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(54) METHODS FOR INHIBITING INTERGRANULAR CORROSION OF METAL SURFACES

VERFAHREN ZUR INHIBIERUNG DER INTERKRISTALLINE KORROSION VON METALLOBERFLÄCHEN

PROCEDES D'INHIBITION DE LA CORROSION INTERGRANULAIRE DES SURFACES METALLIQUES

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Description

FIELD OF THE INVENTION

[0001] The present invention is directed to the use of the reaction product of alkynediols and polyalkylene polyamine compounds to inhibit intergranular corrosion of metal surfaces in industrial water and process systems, which surfaces are in contact with spray water or condensation.

BACKGROUND OF THE INVENTION

[0002] The microstructure of metals and alloys is made up of grains, separated by grain boundaries. Intergranular corrosion may be defined as localized attack along the grain boundaries, or immediately adjacent to grain boundaries. Such precipitation can produce zones of reduced corrosion resistance in the immediate vicinity.

[0003] An example of intergranular corrosion is the sensitization of stainless steels or weld decay. Chromium-rich grain boundary precipitates lead to a local depletion of Cr adjacent to these precipitates, leaving these areas vulnerable to corrosive attack.

[0004] Exfoliation corrosion is a particular form of intergranular corrosion. Exfoliation or delainination presents itself as a loss of metal in layers that appear to follow grain boundaries along the surface. The exfoliation in the casters, for instance, occurs on the non-wetted structures of the lower segments where direct spray water contact does not occur. The steel is exposed to a hot, humid environment in which the surfaces are wetted only by spray water mist or condensation. The corrosion propagates rapidly along the steel surfaces, resulting in the loss of structural integrity of the secondary supporting structure.

[0005] The mechanism for exfoliation corrosion is related to the presence of chlorides in the spray water. When used in the spray water system, the mist (steam) travels throughout the steam chamber and concentrates on steel surfaces. The heat and humidity evaporates the water from the steel surface, leaving behind a concentrated chloride ion. This process continues, concentrating more and more chloride ions to the point where exfoliation occurs.

[0006] Coupon analysis reveals that the corrosion mechanism occurs as follows: The chloride ion that is deposited on the metal surface migrates through the brittle layer of corrosion product/deposit that is generated. Under the deposit, a transient iron chloride salt is generated. The salt is hygroscopic (moisture absorbing) and undergoes hydrolysis, creating acid chloride conditions. Additional iron oxide corrosion products are left behind as the acidic corrosion front advances deeper into the metal surface.

[0007] In view of the forgoing, industry is looking for techniques and inhibitors to combat exfoliation corrosion present in industrial processing systems.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0008] The present invention is directed toward methods for inhibiting the intergranular corrosion of metal surfaces in industrial processing systems, e.g., steam and cooling water systems, which surfaces are in contact with spray water or condensation, which comprises adding to the spray water a sufficient corrosion inhibiting amount of the reaction product of an alkynediol and a polyalkylene polyamine.

[0009] The conditions under which the reaction product are formed are described in U.S. Patent No. 3,211,667, the contents of which are wholly incorporated herein.

[0010] The alkynediols and alkenediols taught to be effective in producing the reaction product are those containing four to twelve carbon atoms. Preferably, the alkynediols contain four carbon atoms. An exemplary alkynediol is butynediol.

[0011] The polyalkylene polyamine compounds taught to be effective in producing the reaction product are those containing two to ten amine groups, and preferably, three to seven amine groups. These amine groups may be substituted or unsubstituted, and each is separated by an alkylene group having from one to six carbon atoms, with two to four being preferred. Exemplary polyamines include ethylene diamine, diethylene triamine, pentaethylene hexamine, pentapropylene hexamine, triheptylene diamine, and the like.

[0012] The weight ratio of the reactants are such as to attain full reaction between the respective ingredients with weight ratios of amine to diol of 4:1 to 1:1, with 3:1 being preferred. An ionizable compound of copper, such as copper acetate, is employed in this reaction in catalytic amounts.

[0013] The reaction product of the present invention may be added to the spray water in an amount which is sufficient to inhibit corrosion of the metal surfaces. The reaction product may be added to a supply line in an amount ranging from 0.5 parts to about 500 parts per million parts of water present in the supply line. Preferably, about 1 to 100 parts per million parts water are added, with about 5 to 10 parts per million parts water particularly preferred.

[0014] The reaction product of the present invention is added to the supply line in either a solvent or in neat form. Preferably, the reaction product is added in an aqueous solvent, of which water is an example. The reaction product

can be added to the spray water along with other suitable ingredients, such as antifoams, corrosion inhibitors, and the like. The spray water is typically at a temperature of from about 43,3 - 82,2°C (110 - 180 °F) in the systems to be treated.

[0015] The data set forth below demonstrate the unexpected results occasioned by use of this invention. The following examples are included as being an illustration of the invention, and should not be construed as limiting the scope thereof.

