Title: IMPROVEMENTS IN OR RELATING TO THE PROCESS FOR THE PREPARATION OF ANTI-TARNISHING LACQUER FOR COPPER AND ITS ALLOYS.

Applicant: COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, Safi Marg, New Delhi-110001, India an Indian registered body incorporated under the Registration of Societies Act (Act XXI of 1860).

Inventors: SUBBIAH GURUVIAH, MEYYAPPA SUNDARAM & VYDIANATHA GANESA SARMA.

The following specification describes the nature of this invention.

PRICE: TWO RUPEES
This invention by Subbaiah Surwitti, Meyyappa Sundarar and Mysranat Srinivasa Sarma, both from the Central Electro-Chemical Research Institute, Karikal, Pondicherry, India, is titled "The Use of Lacquers Prepared by Dissolving Film Forming Material in Volatile Solvents and Some of Them Are Imported. This Has a Drawback That Copper and Brass Materials Coated with This Lacquer and Exposed to Atmosphere Containing Sulphur and Other Acidic Substances Undergo Tarnishing and Staining."

The object of this invention is to obviate these disadvantages and to provide a process in which lacquers are formulated with incorporation of suitable additives.

With the above object in view of the present invention broadly consists in preparing lacquers containing 40-50% film forming materials such as rosin modified phenolics (melting point 118-130°C, acid value 15-20, iodine value 20-25) epoxies (Mol. weight 900-1000) & nitro cellulose in solvents such as xylene, benzene, white spirit, methyl isobutyl ketone. 0.20 to 0.25% of benzotriazole or monoethanol amine is added to the lacquer and thoroughly mixed to dissolve the additives and form a homogeneous mixture.

The following typical examples are given to illustrate the invention.
Example -I

50 gm. of resin modified phenolic resin is dissolved in 50 gm. white spirit and mixed thoroughly. To this 0.25 gm of monoethanol amine/benzotriazole is added. The product thus obtained was applied on to the polished and degreased copper or brass panels by brush. The thickness of the film is of the order of 7 - 10 μ.

Example -II

50 gm of epoxy resin (70% epoxy resin and 30% polyamide) is dissolved in 50 gm of mixed solvent (equal volumes of xylene and methyl isobutyl ketone) and mixed thoroughly. To this 0.25 gm of either amine or benzotriazole is added. The lacquer thus obtained was applied to the polished and degreased surfaces by brush. The thickness of the film is of the order of 7 - 10 μ.

In all the cases the lacquer dried in an hour and the lacquer coated panels were tested by total immersion tests in 0.5% Na₂S solution at room temperature for 24 hours, following tables I and II.

Table 1

<table>
<thead>
<tr>
<th>PHYSICAL PROPERTIES OF THE LACQUER</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Film thickness of coat</td>
</tr>
<tr>
<td>2. Drying time</td>
</tr>
<tr>
<td>3. Specific gravity</td>
</tr>
<tr>
<td>4. Coverage</td>
</tr>
</tbody>
</table>
**Table 2**

**Observations of the Lacquered Copper and Brass Specimens after Total Immersion Test in 0.5% Na<sub>2</sub>S Solution at Room Temperature after 24 Hours.**

<table>
<thead>
<tr>
<th>S.No.</th>
<th>System</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Control (without lacquer coating)</td>
</tr>
<tr>
<td>2.</td>
<td>Rosin modified phenolic resin</td>
</tr>
<tr>
<td>3.</td>
<td>Rosin modified phenolic resin + mono ethanol amine</td>
</tr>
<tr>
<td>4.</td>
<td>Rosin modified phenolic resin + Benzo triazole (0.25%)</td>
</tr>
<tr>
<td>5.</td>
<td>Epoxy polyamide</td>
</tr>
<tr>
<td>6.</td>
<td>Epoxy-polyamide + Mono-ethanol amine (0.25%)</td>
</tr>
<tr>
<td>7.</td>
<td>Epoxy polyamide + Benzo-triazole (0.25%)</td>
</tr>
</tbody>
</table>

**Visual Observations**

- **1.** Tarnished in 10 secs.
- **2.** Transparent coating turns to opaque
- **3.** White patches at random
- **4.** Very few white patches
- **5.** Coating softens, but surface remains
- **6.** Even before immersion the coating becomes black - its transparent (10 secs) nature
- **7.** No change

The following are the main advantages of the lacquer.

