Yet another object is to provide a composition in which the quaternary ammonium compound may be one hundred percent active. Other specific objects and advantages will appear as the specification proceeds.

In one embodiment of the invention, dibutylthiourea is mixed with a compound having the following structure:



wherein R is an aliphatic hydrocarbon radical having between 6 and 22 carbon atoms, R' is an alkylene radical having between 2 and 3 carbon atoms, R'' is an alkyl radical having between 1 and 3 carbon atoms, X is a halogen, and x and y are integers having a sum total varying between 2 and 50.

It is preferred to employ in combination with the dibutylthiourea, an ethoxylated quaternary ammonium compound or a propoxylated quaternary ammonium compound, and the range of moles for the ethylene oxide or propylene oxide is 2 to 50 moles. I prefer to employ 2 to 25 moles of the ethylene oxide or propylene oxide. Best results have been obtained when there are about 2 to 15 moles of the ethylene oxide or propylene oxide.

The ethoxylated quaternary ammonium compound or propoxylated quaternary ammonium compound may be used with the dibutylthiourea in varying proportions, the preferred range being 10–50% by weight of the dibutylthiourea to 90–50% by weight of the ethoxylated quaternary ammonium compound. Best results have been obtained where the dibutylthiourea is 25% and the ethoxylated ammonium compound is 75% by weight.

New results achieved by the new formulation or composition are that solubility is provided without the use for a solvent and the flash point of the composition or mixture is in excess of 340° F. Further, the formulation may contain a 100% active quaternary ammonium compound.

The composition consisting of the ethoxylated quaternary ammonium compound and the dibutylthiourea may be used without further additives. However, the composition may be usefully employed with a dispersant material, such as a cationic or non-ionic surface active agent, including a polyethoxylated fatty acid, polyethoxylated diamines, etc. Usually good results have been obtained by the use of polyethoxylated rosin-fatty acids.

As a specific example, the following may be set out:

	Percent
Ethoquad C/25 (ethoxylated quaternary ammonium compound of coco origin having 15 moles of ethylene oxide)	71.2
Dibutylthiourea	23.8
Ethofat 242/25 (polyethoxylated 70% rosin-fatty acids having 15 moles of ethylene oxide)	5.0

In the above formulation, Propoquad C/25 (quaternary ammonium compound from coco origin having 15 moles of propylene oxide) is substituted with equal results for Ethoquad C/25.

The compositions described may be employed with any of the pickling or cleaning acids, including sulfuric, phosphoric, sulfamic, citric, etc. acids.

In preparing the composition, I prefer to acidulate the ethoxylated or propoxylated quaternary ammonium compound with hydrochloric or sulfuric acid to a pH of about 4.5–5.5 before the dibutylthiourea is added. By this procedure, it is found that superior corrosion protection is obtained.

Specific examples illustrative of the processes and compositions may be set out as follows:

Example I

Mild steel coupons were exposed to an acid at a previously determined concentration and at a given temperature for 6 hours. At the end of the test period, the coupon was removed from the acid, cleaned, and reweighed. The corrosion rate is calculated on a weight loss basis and expressed in lb./ft.^{2}/day.

The mild steel coupons were wiped free of excess grease with a clean cloth, degreased in isooctane, and agitated in a ball mill in the presence of 150 mesh Alundum powder for 3 days. Just before using, the coupons were removed from the ball mill, washed in hot alcohol, and dried in hot acetone.

A number of compositions were prepared and tested in a 15% sulfuric acid solution; 0.25% inhibitor concentration (basis acid concentration), and at a temperature of 200° F., using the mild steel coupons described above. The compositions were as follows:

	Percent
(1) Ethoquad C/25	71.2
Dibutylthiourea	23.8
Ethofat 242/25	5.0

(2) The composition was as in (1) except that Ethoquad C/12 (ethoxylated quaternary ammonium compound of coco origin having 2 moles of ethylene oxide) was substituted for Ethoquad C/25.

(3) The composition was as in (1) except that Propoquad C/12 (propoxylated quaternary ammonium compound of coco origin having 2 moles of propylene oxide) was substituted for Ethoquad C/25.