Examples

[0016] In order to inhibit the corrosion mechanism from occurring on metal surfaces, the addition of a filming material to isolate the surfaces from water and chlorides was postulated. The addition of 2-butyne-1, 4-diol-polyethylenepolyamine (Product A) reduced corrosion rates of steel significantly (as shown in Tables 1 and 2). In all tests, coupon trees were constructed, in order to place a variety of corrosion coupons within a spray chamber. The solution was injected into the supply line to the caster sprays. This distributed the material throughout the spray chamber.

Table 1 (coupons submitted for SEM)

Strand #1 - Untreated Side	Strand #2 - Treated Side
151 mpy (*)	20.9 mpy
(*) 1 mpy (milli-inch per year) equals 25.4 micrometer per year	

[0017] The iron level was greatly reduced in the deposit.

Table 2 (coupons submitted for SEM)

Strand #1 - Untreated Side	Strand #2 - Treated Side
Fe - 88%	Ca - 52%
Cl - 5%	Fe - 23%
Ca - 1%	Na - 6%
Na - 1%	Cl - 6%
Mg - Trace (<1%)	Al - 2%
Al - Trace (<1%)	Si - 2%
Si - Trace (<1%)	S - 2%
S - Trace (<1%)	K - <1%

[0018] The results showed that while the chloride concentration was similar for both the untreated (5%) and treated side (6%), the other components were dramatically different. The iron level on the untreated side was 88%; the level of exfoliation was also significant. On the treated side, the iron level was only 23% and exfoliation was not present. The treated side had 52% calcium, indicating the presence of corrosion inhibition.

[0019] In additional tests, a corrosion coupon was dipped in Product A and placed next to an untreated coupon in both the treated and untreated strands. In the untreated strand, the dipped coupon showed very little corrosion, while the untreated coupon was exfoliated. In the treated strand there was a significant improvement in corrosion control versus the undipped coupon.

[0020] In other testing of the present invention, alternative coupon trees were constructed. Coupons tested included: mild steel, stainless steel, copper and coated mild steel.

[0021] A single set of mild steel coupons was removed after eight days as an initial inspection. Coupon results are shown in Table 3, below. Coupons from Strand #2 showed signs of exfoliation, while coupons from Strand #1 showed only a general corrosion mechanism.

Table 3 - Eight day Coupon Results (mpy)

	Strand #1	Strand #2
Mild Steel	**29.9**	**91.7**

[0022] As further shown in Table 4 below, there was a significant reduction in the rate of corrosion on the corrosion coupon tree in Strand #1, where Product A was injected. Product A was fed at 15 ppm through the system. Mild steel corrosion rates were reduced by approximately 50 to 80% on most of the locations. As above, coupons from Strand #2 showed signs of exfoliation, while coupons from Strand #1 showed only a general corrosion mechanism (exfoliation was not present).

Table 4 - Coupon Corrosion Results (mpy)

	Position	Days Exposed	Strand #1	Strand #2
Mild Steel	4	19	**20.6**	**107.5**
Mild Steel	7	28	**20.6**	**58.9**
Mild Steel	9	28	**29.1**	**34.4**
Copper	1	28	**1.6**	**6.3**

[0023] Note that all of the remaining coupons were either stainless steel or coated coupons; no significant corrosion was visible on any of these coupons. Additionally, the treatment of the present invention did not adversely impact nozzle performance in the spray water system.

[0024] While this invention has been described with respect to particular embodiments thereof, it is apparent that numerous other forms and modifications of this invention will be obvious to those skilled in the art. The appended claims and this invention generally should be construed to cover all such obvious forms and modifications which are within the true spirit and scope of the present invention.

Claims

1. A method for inhibiting the intergranular corrosion of metal surfaces in industrial processing systems, which surfaces are in contact with spray water, which comprises adding to the spray water a sufficient corrosion inhibiting amount of the reaction product of an alkynediol and a polyalkylene polyamine.

2. The method as recited in claim 1, wherein said intergranular corrosion is exfoliation corrosion.

3. The method as recited in claim 1, wherein said metal surfaces comprise continuous caster surfaces.

4. The method as recited in claim 2, wherein said exfoliation corrosion occurs on metal surfaces wetted by spray water mist or condensation.

5. The method as recited in claim 1, wherein said alkynediol contains an alkyne group having from about 4 to 12 carbon atoms.

6. The method as recited in claim 1, wherein said alkynediol is butynediol.

7. The method as recited in claim 1, wherein said polyalkylene polyamine contains from 2 to 10 amine groups, each separated from another by an alkylene group having from 1 to 6 carbon atoms.

8. The method as recited in claim 1, wherein said polyalkylene polyamine is pentaethylene hexamine.

9. The method as recited in claim 1, wherein said reaction product is added to said spray water in an amount ranging from 0.5 parts to about 500 parts per million parts water.

10. The method as recited in claim 1, wherein said spray water is at a temperature from about 43,3°C (110°F) to about 82,2°C (180°F).

