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

(57) There is disclosed a cleaning and passivating treatment solution for ferrous metal surface comprising an essentially amine ; alkanol amine and phosphate free aqueous solution of (a) from about 0.05 to 5.0% by weight of a caprylic acid derivative of imidazoline amphoteric surfactant, (b) a borate ion and (c) a molybdate ion wherein the ratio of imidazoline amphoteric surfactant to borate ion is from about 1 :0.4 to 1 :5 and the ratio of sodium molybdate to imidazoline amphoteric surfactant and borate ion is more than about 1 :4. There is also disclosed a method of cleaning and passivating a ferrous metal surface.

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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.

"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, anti-foam agents and/or phosphonates and possibly biocides and builders. 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.

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, non-ferrous metal inhibitors and biocides.

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

SUMMARY OF THE INVENTION

The present inventors discovered that a specific class of amphoteric surfactants provides excellent passivation of ferrous metals when substituted for alkanolamines. 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 caprylic acid derivatives of imidazoline compounds provide efficacious passivation of ferrous metal surfaces. The treatment solution of the present invention is substantially free of amines, 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 also includes small quantities of a borate ion and 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.

DESCRIPTION OF THE PREFERRED EMBODIMENT

The present inventors discovered a clean and passivate treatment formulation for use in treating ferrous metal surfaces which is substantially free of amines, alkanolamines, and phosphates. The clean and passivate formulation of the present invention is an aqueous solution of a caprylic acid derivative of an imidazoline. The formulation preferably also includes a borate ion, sodium molybdate and a nonionic surfactant defoamer. The inventors found that aqueous solutions of caprylic acid derivatives of an imidazoline provide effective rust protection. It was further discovered that when such amphoteric surfactants were used in combination with a borate ion and sodium molybdate significantly lower concentrations of the amphoteric surfactant could be employed with good rust inhibition results. The borate ion may be provided by a borate salt or by boric acid.

The formulation of the present invention includes amphoteric surfactants which are caprylic acid derivatives of an imidazoline compound. 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 include Monateric Cy-Na 50%, a sodium salt of 2-caprylic-1 (ethyl beta oxypropanoic acid) imidazoline; Monateric LF-100, a C_{5-9} methyl alkyl imidazoline; Monateric LF-Na 50, a sodium salt of LF-100 but 50% active; 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.

When a caprylic acid derivative of an imidazoline is used alone, the preferred treatment concentration is

about 5% by weight. When a caprylic acid derivative of an imidazoline is employed in the preferred combination which includes a borate ion (such as sodium metaborate octahydrate) and a molybdate ion (such as sodium molybdate), the concentration of the surfactant can be decreased to 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. The ratio of imidazoline to borate ion is from about 1:0.4 to 1.5 and the ratio of molybdate ion to imidazoline and borate ion is more than about 1:4

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 derivative of imidazoline compound; sodium molybdate and sodium metaborate octahydrate in deionized water. The second package comprises a nonionic surfactant defoaming agent.

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.

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

A variety of amphoteric surfactants which are imidazoline compounds were tested in the above manner. Table I summarizes the results.

TABLE I

Bath Composition	Chip Test
99% water 1% Monateric 1000	20+ rust spots
95% water 5% Monateric 1000	0 rust spots
99% water 1% Monateric CY Na-50	2 rust spots
95% water 5% Monateric CY NA-50	0 rust spots
99% water 1% Monateric LF Na-50	5 rust spots
95% water 5% Monateric LF Na-50	0 rust spots
95% water 5% Monateric CEM-38*	20+ rust spots

*Monateric CEM-38 is a sodium salt of a coconut fatty acid derivative of an imidazoline compound available from Mona Industries.

The data in Table I shows that amphoteric surfactants which are caprylic acid derivatives of an imidazoline

will provide chip protection while a C12-C14 fatty acid derivative of an imidazoline (Monateric CEM-38) does not provide such protection.

Example 2

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

TABLE II

Clean/Passivate Bath Composition (weight %)				Chip Evaluation
Monateric CY Na-50	$NaBO_2 \cdot 8H_2O$	Sodium Molybdate	Water	
1	----	----	99.0	2 rust spots
1	0.2	----	98.8	3 rust spots
1	0.4	----	98.6	no rust spots
0.8	0.5	----	98.7	no 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

TABLE II (cont'd)

Clean/Passivate Bath Composition (weight %)				Chip Evaluation
Monateric CY Na-50	$NaBO_2 \cdot 8H_2O$	Sodium Molybdate	Water	
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

The data in Table II shows that efficacious results are obtained at a relatively low treatment concentration with the preferred combination of the present invention.

