

PATENT SPECIFICATION

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 (72) Inventors EDWIN ARTHUR CHANDROSS and
 CORALIE ANNE PRYDE



(54) CORROSION INHIBITOR FOR A METAL SURFACE

(71) We, WESTERN ELECTRIC COMPANY, INCORPORATED, of 222 Broadway (and formerly of 195 Broadway), New York City, New York State, United States of America, a Corporation organised and existing under the laws of the State of New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a technique for retarding corrosion of copper and copper alloy surfaces.

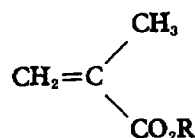
The corrosion of metal surfaces has been a matter of concern to the electronics industry for many years. Unfortunately, the metals most commonly employed in electronic applications, namely, copper and its alloys, tend toward instability under the influence of heat and moisture, so resulting in the formation of an unattractive and unevenly oxidized surface. Furthermore, oxides so formed enhance the difficulties encountered in making acceptable solder connections to the metal surfaces.

In the past, a wide variety of chemical compositions have been used as ambient atmosphere protectants for such metals. The majority of those compositions have been found unsatisfactory for even short periods of exposure and, thus, not suited for the relatively long exposures required for many conventional applications. Accordingly, the most commonly used procedure for effecting the desired end has involved plating the metal surfaces with either a noble metal or solder, neither procedure having proven ideal.

More recently, a technique for obviating such limitations was described wherein a thin coating of a siloxane prepolymer formed by hydrolysis and partial condensation of an acylated aminoalkyltrialkoxysilane was deposited upon the metal surface of interest. The coating so deposited was found to effectively retard corrosion while maintaining satisfactory solderability, characteristics.

Although this system appears to have merit, workers in the art have continued their search for suitable alternatives.

The invention provides a method of treating a surface containing copper or an alloy thereof, wherein the surface in a clean condition is contacted with a benzotriazole solution and a layer of polymer is then formed on the surface, the polymer being selected from homopolymers formed by polymerization of a methacrylate monomer of the general formula



in which R is an alkyl radical represented by the formula $\text{C}_n\text{H}_{2n+1}$ where n is an integer from 1 to 6, and from copolymers formed by copolymerization of at least one methacrylate monomer of the said general formula in which R is a glycidyl radical or an alkyl radical represented by the said formula $\text{C}_n\text{H}_{2n+1}$, the glycidyl monomer, if present in the copolymer, being in an amount from 0 to 10 per cent by weight.

Studies have revealed that the deposited coating deposited can effectively protect clean copper and alloys thereof from atmospheric corrosion without adversely affecting solderability. Although these films, standing alone, cannot always protect the copper from tarnishing induced by contaminants present on the surface before coating or introduced during the coating procedure, it has been found that such limitations can be effectively obviated by rinsing the surface to be coated with an aqueous solution of benzotriazole prior to coating. The combination of the methacrylate polymer and benzotriazole rinse has been found to yield a synergistic effect and hence the rinse is considered to be important.

The invention will be more readily under-

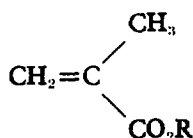
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stood by reference to the accompanying drawing wherein:—

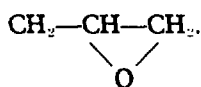
The Figure is a perspective view of a typical electrical component having copper surfaces destined for subsequent soldering.

With reference now more particularly to the Figure, there is shown an encapsulated component 11 including a plurality of copper containing fingers 12 destined for soldering. Shown deposited upon the surface of fingers 12 is a thin coating 13 of the polymer described herein.

As noted, the polymer described is formed by polymerizing a methacrylate monomer or mixture of at least two methacrylate monomers. The methacrylates employed are of the general formula



wherein R is selected from the group consisting of (a) alkyl radicals of the general formula $\text{C}_n\text{H}_{2n+1}$ wherein n is an integer from 1—6, and (b) glycidyl radicals of the formula



The methacrylate employed herein may be polymerized alone or in combination with other methacrylates by any well known procedure. A convenient technique for achieving this end involves dissolving the monomers in a suitable solvent and bringing the resultant solution to reflux in the presence of an inert gas. Then, a polymerization initiator is added to the solution and refluxing continued. The solution may then be added to a suitable solvent from which the desired polymer precipitates upon cooling. Studies have revealed that the polymers may comprise mixtures of any members of the recited group in varying proportions dependent upon the desired hardness and relative flexibility desired. The glycidyl methacrylate may be employed in amounts ranging up to ten percent, by weight, based on the weight of the polymer, such limit being dictated by crosslinking considerations beyond that point, which make the film too stable to solder under the mild soldering conditions employed.

As indicated, the invention contemplates coating metal surfaces of copper or alloys thereof, the materials most commonly employed in the fabrication of electronic components. Prior to coating the surface of interest, a conventional cleansing technique is preferably employed for the purpose thereof of removing surface contaminants. The cleansed surface may then be rinsed in water and

either immediately placed in ethanol to be used sometime later, or it may be placed for two to five minutes in an aqueous solution of benzotriazole at substantially 20°C, then rinsed and stored in ethanol. When the sample is to be coated, the ethanol is removed. A preferred method of coating is to dip-coat the sample in the polymer solution, and it is then preferably air-dried and heated to a temperature within the range of 85 to 115°C for a time period ranging from 15—30 minutes, the lower temperature corresponding with the longer time period, thereby resulting in effective adherence of the polymer to the metal surface. Although the temperature range is not absolute, it will be understood that the use of temperatures appreciably in excess of 115°C may result in thermal oxidation of the surface whereas temperatures less than 85°C may not result in effecting adhesion of the polymer film to the metal surface. The thickness of the coating is preferably within the range of 1—2 microns. After coating, testing may be implemented to evaluate retardation of oxidative degradation and degradation occurring under conditions normally encountered during storage prior to soldering operations.

