United States Patent

Borchert et al.

[54] ANTI-TARNISH COMPOSITION FOR METAL SURFACES AND PROCESS FOR ITS USE

- [72] Inventors: Peter Jochen Borchert, Elkhart, Ind.; James Edward Slager, Edwardsburg, Mich.; Ronald George Sommer, Mishawaka; Mitchell Frank Zienty, Elkhart, both of Ind.
- [73] Assignee: Miles Laboratories, Inc., Elkhart, Ind.
- [22] Filed: Dec. 30, 1970
- [21] Appl. No.: 102,988
- [52] U.S. Cl......106/3, 106/14, 117/127,
- 252/390, 252/394
- [51]
 Int. Cl.
 C09g 1/14

 [58]
 Field of Search
 106/3, 14; 252/390, 387, 394, 252/33.6, 80, 82, 84, 85, 87, 175, 178; 117/127

[56] References Cited

UNITED STATES PATENTS

3,265,620 8/1966 Heiman252/33.6

Primary Examiner—Donald J. Arnold

Assistant Examiner-David A. Jackson

Attorney—Joseph C. Schwalbach, Louis E. Davidson, Harry T. Stephenson and George R. Caruso

[57] ABSTRACT

The clean surface of metals, such as copper and copper-containing alloys, can be protected from tarnishing by a composition containing a mixture of a surfactant, benzotriazole, sodium bisulfite and ethylenediaminetetraacetic acid. This composition is generally mixed with water and the clean metal surface is dipped in or otherwise contacted with the aqueous solution.

6 Claims, No Drawings

[15] 3,653,931
[45] Apr. 4, 1972

5

ANTI-TARNISH COMPOSITION FOR METAL SURFACES AND PROCESS FOR ITS USE

BACKGROUND AND PRIOR ART

Metal objects, such as fittings, tubing and the like formed from copper and copper-containing alloys, often are severely tarnished in their finished form, and it is commercially desirable to remove such tarnish before they are supplied to the ultimate users of such items. The prior art cleansing techniques for removing tarnish generally consisted of first treating the tarnished article with a detergent cleaning bath to remove greases, oils, soap, borax and waxes which resulted from the operations employed to form the article. The "cleaned" item was then exposed to a descaling bath, which in the case of 15 copper articles generally contained sodium cyanide. Sulfuric acid had also been used in prior art descaling baths. After passing through the descaling bath, the item was treated with a bright dip bath, which, in the case of copper articles, generally contained nitric acid or a mixture of chromic acid and sodium 20 bisulfate. The finished item had a clean bright surface.

When the bright dip bath contains chromic acid, the resulting bright copper surface, for example, is "passivated" and will not readily tarnish through subsequent handling or atmospheric reaction. However, if nitric acid is used in the 25 bright dip bath, the resulting bright copper surface, for example, is "activated" and will readily tarnish through subsequent handling or atmospheric reaction. A similar situation exists when the prior art descaling and bright dip baths are replaced by a single cleaning composition containing citric acid, a 30 metal chloride, a ferric salt and a nonionic surfactant. This latter composition produces a clean bright metal surface which is somewhat activated.

The prior art has suggested the use of benzotriazole to treat such activated metal surfaces, such as copper surfaces, in 35 order to prevent tarnishing, but this treatment has not been entirely satisfactory since it is difficult to get uniform protection with this material. Even with a reasonably good coating, the article can still tarnish in an undesirably short time.

SUMMARY OF THE INVENTION

In accordance with the present invention an anti-tarnish composition for metal surfaces is provided which consists essentially of a mixture of nonionic or anionic surfactant, 45 bisulfite and benzotriazole. sodium ethylenediaminetetraacetic acid. A metal surface is protected from tarnishing by contacting such surface with the above composition to form a protective coating thereon.

DESCRIPTION OF THE INVENTION

The anti-tarnish composition of the present invention is a mixture consisting essentially of components having the proportion of 0.05 to 1 weight parts nonionic or anionic surfactant, 0.5 to 2 weight parts benzotriazole, 0.1 to 1 weight parts 55 parts sodium bisulfite and 0.1 to 1 weight ethylenediaminetetraacetic acid. This composition can be dissolved in water to form an aqueous solution containing 0.005 to 0.1 weight percent surfactant, 0.05 to 0.2 weight percent benzotriazole, 0.01 to 0.1 weight percent sodium bisulfite and 60 0.01 to 0.1 weight percent ethylenediaminetetraacetic acid. The above aqueous solution should have an initial pH from about 3.5 to about 8.0. Preferably the initial pH should be from about 4.5 to about 6.0. If necessary, appropriate acidic the above values.