(4) The composition was as in (1) except that for the Ethoquad C/25, Propoquad C/25 (propoxylated quaternary ammonium compound of coco origin having 15 moles of propylene oxide) was substituted.

(5) The composition was as in (1) except that for

the Ethoquad C/25, Propoquad HT/12 (propoxylated quaternary ammonium compound of hydrogenated tallow origin having 2 moles of propylene oxide) was substituted.

(6) The composition was as in (5) except that Propoquad HT/25 (propoxylated quaternary ammonium compound having 15 moles of propylene oxide) was used in place of Propoquad HT/12.

The results were as follows:

	Lb./ft.²/day
Control	2.52
Propoquad HT/12	.0272
Propoquad HT/25	.0462
Propoquad C/12	.0219
Propoquad C/25	.0242
Ethoquad C/12	.0196
Ethoquad C/25	.0114

Example II

Armohib 31 was made up of the following chemicals:

	Percent
Ethoquad C/25	71.2
Dibutylthiourea	23.8
Ethofat 242/25	5.0

In preparing the composition, the Ethoquad C/25 was acidulated to a pH of 4.5–5.5, as indicated by a pH meter, the acidulation being with concentrated sulfuric acid. The correct amounts of Ethofat 242/25 and dibutylthiourea were then added to the Ethoquad C/25 and the mixture heated to approximately 150° F. until the dibutylthiourea was melted. The mixture was stirred during the heating period. A test made after a 48-hour period showed that no unpleasant or offensive odor was developed.

In testing the above composition, 160 ml. of 15% sulfuric acid were placed in an 8 oz. French square bottle and a 0.06% concentration (on the basis of total solution) of Armohib 31 added. The test cell was placed in a constant temperature oil bath and heated to 200° F. When the test cell reached the desired temperature, a metal coupon which had previously been cleaned and weighed was placed in the acid mixture. At the end of a 6-hour test period, the coupon was removed, cleaned, and reweighed. The corrosion rate was calculated on a weight loss basis and expressed in lb./ft.²/day. In a series of tests, it was found that the corrosion rate was always less than .027.

The above composition (Armohib 31) was found to have the following physical properties.

Activity	100%.
Cloud point	28° F.
Pour point	24° F.
Flash point	Over 340° F.
Specific gravity @ 25° C.	1.042.
Solubility:	
Water	Dispersible to 1%.
Acid	Dispersible (soluble at use concentration).
Physical appearance	Viscous amber colored liquid.
Lb./gal.	8.72.

Example III

The test was carried on as described in Example II except that phosphoric acid at temperatures of 165° F. and 200° F. and at acid percents varying from 20–10% was employed, the results in terms of lb./ft.²/day being substantially less than .027.

Example IV

Tests were made as described in Example II with citric acid at temperatures of 165° F. and at 200° F., with the citric acid being used at 10–20%, and with the results

in the terms of lb./ft.²/day being again substantially less than .027.

Example V

A further test was made using a mixture of phosphoric acid and sulfuric acid at room temperatures and with results comparable to those described in Example II.

Example VI

Tests employing a composition consisting of 25% dibutylthiourea and 75% Ethoquad C/25 were carried out as described in Example II, no dispersant chemical being employed, and the corrosion rate was found to be substantially less than .027 lb./ft.²/day.

Example VII

Tests as described in Example VI, substituting Propoquad C/25 and C/12 and Propoquad HT/12 and HT/25, likewise give a corrosion rate of .0272 lb./ft.²/day.

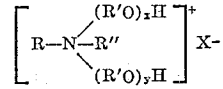
Example VIII

Tests made with varying amounts of dibutylthiourea in ranges between 10% and 50% by weight and of the Ethoquad and Propoquad compounds in ranges between 90% and 50% by weight demonstrated that the ranges were not critical in that improvement was obtained throughout these ranges, but the solubility was best, and best results were obtained in the proportions of about ¼ to ⅓ of the dibutylthiourea to about ¾ to ⅔ of the ethoxylated quaternary ammonium compound. As already stated, the best results were obtained when the proportions were 25% of the dibutylthiourea and 75% of the propoxylated quaternary ammonium compound.

