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(54) **Cleaning and passivation treatment for metals**

Reinigungs- und Passivierungsbehandlung von Metallen

Traitement de nettoyage et de passivation de métaux

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Description

[0001] The present invention relates to cleaning and passivating treatments for metals. More particularly, the present invention relates to cleaning and passivating treatments for metals which are essentially free of amines, alkanolamines, and phosphates. The aqueous treatments of the present invention comprise amphoteric surfactants which were found to provide an excellent passivating film on ferrous surfaces. The amphoteric surfactants of the present invention are caprylic acid derivatives of imidazoline compounds or sodium salts thereof.

[0002] "In process" cleaners are employed in the metal treatment industry to clean and passivate a metal surface. These types of aqueous cleaners are typically based on organic rust-proofing or passivating agents such as combinations of alkanolamines and fatty acids, surfactants, antifoam agents and/or phosphonates and possibly biocides and builders.

[0003] In order to passivate a metal surface to prevent rusting during process breaks and storage, appropriate additives are used. Cleaning and passivating agents which inhibit the corrosion of ferrous metal surfaces contain for example alkali nitrites, alkanolamines, soaps and benzoates.

[0004] Clean and passivate treatments are typically employed in applications which require good cleaning and temporary metal passivation. Treated parts may need to remain rust-free, while exposed in the manufacturing plant for from several hours up to 30 days. In order to maintain their rust prevention ability, these cleaners are not rinsed. Current commercial cleaners typically employ alkanolamines such as monoethanolamine, diethanolamine or triethanolamine as a passivating agent for ferrous surfaces. The alkanolamine component inhibits flash rusting of ferrous iron parts during line stops or storage. Typical cleaners also will include surfactants such as glycol ether compounds and phosphonate compounds which aid in cleaning of the parts. For example, U.S. Patent No. 4,578,208 which issued to Geke et al. discloses a cleaning and/or passivating composition and process which employs a phosphoric acid ester, an alkanolamine and a surfactant and optionally builders, nonferrous metal inhibitors and biocides.

[0005] Currently, environmental objections are being raised concerning the use of alkanolamines, phosphates and glycol ethers as raw materials for industrial processes.

[0006] U.K. Patent Specification 1,133,385 discloses a method of storage of corrodible metals wherein a layer of an aqueous solution of corrosion inhibitor is maintained in a wet condition on the surfaces to be protected. The wet condition of the treated surfaces is maintained by capillary action between surfaces in face-to-face contact. Example 5 of this specification discloses a passivating solution which is free from amine, alkanolamine and phosphate, and which comprises sodium borate, sodium benzoate and polyoxyethylene-sorbitanmonooleate. The effective use of solutions containing a caprylic acid derivative of imidazoline is not disclosed.

[0007] The use of amphoteric surfactants in accordance with the present invention obviates the need for amines, alkanolamines, phosphates and other currently environmentally undesirable materials in clean and passivate formulations. The inventors found that compositions of a caprylic acid derivative of an imidazoline compound or a sodium salt thereof together with a borate ion and a molybdate ion as defined in claim 1 provide efficacious passivation of ferrous metal surfaces. The treatment solution of the present invention is substantially free of amines and alkanolamines, and phosphates. By substantially free, it is meant that these materials are not intentionally added as active components of the treatment solution. The preferred treatment solution includes sodium molybdate. These compounds were found to allow reductions in the concentration of the amphoteric surfactant component without adversely affecting efficacy. In addition, a defoamer such as a nonionic surfactant may be desirable in spray applications.

[0008] The molybdate ion is preferably added as sodium molybdate. Preferably the formulation also includes a nonionic surfactant defoamer. The inventors found that such aqueous solutions provide effective rust protection. The borate ion may be provided by a borate salt or by boric acid.

[0009] According to the present invention there is provided a cleaning and passivating treatment solution for ferrous metal surface comprising an aqueous solution of (a) from 0.05 to 5.0% by weight of a caprylic acid derivative of imidazoline amphoteric surfactant or sodium salt thereof, (b) a borate ion and (c) a molybdate ion wherein the weight ratio of caprylic acid derivative of imidazoline amphoteric surfactant or sodium salt thereof to borate ion (calculated as metaborate ion) is from 1:0.4 to 1:5 and the weight ratio of molybdate ion to caprylic acid derivative of imidazoline amphoteric surfactant or sodium salt thereof plus metaborate ion (BO_2) is more than 1:4, and said solution being essentially free of amine, alkanol amine and phosphate.