1. The lacquer based on epoxy polyamide and benzo triazole can be used for prevention of tarnishing of copper and brass in industrial and other polluted atmospheres.
2. It gives a transparent uniform coating.
3. All the raw materials are indigenously available.
4. It reduce the import of lacquer.

Dated this 19<sup>th</sup> day of January 1984

(N.R. Subbaram)

J OINT ADVISER (PATENTS)
COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH
COMPLETE SPECIFICATION

(Section-10)

Title: IMPROVEMENTS IN OR RELATING TO THE PROCESS FOR THE PREPARATION OF ANTI-TRANISHING LACQUER FOR COPPER AND ITS ALLOYS.

Applicant: COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, Rafi Marg, New Delhi-110001, India, an Indian registered body incorporated under the Registration of Societies Act (Act XXI of 1860).

Inventors: GURUVIAH, SUNDARAM & VYDIANATHA GANESHA SARS.

The following specification particularly describes and explains the nature of this invention and the manner in which it is to be performed:—
This invention relates to the improvements in or relating to a process for the preparation of anti-tarnishing lacquer for copper and its alloys.

Ritherto it has been proposed to use lacquers prepared by dissolving film formers in solvents. Copper and brass materials coated with this lacquer and exposed to atmosphere containing sulphur, and/or other acidic constituents undergo tarnishing and staining.

The object of this present invention is to provide a process to prepare a lacquer by incorporating suitable additives in film forming materials so that a lacquer film with anti-tarnishing properties in highly polluted environments is formed.

The main finding of this invention is that when a film forming material is dissolved in a suitable solvent a lacquer is formed. To this lacquer suitable additives are added which prevents the tarnishing of copper and its alloys in industrial and marine environments. An abrasion resistant coating is formed on the surface and this excludes the reaction between the metal surface and the environment. The coating dries quickly and the additive acts as an inhibitor - both as a contact and vapour phase inhibitor under immersed and atmospheric conditions, to prevent the tarnishing of copper and its alloys.

Accordingly, the present invention provides a process for the preparation of an anti-tarnishing lacquer for copper and its alloys which comprises mixing 40 to 60% of film forming material
selected from (1) rosin modified phenolic resin of acid value 15–
20, iodine value 20–25 and melting point 110–120°C; (2)
diglycidyl ether of bisphenol A type epoxides of molecular weight
ranging from 900–1000 or (3) cellulose nitrate with 60 to 40%
organic solvent such as herein described, then adding 0.2 to
0.5% an additive selected from benzotriazole and monoethanol
amine to the resultant solution.

The organic solvent may be selected from toluene, xylene, white
spirit, methyl isobutyl ketone mixture thereof.

The lacquer prepared by the process of this invention may
preferably contain 50% of film forming material, 50% of solvent
and .25 gm of additive. The lacquer thus obtained could be used
for prevention of tarnishing of copper and its alloy materials.

The invention is further illustrated by the following examples
which should not, however, be construed to limit the scope of the
invention.

**Example 1**

50 gm Rosin modified phenolic resin dissolved in 50 gm white
spirit and mixed thoroughly. To this was added 0.25 gm of
benzotriazole. The product so obtained was applied on to the
polished, degreased copper by brush. The thickness of the film
is of the order of 7–10 μm.
Example 2

50 gms of diglycidyl ether of bisphenol A type epoxy of molecular weight 900-1000 (70% epoxy resin, 30% polyamide) was dissolved in a mixture of xylene : methyl isobutyl ketone and mixed thoroughly. To this 0.25 gms of benzotrisole was added. The lacquer thus obtained was applied by brush on polished and degreased copper. The thickness is of the order of 7-10µm.

Example 3

Similarly a 10% solution of cellulose nitrate with 0.25 gms of benzotrisole in toluene/xylene was prepared and applied on copper to obtain a film of 7-10µm thick.