While in the foregoing specification I have set forth composition ingredients and procedure in considerable detail for the purpose of illustrating embodiments of my invention, it will be understood that such details of composition and procedure may be varied widely by those skilled in the art without departing from the spirit of my invention.

I claim:

1. A composition for inhibiting corrosion of ferrous metals in contact with aqueous solutions of corroding acids, consisting essentially of dibutylthiourea and from about 50 to 90 weight percent, based upon total weight of the composition, of a compound having the structure:



wherein R is an aliphatic hydrocarbon radical having between 6 and 22 carbon atoms, R′ is an alkylene radical having between 2 and 3 carbon atoms, R″ is an alkyl radical having between 1 and 3 carbon atoms, X is a halogen, and x and y are integers having a sum total varying between 2 and 50.

2. A composition for inhibiting corrosion of ferrous metals in contact with aqueous solutions of corroding acids, consisting essentially of dibutylthiourea and an ethoxylated quaternary ammonium compound having an aliphatic hydrocarbon radical with between 6 and 22 carbon atoms in the ratio of 10–50% by weight of dibutylthiourea and 90–50% by weight of the ethoxylated quaternary ammonium compound.

3. The composition of claim **2** in which the proportion by weight of the dibutylthiourea is ¼ to ⅓ of the composition and the proportion by weight of the ethoxylated compound is about ¾ to ⅔ of the composition.

4. The composition of claim **2** in which the proportion by weight of the dibutylthiourea is about 25% and that of the ethoxylated quaternary ammonium compound is about 75% of the composition.

5. The composition of claim **2** in which the ethoxylated quaternary ammonium compound is an ethoxylated quaternary ammonium compound having 2 to 50 moles of ethylene oxide.

6. The composition of claim 5 in which the ethoxylated compound has 2 to 15 moles of ethylene oxide.

7. A composition for inhibiting corrosion of ferrous metals in contact with aqueous solutions of corroding acids, consisting essentially of dibutylthiourea and a propoxylated quaternary ammonium compound having an aliphatic hydrocarbon radical of from 6 to 22 carbon atoms in the ratio of 10–50% by weight of dibutylthiourea and 90–50% by weight of the propoxylated quaternary ammonium compound, said quaternary ammonium compound being propoxylated with from 2 to 50 moles of propylene oxide.

8. The composition of claim 7 in which the propoxylated quaternary ammonium compound has about 2 to 15 moles of propylene oxide.

9. In a process for inhibiting corrosion of ferrous metals in contact with aqueous solutions of corroding acids, the steps of adding to such solutions a corrosion inhibiting composition consisting essentially of dibutylthiourea and an ethoxylated quaternary ammonium compound having an aliphatic hydrocarbon radical with between 6 and 22 carbon atoms in the proportions of 10–50% by weight of dibutylthiourea and 90–50% of the ethoxylated quaternary ammonium compound.

10. The process of claim 9 in which the dibutylthiourea is added in the proportion of about 25% and the ethoxylated quaternary ammonium compound in the proportion of about 75%.

11. In the preparation of a corrosion inhibiting composition, the steps of acidulating an ethoxylated quaternary ammonium compound having an aliphatic hydrocarbon radical with between 6 and 22 carbon atoms to a pH of 4.5–5.5, and then mixing therewith dibutylthiourea in the proportions of about 10–50% of the dibutylthiourea to 90–50% by weight of the ethoxylated quaternary ammonium compound.

12. In a process for inhibiting corrosion of ferrous metals in contact with aqueous solutions of corroding acids, the steps of adding to such solutions a corrosion inhibiting composition consisting essentially of dibutylthiourea and a propoxylated quaternary ammonium compound having an aliphatic hydrocarbon radical with between 6 and 22 carbon atoms in the proportions of 10–50% by weight of dibutylthiourea and 50–90% of the propoxylated quaternary ammonium compound.

13. In the preparation of a corrosion inhibiting composition, the steps of acidulating a propoxylated quaternary ammonium compound having an aliphatic hydrocarbon radical with between 6 and 22 carbon atoms to a pH of 4.5–5.5, and then mixing therewith dibutylthiourea in the proportions of about 10–50% of the dibutylthiourea to 50–90% by weight of the propoxylated quaternary ammonium compound.

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