[0010] The formulation of the present invention includes amphoteric surfactants which are caprylic acid derivatives of an imidazoline compound or a sodium salt thereof. The surfactants are present in the treatment solution at concentrations of from about 0.05% up to about 5% by weight. Examples of commercially available amphoteric surfactants which are caprylic acid derivatives of an imidazoline (or sodium salts) include Monateric Cy-Na 50%, a sodium salt of 2-caprylic-1 (ethyl beta oxypropanoic acid) imidazoline; Monateric CYA-50, a capryl ampho-propionate; Monateric 1000, a capryl amphopropionate; and Miranol JAS concentrate which is a carboxylate derivative of capryl imidazoline. Miranol is a trademark of Rhone-Poulenc and Monateric is a trademark of Mona Industries. Amphopropionate is another name for imidazoline.

[0011] The preferred concentration of the surfactant is about 0.1 to 0.3% by weight. The preferred concentration of sodium molybdate is from about 0.1 to 0.5% by weight. The preferred concentration of sodium metaborate octahydrate is from about 0.1 to 0.5% by weight.

[0012] The clean and passivate formulation of the present invention is typically supplied in two concentrate packages which are diluted and mixed prior to application. The first comprises the caprylic acid derivative of imidazoline compound or sodium salt thereof: sodium molybdate and sodium metaborate octahydrate in deionized water. The second package comprises a nonionic surfactant defoaming agent.

[0013] Efficacy of the treatment solution of the present invention was evaluated in a chip test evaluation. The test involved placing 4 g of cast iron chips on a filter paper in a plastic weighing dish, adding 50 ml of the test solution, allowing the solution to stand for 24 hours. The filter paper is rinsed with tap water and examined for rust spots. Refer to ASTM D4627-92.

[0014] The effectiveness of the composition and method of the present invention is demonstrated by the following examples which are provided as illustrative and are not intended to limit the scope of the invention as set forth in the claims.

Example 1

[0015] The above described chip test was employed to evaluate various treatment concentrations of the surfactant, the borate, and the molybdate. Table I summarizes the results.

TABLE I

Clean/Passivate Bath Composition (weight %)				Chip Evaluation
Monateric CY Na-50	NaBO ₂ .8H ₂ O	Sodium Molybdate	Water	
1	—	—	99.0	2 rust spots *
1	0.2	—	98.8	3 rust spots *
0.5	0.5	—	99.0	8 rust spots *
0.3	0.5	—	99.2	18 rust spots *
0.3	0.5	0.1	99.1	no rust spots
0.3	0.5	0.2	99.0	no rust spots
0.3	—	0.2	99.5	20 ⁺ rust spots *
0.2	0.5	0.1	99.2	no rust spots
0.1	0.5	0.1	99.3	no rust spots
0.1	0.4	0.1	99.4	no rust spots
0.1	0.3	0.1	99.5	no rust spots
—	0.5	0.1	99.4	6 rust spots *
—	0.5	—	99.5	20 ⁺ rust spots *
—	—	0.1	99.9	20 ⁺ rust spots *

* comparative examples

[0016] The data in Table I shows that efficacious results are obtained at a relatively low treatment concentration with the combination of the present invention.

[0017] For economies of shipping and handling, the treatment solution of the present invention is preferably supplied as a concentrate which is diluted with deionized water to form a working bath.

Claims

1. A cleaning and passivating treatment solution for ferrous metal surface comprising an aqueous solution of (a) from 0.05 to 5.0% by weight of a caprylic acid derivative of imidazoline amphoteric surfactant or a sodium salt thereof, (b) a borate ion and (c) a molybdate ion wherein the weight ratio of caprylic acid derivative of imidazoline amphoteric surfactant or sodium salt thereof to borate ion (calculated as metaborate ion) is from 1:0.4 to 1:5 and the weight ratio of molybdate ion to caprylic acid derivative of imidazoline amphoteric surfactant or sodium salt thereof plus metaborate ion (BO₂) is more than 1:4, and said solution being essentially free of amine, alkanol amine and phosphate.

