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PREVENTION OF CORROSION ON ALUMINUM METAL AND ITS ALLOYS

William A. Erby and Paul W. Thorsell, Downers Grove, and Perlita A. Hagan, Chicago, Ill., assignors to Daubert Chemical Company, Oak Brook, Ill.
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10 Claims

ABSTRACT OF THE DISCLOSURE

Compositions for, and a method of, preventing the oxidation and/or pitting of the surface of aluminum metal and aluminum metal alloys, the compositions comprising as their essential active ingredient a morpholine salt of a C₅-C₂₂ monocarboxylic or fatty acid exemplified by morpholine caprylate. The morpholine salt advantageously is utilized in conjunction with an aluminum metal lubricant such as a mineral oil, the concentration of the salt in the lubricant being about 0.1% to about 99%, by weight.

The present invention relates to compositions for, and a method of, preventing or inhibiting attack on the surfaces of aluminum metal and aluminum metal alloys, especially newly fabricated aluminum metal and aluminum metal alloys (hereinafter called "aluminum metal") by elements normally found in the atmosphere.

Newly rolled, cast, or milled aluminum metal has a tendency to condense moisture on the surface thereof which will eventually cause corrosion. Normally, the corrosion manifests itself as a white, powdery formation on the surface of the metal which, in turn, is accompanied by surface pitting. The powdery formation and the pitting detract from the appearance of the metal, and are a cause of considerable concern to manufacturers and fabricators of aluminum metal products. Apart from the unfavorable aesthetic aspects of the surface corrosion of aluminum metal, such corrosion can impair the function of aluminum metal products in certain environments. Thus, for example in the case of heat exchangers fabricated of aluminum, the formation of corrosion on the surface of the heat exchangers can adversely affect the heat transfer properties of the exchangers and can shorten their useful life.

In accordance with the present invention, compositions have been evolved which effectively prevent the corrosion of aluminum metal surfaces caused by moisture or exposure to the atmosphere. The compositions, in liquid form, can be applied in any manner known in the art to the surface of the aluminum metal during the fabrication thereof, or, in the case of heat exchangers formed of aluminum metal, can be incorporated into the fluid acted upon by the exchangers. In either case, only small quantities of the compositions are required to achieve the desired results. The compositions, also, can be used in the form of coolants, lubricating and cutting oils, and as metal working compositions.

The compositions of this invention contain as an essential active ingredient a morpholine salt of a C₅ to C₂₂, especially desirably a C₆ to C₁₃, straight or branched carbon chain, monocarboxylic acid. Exemplary of such acids are caproic acid, enanthic acid, caprylic acid, pelargonic acid, capric acid, undecylic acid, lauric acid, tridecoic acid, myristic acid, pentadecanoic acid, palmitic acid, margaric acid, stearic acid, nondecylic acid, arachidic acid and behenic acid. Of this group morpholine salts of caprylic acid, i.e., morpholine caprylate, pelargonic acid, i.e., morpholine pelargonate, and capric acid, i.e., morpholine caprate, or a mixture thereof, are preferred.

The morpholine salts can be incorporated directly into

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the surface lubricants utilized in the fabrication of aluminum metal, or, as indicated, into the fluid acted upon by heat exchangers formed of the metal. In accordance with a preferred practice of the invention, the morpholine salts are employed in conjunction with an inert liquid carrier which is a solvent for the salt, or mixture of salts, used. Among the various liquid carriers which can be utilized in this connection are water; hydrocarbons exemplified by paraffinic and aromatic hydrocarbons such as mineral oil, lubricating oil, benzene, toluene, xylenes, hexane, heptane, mineral spirits, and the like; C₃ to C₁₈ straight and branched carbon chain alcohols specific examples of which are isopropyl alcohol, isobutyl alcohol, amyl alcohol, isoamyl alcohol, octyl alcohol, decyl alcohol, dodecyl alcohol, cetyl alcohol, octadecyl alcohol, 2-ethylhexyl alcohol, ethylene glycol, propylene glycol, glycerol, diglycerol, hexitols, and the like; esters of monohydric and polyhydric alcohols with C₄ to C₂₂ carboxylic acids, such as isopropyl laurate, butyl stearate, isobutyl stearate, di-n-octyl sebacate, diglycol stearate, glyceryl monostearate, and the like; esters of polymerized polyhydric alcohols with C₄-C₂₂ carboxylic acids exemplified by polyethylene glycol monostearate, polypropylene glycol monolaurate, polyisobutylene glycol stearate, and the like; Cellosolves such as ethyl Cellosolve, propyl Cellosolve and butyl Cellosolve; and compatible mixtures of the foregoing.

The following examples are illustrative of the compositions of the present invention. It will be understood that various changes may be made therein in relation to proportions of ingredients and numerous other compositions can readily be evolved in the light of the teachings disclosed herein. All parts given are by weight.