Example 3

Monateric LF-Na 50 was tested in a treatment solution including sodium metaborate octahydrate, sodium molybdate and Macol LF 110 (a nonionic polyoxyalkylated aliphatic ether available from PPG Industries, Inc. which was added as a defoamer). The addition of the borate and molybdate was found to allow excellent passivation, i.e., no chip rusting, in the above described chip test with a relatively low concentration of amphoteric surfactant. The treatment solution tested is set out in Table III in weight percent.

TABLE III

Sodium meta borate octahydrate	0.5%
Sodium molybdate	0.1%
Monateric LF-Na-50	0.1% as 100% actives
Macol LF 110	0.04%

Example 4

The presence of Macol LF 110 in the composition of Example 3 is included to inhibit foaming tendencies of the imidazoline surfactant. The presence of the defoamer does not effect the passivating activity of the imidazoline surfactant. Table IV summarizes chip testing as described above of a treatment in accordance with the present invention with and without a nonionic polyoxyalkylated aliphatic ether defoamer (Macol LF 110 available from PPG Industries, Inc.).

TABLE IV

Composition (grams/100 grams)					Chip Test
Monateric LF Na-50	NaBO2.8H20	Sodium Molybdate	Water	Macol LF 110	
1. 0.075	0.37	0.075	99.48	-----	no rust spots
2. 0.075	0.37	0.075	99.44	0.04	no rust spots
3. 0.10	0.50	0.10	99.30	-----	no rust spots
4. 0.10	0.50	0.10	99.26	0.04	no rust spots

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. A preferred concentrate comprises 12.5% sodium metaborate octahydrate, 2.5% sodium molybdate, 5.0% Monateric LF-Na 50 and 80% deionized water. The Macol LF 110 defoamer is supplied separately. A 4% v/v dilution of the preferred concentrate with 0.04% v/v of Macol LF 110 results in the treatment solution described in Example 3. This preferred treatment solution has been found to be effective when diluted with DI, soft or hard water.

While the present 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 cleaning and passivating treatment solution for ferrous metal surface comprising an essentially amine; alkanol amine and phosphate free aqueous solution of (a) from about 0.05 to 5.0% by weight of a caprylic acid derivative of imidazoline amphoteric surfactant, (b) a borate ion and (c) a molybdate ion wherein the ratio of imidazoline amphoteric surfactant to borate ion is from about 1:0.4 to 1:5 and the ratio of sodium molybdate to imidazoline amphoteric surfactant and borate ion is more than about 1:4.

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.

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 comprising (a) from about 0.05 to 5.0% by weight of a caprylic acid derivative of imidazoline amphoteric surfactant, (b) a borate ion, and (c) a molybdate ion wherein the ratio of imidazoline amphoteric surfactant to borate ion is from about 1:0.4 to 1:5 and the ratio of sodium molybdate to imidazoline amphoteric surfactant and borate ion is more than about 1:4.

6. A method as claimed in claim 5, wherein said borate ion is provided by sodium metaborate octahydrate.

7. A method as claimed in claim 5 or 6, wherein said molybdate ion is provided by sodium molybdate.

8. A method as claimed in any of claims 5 to 7, wherein said treatment solution further includes a nonionic surfactant defoaming agent.

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EUROPEAN SEARCH REPORT

Application Number
EP 95 30 1519

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	US-A-4 450 088 (WILSON JOE C ET AL) 22 May 1984 * claims 1,3; example 1 *	1	C23F11/08 C23G1/24
A	EP-A-0 229 440 (TEXACO DEVELOPMENT CORP ;TEXACO PETROLEUM (BE)) 22 July 1987 * claims 1,5; example 19C *	1	
A	EP-A-0 328 872 (BURDA PAUL A) 23 August 1989 * claim 1 *	1	
A	GB-A-1 133 385 (FIJI IRON & STEEL) 13 November 1968 * example 5 *	5	
D,A	EP-A-0 124 851 (HENKEL KGAA) 14 November 1984 * claim 1 * & US-A-4 578 208	5	
A	EP-A-0 552 988 (BP CHEM INT LTD ;BP CHEMICALS SNC (FR)) 28 July 1993 * claims 1,8 *	1	

TECHNICAL FIELDS SEARCHED (Int.Cl.6)
C23F
C23G

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	23 August 1995	Torfs, F

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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