2. A treatment solution as claimed in claim 1, wherein said borate ion is provided by sodium metaborate octahydrate.
3. A treatment solution as claimed in claim 1 or 2, wherein said molybdate ion is provided by sodium molybdate.
- 5 4. A treatment solution as claimed in any one of the preceding claims, wherein said treatment solution further includes a nonionic surfactant defoaming agent.
5. A method of cleaning and passivating a ferrous metal surface comprising contacting the ferrous metal surface with an aqueous treatment solution as claimed in any one of the preceding claims.

Patentansprüche

- 15 1. Behandlungslösung zur Reinigung und Passivierung für Eisenmetalloberflächen, die eine wässrige Lösung umfasst aus: (a) von 0,05 bis 5,0 Gew.-% eines Caprylsäurederivats von einem amphoteren Imidazolin-Tensid oder eines Natriumsalzes davon, (b) einem Boration und (c) einem Molybdat, worin das Gewichtsverhältnis von Caprylsäurederivat von einem amphoteren Imidazolin-Tensid oder einem Natriumsalz davon zu Boration (berechnet als Metaboration) von 1:0,4 bis 1:5 beträgt und das Gewichtsverhältnis von Molybdat zu Caprylsäurederivat von einem amphoteren Imidazolin-Tensid oder einem Natriumsalz davon plus Metaboration (BO_2) mehr als 1:4 beträgt und wobei genannte Lösung im wesentlichen frei von Amin, Alkanolamin und Phosphat ist.
- 20 2. Behandlungslösung nach Anspruch 1, worin genanntes Boration durch Natriummetaboratoctahydrat vorgesehen ist.
- 25 3. Behandlungslösung nach Anspruch 1 oder 2, worin genanntes Molybdat durch Natriummolybdat vorgesehen ist.
4. Behandlungslösung nach einem der vorangehenden Ansprüche, worin genannte Behandlungslösung überdies einen nichtionischen Tensidentschäumer einschließt.
- 30 5. Verfahren zur Reinigung und Passivierung einer Eisenmetalloberfläche, welches das Kontaktieren der Eisenmetalloberfläche mit einer wässrigen Behandlungslösung nach einem der vorangehenden Ansprüche umfasst.

Revendications

- 35 1. Solution de traitement de nettoyage et de passivation pour une surface de métal ferreux comprenant une solution aqueuse (a) de 0,05 à 5,0% en poids d'un dérivé acide caprylique d'imidazoline tensio-active amphotère ou d'un sel de sodium de celle-ci, (b) un ion de borate et (c) un ion de molybdate, dans laquelle le rapport de poids du dérivé acide caprylique d'imidazoline tensio-active amphotère ou de sel de sodium de celle-ci à ion de borate (calculé en tant qu'ion de metaborate) est de 1:0,4 à 1:5 et le rapport de poids d'ion de molybdate à dérivé acide caprylique d'imidazoline tensio-active amphotère ou sel de sodium de celle-ci plus ion de metaborate (BO_2) est de plus de 1:4, et ladite solution étant essentiellement sans amine, alcanolamine et phosphate.
- 40 2. Solution de traitement telle que revendiquée dans la revendication 1, dans laquelle ledit ion de borate est fourni par du sodium metaborate octahydrate.
3. Solution de traitement telle que revendiquée dans la revendication 1 ou 2, dans laquelle ledit ion de molybdate est fourni par du sodium molybdate.
- 50 4. Solution de traitement telle que revendiquée dans l'une quelconque des revendications précédentes, dans laquelle ladite solution de traitement comprend en outre un agent antimousse tensio-actif non ionique.
- 55 5. Procédé de nettoyage et de passivation d'une surface de métal ferreux comprenant l'action de mettre en contact la surface de métal ferreux avec une solution de traitement aqueuse telle que revendiquée dans l'une quelconque des revendications précédentes.