EXAMPLE 1

Morpholine caprylate	0.1
Di-n-octyl sebacate	99.9

EXAMPLE 2

Morpholine caprate	0.2
Isopropyl alcohol	99.8

EXAMPLE 3

Morpholine caprate	5
Polyethylene glycol monostearate	95

EXAMPLE 4

Morpholine caprylate	5
Mineral oil	95

EXAMPLE 5

Morpholine caprylate	5
Water	95

EXAMPLE 6

Morpholine caprate	1
Decyl alcohol	99

EXAMPLE 7

Morpholine caprylate	20
Mineral oil	80

EXAMPLE 8

Morpholine caprylate	50
Water	50

EXAMPLE 9

Morpholine caprate	10
Isobutyl stearate	90

EXAMPLE 10

Morpholine laurate	15
MacMillan 200 oil	85

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EXAMPLE 11

Morpholine myristate -----	10
Mineral oil -----	90

EXAMPLE 12

Morpholine caprylate -----	4
MacMillan 200 oil -----	96

EXAMPLE 13

Morpholine stearate -----	25
Glycerol -----	75

EXAMPLE 14

Morpholine palmitate -----	40
Butyl Cellosolve -----	60

EXAMPLE 15

Morpholine pelargonate -----	7
Ethylene glycol -----	93

The proportion of morpholine salt, or mixture of salts, used in the compositions of this invention are variable. Generally speaking, the compositions comprise from about 0.1% to about 99%, by weight, of the salt, or mixture thereof. Compositions containing higher proportions of the salt, or mixture thereof, can be diluted to achieve the objectives of this invention.

The quantity of morpholine salt deposited, or retained, on the surface of aluminum metal treated with the compositions of this invention will depend, among other things, upon the proportion of the salt or salts in the composition, the nature of the inert carrier and the method employed in applying the composition on the surface of the metal. Thus, by way of illustration, a water solution, containing 4%, by weight, of morpholine caprylate, when applied to aluminum metal, as by dipping, will provide a concentration of the salt of about 6 milligrams per square foot of surface area of the metal. The same weight percent of morpholine caprylate in MacMillan 200 SUS at 100° F. oil, when applied to aluminum metal in the same manner, will provide a concentration of the salt of about 26.8 milligrams per square foot of surface area of the metal.

While concentrations of the order of about 6 milligrams per square foot of surface area will provide substantially complete protection for the metal against corrosion, i.e., formation of so called "white rust" and water spotting, substantially complete protection against water spotting, alone, for example, can be obtained at concentrations of the order of between about 0.4 to about 0.5 milligram per square foot of surface area.

As indicated hereinabove, the compositions of this invention may be applied to the surface of the aluminum metal in a manner known in the art including dipping, brushing, spraying, wiping, roller coating, curtain coating, or the like. In those instances where the compositions comprise a paraffinic hydrocarbon oil such as "MacMillan 200 Oil," an antioxidant advantageously is employed. Any of a number of such agents may be used. The compound 2,6 - di-tert-butyl-p-cresol, sold under the trademark "Parabar-441" (En-Jay Company), is exemplary of an antioxidant having excellent utility in this connection. In addition, surface active agents of the anionic or nonionic type, for example, may be incorporated into the compositions to enhance, among other things, the distribution of the compositions on the surface of the treated aluminum metal. Specific examples of surface active agents having utility for the purposes of this invention are the alkylaryl-polyethers sold under the trademark "Immersol" (Nyanza Inc.), the nonyl phenyl polyethylene glycol ethers sold under the trademark "Tergitol" (Union Carbide), and the like. The proportion of antioxidant and/or surface active agent incorporated in the compositions is small, and, generally speaking, will comprise from about 0.5% to about 5%, by weight, of the compositions.

In order to determine the corrosion preventive prop-

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erties of the compositions of this invention on aluminum metal, the following tests were carried out. One test was directed to the prevention of "white rust" on the metal. The second test was directed specifically to the prevention of water spotting on the metal. The third test was directed to the prevention of corrosion of aluminum metal in a cooling system.

Test I.—Prevention of "White Rust"

Ten aluminum metal test panels were cleaned, dipped in test solution, dried, spotted with water, stacked and stored for two weeks.

The test panels used measured $\frac{3}{4}$ " x 1" x 3". The panels were cleaned by wiping each with a clean, lint-free tissue wet with acetone. They were then polished with a coarse ink eraser until a smooth finish was obtained. The panels were then cleaned thoroughly with acetone using a lint-free tissue to remove debris left by the polishing operation.

The panels were then dipped in the test solution and allowed to dry for 24 hours in a dust free atmosphere at room temperature. The solutions tested were blends of morpholine caprylate in distilled water and in MacMillan 200 SUS at 100° F. pale oil. The concentrations of salt used in this testing sequence were 0, 1, 2, 3 and 4 percent by weight.

After drying, the panels were sprinkled with ten drops of distilled water and stacked. The stacked panels were placed in a desiccator with a ten pound weight on top. The desiccator was stored at 90° F. with enough distilled water to insure an atmosphere of 100% relative humidity. The test duration was two weeks.

The panels were then separated, dried, and an estimation of percentage of the panel surfaces covered with corrosion was made.