In all the cases the lacquer dried in about an hour giving rise to a transparent coating on the substrate. The physical properties of the lacquer are given in Table 1. The coated panels were exposed to the atmosphere and subjected to total immersion tests in 0.5% Na₂S solution. The atmospheric tests show that the lacquer based on epoxy resin is completely freed from tarnishing even after 90 days test, whereas tarnishing has been observed in the other two cases. The results of the immersion tests after 24 hrs at room temperature are given in Table 2. Test also was carried out with samples coated with commercial lacquer.

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### Table 1: Physical properties of the lacquer

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Property</th>
<th>Rosin modified phenolic</th>
<th>Epoxy polyamide</th>
<th>Nitrocellulose lacquer</th>
<th>Commercial lacquer</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Colour</td>
<td>Amber</td>
<td>Light amber</td>
<td>Colourless</td>
<td>Amber</td>
</tr>
<tr>
<td>2.</td>
<td>Film thickness per cm</td>
<td>7-10</td>
<td>7-10</td>
<td>7-10</td>
<td>7-10</td>
</tr>
<tr>
<td>3.</td>
<td>Drying time</td>
<td>1 hour</td>
<td>1 hour</td>
<td>50 seconds</td>
<td>1 hour</td>
</tr>
<tr>
<td>4.</td>
<td>Specific gravity</td>
<td>0.89</td>
<td>0.9</td>
<td>0.8</td>
<td>0.8</td>
</tr>
<tr>
<td>5.</td>
<td>Coverage</td>
<td>10 sqm/l</td>
<td>10 sqm/l</td>
<td>10 sqm/l</td>
<td>10 sqm/l</td>
</tr>
</tbody>
</table>

### Table 2: Observations of the lacquered copper immersed in sodium sulphide solution at room temperature for 24 hrs.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>System</th>
<th>Observation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Control (without lacquer)</td>
<td>Tarnished in 10 seconds</td>
</tr>
<tr>
<td>2.</td>
<td>Rosin modified phenolic</td>
<td>Complete failure, surface lost its lustre</td>
</tr>
<tr>
<td>3.</td>
<td>Rosin modified phenolic + benzotriazole</td>
<td>Very few white patches</td>
</tr>
<tr>
<td>4.</td>
<td>Epoxy polyamide</td>
<td>Coating softens but, surface remains bright</td>
</tr>
<tr>
<td>5.</td>
<td>Epoxy polyamide + benzotriazole</td>
<td>No change even after 48 hrs.</td>
</tr>
<tr>
<td>6.</td>
<td>Nitrocellulose lacquer</td>
<td>Softens, surface remains bright</td>
</tr>
<tr>
<td>7.</td>
<td>Nitrocellulose lacquer + benzotriazole</td>
<td>Practically no change</td>
</tr>
<tr>
<td>8.</td>
<td>Commercial lacquer</td>
<td>No change up to 48 hrs.</td>
</tr>
</tbody>
</table>
We claim:

1. A process for the preparation of an anti-tarnishing lacquer for copper and its alloys which comprises mixing 40 to 60% of film forming material selected from (1) rosin modified phenolic resin of acid value 15-20, iodine value 20-25 and melting point 118-120°C, (2) diglycidyl ether of bisphenol A type epoxides of molecular weight ranging from 900-1000 or (3) cellulose nitrate with 60 to 40% of organic solvent such as herein described, then adding 0.2 to 0.5% of an additive selected from benzotriazole and monoethanol amine to the resultant solution.

2. A process as claimed in claim 1 wherein the organic solvent is selected from toluene, xylene, white spirit, methyl, isobutyl ketone or mixture thereof.

3. A process as claimed in claims 1 and 2 wherein the lacquer contains 50% of the film forming material, 50% of the solvent and .25% gm of the additive.

4. A process for the preparation of an anti-tarnishing lacquer for copper and its alloys substantially as herein described with reference to the examples.

Dated this 19th day of October, 1987.

[Signature]

JOINT ADVISOR (PATENTS)
COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH

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