The nonionic or anionic surfactants useful in the present composition are well known materials. Typical nonionic surfactants are N-(beta-hydroxyethyl)laurylamide, nonylphenylpolyethylene glycol ether, octylphenylpolyethylene glycol 70 ether, sorbitan monooleate, polyoxyethylene sorbitan tristearate, ethoxylated isomeric linear alcohols and the like. The preferred nonionic surfactant is an octylphenylpolyethylene glycol ether having the formula:

(C₈H₁₇) (C₆H₄) O [CH₂CH₂O]₄₀ CH₂CH₂OH

2

This material is commercially available under the trade name Triton X-705 from the Rohm and Haas Co.

Typical anionic surfactants useful in the present composition are C8--C24 straight-chain saturated carboxylic acids, alkali metal salts of C8-C24 straight-chain saturated carboxylic acids, such as sodium stearate, dodecylbenzene sulfonic acid, sodium lauryl sulfoacetate, monoethanolamine lauryl ether sulfate and the like.

The benzotriazole, sodium bisulfite and 10 ethylenediaminetetraacetic acid are well known materials and are readily available.

Another aspect of the present invention is the process for using the above-described composition to form an anti-tarnish coating on a treated article. The anti-tarnish compositions of the present invention can be used at temperatures from about 25° to about 95° C., preferably at a temperature of about 85° to 95° C. The article to be treated is contacted with a solution of the composition, for example, for from 30 seconds to about 3 minutes, preferably from about 1.5 to about 3 minutes, and then air dried, oven dried at 60° C. or dried in a stream of hot or warm air. This contact can take place by immersing the article in the solution, or the solution can be sprayed, for example, onto the metal surface. The metal surface can also be contacted with a viscous gel or paste containing the anti-tarnish composition.

The invention is described in further detail in the following example.

EXAMPLE

A mixture of Triton X-705 nonionic surfactant, benzotriazole. sodium bisulfite and ethylenediaminetetraacetic acid was blended and mixed with sufficient water to form an aqueous solution containing 0.03 weight percent surfactant, 0.1 weight percent benzotriazole, 0.06 weight percent sodium bisulfite and 0.06 weight percent ethylenediaminetetraacetic acid.

Tarnished copper articles were degreased and then cleaned with a mixture of citric acid, sodium chloride, ferric sulfate 40 and nonionic surfactant until the surface was bright. These cleaned bright articles were then immersed with agitation in the above anti-tarnish solution at 85°-95° C. for 1.5 minutes. The articles were then removed from the solution, drained and air dried. The resulting treated articles had a uniform pinkishcopper color without water marks and were satisfactorily stable against tarnishing by atmospheric moisture, carbon dioxide, casual amounts of atmospheric contaminants and intermittent handling with bare hands. Parts stored up to 1 year without any special precautions still show resistance to 50 tarnishing and possess an acceptable level of brightness. The anti-tarnish coating also did not interfere with any soldering or brazing procedures employing the treated articles.

While the above disclosure is directed principally at antitarnish treatment of copper and copper-containing alloys, such as brass and bronze, it should be understood that the anti-tarnish composition and process of the present invention is useful for protection of any metal surface subject to tarnishing.

What is claimed is:

1. An anti-tarnish composition for metal surfaces consisting essentially of a mixture of components having the proportion of 0.05 to 1 weight part of a surfactant selected from the group consisting of N-(beta-hydroxy ethyl) laurylamide, nonylphenor alkaline materials can be added to adjust the pH to within 65 yl poly-ethylene glycol ether, octylphenyl-polyethylene glycol ether, sorbitan monooleate, polyoxyethylene sorbitan tristearate, ethoxylated isomeric linear alcohols, $C_8 - C_{24}$ straight-chain saturated carboxylic acids, the alkali metal salts of C8-C24 straight-chain saturated carboxylic acids, dodecylbenzene sulfonic acid, sodium lauryl sulfoacetate, and monoethanolamine lauryl ether sulfate 0.5 to 2 weight parts, benzotriazole, 0.1 to 1 weight parts sodium bisulfite and 0.1 to weight parts ethylenediaminetetraacetic acid.

> 2. A composition according to claim 1 wherein the surfac-75 tant is a nonionic octylphenylpolyethylene glycol ether.

3

3. A composition according to claim 2 wherein the surfactant has the formula:

 $(C_8H_{17}) (C_6H_4) O [CH_2CH_2O]_{40} CH_2CH_2OH$

4. An anti-tarnish liquid comprising an aqueous solution of the composition of claim 1, the components of said composition being present in said solution in the concentrations of 0.005 to 0.1 weight percent surfactant, 0.05 to 0.2 weight percent benzotriazole, 0.01 to 0.1 weight percent sodium bisulfite

and 0.01 to 0.1 weight percent ethylenediaminetetraacetic acid.

5. An anti-tarnish liquid according to claim 4 having a pH from about 3.5 to about 8.0.

6. An anti-tarnish liquid according to claim 4 having a pH from about 4.5 to about 6.0.

*

20

25

30

35

40

45

50

55

60

65

70

75

101030

^***

15

10