The following table contains a summary of the data obtained.

	Water				MacMillan 200 oil					
	0	1	2	3	4	0	1	2	3	4
Morpholine caprylate, wt. percent....	0	1	2	3	4	0	1	2	3	4
White rust after 14 days, percent surface corroded	75	20	15	6	0	90	5	3	1	0

While not indicated in the table, the concentration of the salt per unit area of the test panels was more than sufficient to provide complete protection against water spotting.

Test II.—Prevention of water spotting

A mixture consisting of 24 weight percent di-n-octyl sebacate (DOS) and 76 weight percent hexane was wiped on an aluminum panel with a tissue moistened with the solution, then immediately wiped off with a clean, dry tissue. This method was found to give an average deposit of 0.86 mg./sq. ft.

Solutions of 50, 55, 60, 65, 70 and 75 percent by weight of morpholine caprylate in DOS were also diluted with 76 wt. percent hexane and applied to cleaned aluminum panels by the above-mentioned method. Drops of tap water were put on the panels and allowed to stand for 72 hours. The spots were wiped with a clean, dry tissue. The test was considered a failure if any of the white stain caused by the water droplet remains after the wiping procedure.

The following table contains the data obtained by this test method:

Salt, wt. percent in DOS...	0	50	55	60	65	70	75
Salt, mg./sq. ft.	0	0.43	0.47	0.52	0.56	0.60	0.65
Water spots.....	Yes	Trace	No	No	No	No	No

Test III.—Prevention of corrosion in cooling system

Solutions of morpholine caprylate were tested for their protection against corrosion of aluminum in the ASTM: D-1384 test. In this test specimens of metal typical of those found in automotive cooling systems are totally immersed in the test solution for 336 hours at 190° F.

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with aeration. The corrosion inhibitive properties of the test solution are evaluated on the basis of the weight losses incurred by the specimens. Each test was run in triplicate, and the average weight loss was determined for each metal.

Test results:	Weight loss of aluminum metal specimen, mg.
Morpholine caprylate, 3% in water -----	1.5
Typical antifreeze and coolant -----	203.0

What is claimed is:

1. A method of preventing the formation of "white rust" and/or water spotting on the surface of aluminum metal and its alloys comprising applying to the surface of the metal, before it has become oxidized and/or wetted by exposure to an oxidizing or wetting atmosphere, a composition consisting essentially of a morpholine salt of a C₅-C₂₂ monocarboxylic acid and an inert liquid carrier, the salt comprising about 0.1% to about 99%, by weight, of the composition, the composition being applied to the surface of the metal in an amount sufficient to provide thereon a concentration of the morpholine salt of at least 0.4 milligram per square foot of surface area of the metal.

2. A method according to claim 1 wherein the morpholine salt is morpholine caprylate, morpholine pelargonate, or morpholine caprate, or a mixture thereof.

3. A method according to claim 1 wherein the inert carrier is selected from the group consisting of water, paraffinic and aromatic hydrocarbons, C₃ to C₁₈ alcohols, esters of monohydric and polyhydric alcohols with C₄ to C₂₂ carboxylic acids, partial esters of polymerized polyhydric alcohols with C₈ to C₂₂ carboxylic acids, and Cello-solves.

4. An aluminum metal or aluminum metal alloy body having a substantially unoxidized surface which is provided with a coating consisting essentially of morpholine salt of a C₅-C₂₂ monocarboxylic acid, the concentration of the morpholine salt being at least about 0.4 milligram per square foot of the said surface of the aluminum metal body.

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5. An aluminum metal body according to claim 4 wherein the morpholine salt is morpholine caprylate, morpholine pelargonate, or morpholine caprate, or a mixture thereof.

6. A composition for preventing the formation of "white rust" and/or water spotting on the surfaces of newly rolled, cast or milled aluminum metal and its alloys comprising a morpholine salt and an inert liquid carrier, the proportion of the salt in the composition being from about 0.1% to about 99%, by weight.

7. A composition as claimed in claim 6 wherein the salt is morpholine caprylate, morpholine pelargonate, or morpholine caprate.

8. A composition as claimed in claim 6 wherein the inert liquid carrier is a mineral oil or di-n-octyl sebacate.

9. A composition as claimed in claim 8 wherein the salt comprises about 4%, by weight, of the inert liquid carrier.

10. A composition as claimed in claim 8 wherein the inert liquid carrier is a metal coolant, metal lubricating, metal cutting or other metal working fluid.

References Cited

UNITED STATES PATENTS

25	2,993,007	7/1961	Andersen -----	252—392
	3,156,687	11/1964	Andersen -----	252—180 X
	2,186,628	1/1940	Dickey -----	260—247.2 X
	3,019,196	1/1962	Andersen -----	252—180 X
30	3,345,299	10/1967	Davidowich -----	252—392 X
	3,469,955	9/1969	Grosse-Oetringhaus	252—392 X
	3,556,718	1/1971	Bachmann -----	252—394 X

ROBERT F. BURNETT, Primary Examiner

35 M. E. MCCAMISH, Assistant Examiner

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