11. The method as recited in claim 1, wherein said reaction product is added to said spray water in an aqueous solvent.

12. The method as recited in claim 1, wherein said metal surfaces are iron-containing metal surfaces.

13. The method as recited in claim 1, wherein said industrial processing systems comprise steam and cooling water systems.

Patentansprüche

1. Verfahren zur Inhibierung der Intergranularkorrosion von Metalloberflächen in industriellen Verarbeitungssystemen, wobei die Oberflächen in Kontakt mit Spritzwasser sind, welches Verfahren umfasst, dass man dem Spritzwasser eine zur Inhibierung der Korrosion ausreichende Menge des Umsetzungsproduktes eines Alkindiols und eines Polyalkylenpolyamins hinzufügt.

2. Verfahren nach Anspruch 1 , wobei die Intergranularkorrosion schichtförmige Korrosionen ist.

3. Verfahren nach Anspruch 1, wobei die Metalloberflächen kontinuierliche Gießflächen umfassen.

4. Verfahren nach Anspruch 2, wobei die schichtförmige Korrosion auf Metalloberflächen geschieht, die durch Spritzwassemebel oder Kondensation benetzt sind.

5. Verfahren nach Anspruch 1, wobei das Alkindiol eine Alkingrupppe enthält, die 4 bis 12 Kohlenstoffatome hat.

6. Verfahren nach Anspruch 1, wobei das Alkindiol Butindiol ist.

7. Verfahren nach Anspruch 1, wobei das Polyalkylenpolyamin 2 bis 10 Amingruppen enthält, die jeweils durch eine Alkylengruppe von einander getrennt sind, die 1-6 Kohlenstoffatome hat.

8. Verfahren nach Anspruch 1, wobei das Polyalkylenpolyamin Pentaethylenhexamin ist.

9. Verfahren nach Anspruch 1, wobei das Reaktionsprodukt dem Spritzwasser in einer Menge im Bereich von 0,5 Teilen bis etwa 500 Teilen pro Million Wasserteilen zugefügt wird.

10. Verfahren nach Anspruch 1, wobei das Spritzwasser eine Temperatur von etwa 43,3°C (110°F) bis etwa 82,2°C (180°F) hat.

11. Verfahren nach Anspruch 1, wobei das Reaktionsprodukt dem Spritzwasser in einem wässrigen Lösungsmittel zugefügt wird.

12. Verfahren nach Anspruch 1, wobei die Metalloberflächen Eisen enthaltende Metalloberflächen sind.

13. Verfahren nach Anspruch 1, wobei die industriellen Verarbeitungsverfahren Dampf- und Kühlwassersysteme umfassen.

Revendications

1. Procédé permettant d'empêcher la corrosion intergranulaire des surfaces métalliques dans des systèmes de traitement industriels, lesquelles surfaces sont en contact avec de l'eau pulvérisée, qui comprend l'addition à l'eau pulvérisée d'une quantité inhibitrice de la corrosion suffisante du produit réactionnel d'un alcynediol et polyalkylène polyamine.

2. Procédé selon la revendication 1, dans lequel ladite corrosion intergranulaire est la corrosion exfoliationte.

3. Procédé selon la revendication 1, dans lequel lesdites surfaces métalliques comprennent des surfaces de coulée continue.

4. Procédé selon la revendication 2, dans lequel ladite corrosion exfoliationte se produit sur des surfaces métalliques humidifiées par une brume d'eau pulvérisée ou par condensation.

5. Procédé selon la revendication 1, dans lequel ledit alcynediol contient un groupe alcyne ayant environ entre 4 et

12 atomes de carbone.

6. Procédé selon la revendication 1, dans lequel ledit alcynediol est du butynediol.

7. Procédé selon la revendication 1, dans lequel ladite polyalkylène polyamine contient de 2 à 10 groupes amine, chacun étant séparé de l'autre par un groupe alkylène ayant de 1 à 6 atomes de carbone.

8. Procédé selon la revendication 1, dans lequel ladite polyalkylène polyamine est de la pentaéthylène hexamine.

9. Procédé selon la revendication 1, dans lequel ledit produit réactionnel est ajouté à ladite eau pulvérisée en une quantité variant de 0,5 partie à environ 500 parties par million de parties d'eau.

10. Procédé selon la revendication 1, dans lequel ladite eau pulvérisée est à une température comprise entre environ 43,3 °C (110 °F) et environ 82,2 °C (180 °F).

11. Procédé selon la revendication 1, dans lequel ledit produit réactionnel est ajouté à ladite eau pulvérisée dans un solvant aqueux.

12. Procédé selon la revendication 1, dans lequel lesdites surfaces métalliques sont des surfaces métalliques contenant du fer.

13. Procédé selon la revendication 1, dans lequel lesdits systèmes de traitement industriels comprennent des systèmes à vapeur et eau de refroidissement.