The following example serves to illustrate the invention.

Preparative Procedure

Eight grams (0.08 mole) of methyl methacrylate, two grams (0.014 mole) of glycidyl methacrylate and ten grams (0.07 mole) of butyl methacrylate were dissolved in a mixture comprising 80 millilitres of benzene and 20 millilitres of toluene. The resultant solution was brought to reflux in a nitrogen ambient atmosphere and 150 milligrams of benzoyl peroxide in 15 millilitres of benzene was added thereto. After three hours, 100 milligrams of benzoyl peroxide was added to the mixture and refluxing continued for an additional three hours. Then, the solution was poured into hot, stirred hexane and, upon cooling, the desired methacrylate copolymer precipitated as a soft, glassy solid from the solvent and was decanted. The resultant polymer was then dissolved in warm methylene chloride and the precipitation in hexane repeated. Following decantation, the polymer was maintained under vacuum overnight at a temperature within the range of 40—45°C to remove the last traces of solvent. Fifteen grams of dry solid methacrylate copolymer was obtained.

The above preparative procedure was repeated with the exception that the glycidyl methacrylate was eliminated from the mixture. Fourteen grams of dry solid methacrylate copolymer was obtained.

The polymers so obtained are soluble in organic solvents, as for example, halogenated hydrocarbons such as trichloroethylene and dichloroethane. Following recovery, the poly-

mers are dissolved in a solvent in an amount sufficient to yield films of the desired thickness.

Aging tests were conducted using oxygen-free high-conductivity copper strips. The strips were initially cleaned by dipping in a 1:1 mixture of nitric acid and water containing a trace of chloride ion which leaves a lustrous surface. Following cleaning, the copper strips were rinsed in running tap water and placed either in ethanol for storage until use or in a benzotriazole solution containing from 150—300 milligrams per 100 millilitres of distilled water. A dip in the benzotriazole solution for 2—5 minutes at substantially 20°C is sufficient to provide adequate protection for samples subsequently coated with the polymer. Following the benzotriazole rinse, the strips were given an aqueous rinse and stored in ethanol until ready for coating.

Immediately before coating, the samples were removed from the ethanol and blown dry with a stream of nitrogen. Following, the surface is dip-coated in the polymer solution, held vertically to drain and, after evaporation of the majority of the solvent, heated to a temperature within the range of 85—115°C for a time period ranging from 30—15 minutes, the shorter periods corresponding with the higher temperatures. As indicated, the temperature range is not absolute. However, temperatures appreciably beyond the 115°C maximum tend to cause degradation of the polymer film.

Solderability tests were performed in the following manner. After dipping first in water and then in white rosin in isopropyl alcohol, the surfaces were immersed for ten seconds in solder at 236°C.

Additionally accelerated aging conditions were employed to test the treated samples using (a) dry heat at 80—90°C and ambient humidity, (b) humid atmosphere (38°C and 100 percent humidity), and (c) humid atmosphere (40—42°C, 100 percent relative humidity) in an ambient atmosphere saturated with elemental sulphur.

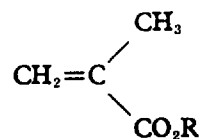
Other tests conducted include sodium chloride, polysulphide and amine tests, the samples being inspected visually for evidence of tarnishing at the conclusion of the test.

Studies of the results obtained from the foregoing tests revealed that samples protected in the described manner evidenced excellent aging characteristics and good solderability after several weeks in the sulphur-100 percent relative humidity ambient atmosphere. Additionally, the samples protected as described were found to be very resistant to attack by sodium chloride. Studies also revealed that benzotriazole treatments alone did not yield satisfactory results but that the

synergistic combination of methacrylate polymer and benzotriazole resulted in a marked enhancement in retention of solderability. Additionally, the methacrylate polymers alone yielded erratic results.

WHAT WE CLAIM IS:—

1. A method of treating a surface containing copper or an alloy thereof, wherein the surface in a clean condition is contacted with a benzotriazole solution and a layer of polymer is then formed on the surface, the polymer being selected from homopolymers formed by polymerization of a methacrylate monomer of the general formula



in which R is an alkyl radical represented by the formula $\text{C}_n\text{H}_{2n+1}$ where n is an integer from 1 to 6, and from copolymers formed by copolymerization of at least one methacrylate monomer of the said general formula in which R is a glycidyl radical or an alkyl radical represented by the said formula $\text{C}_n\text{H}_{2n+1}$, the glycidyl monomer, if present in the copolymer, being in an amount from 0 to 10 percent by weight.

2. A method according to claim 1, wherein the layer comprises a copolymer of methyl methacrylate and butyl methacrylate.

3. A method according to claim 2, wherein the layer further comprises up to 10 percent by weight glycidyl methacrylate.

4. A method according to claim 1, 2, or 3 wherein the layer is heated to within the range 85 to 115°C.

5. A method according to claim 4, wherein the layer is heated for a period ranging from 15 to 30 minutes, the shorter periods corresponding to the higher temperatures.

6. A method according to any one preceding claim, wherein the benzotriazole solution is an aqueous solution and the surface is dipped into the solution at substantially 20°C for a period of from 2 to 5 minutes.

7. A method of treating a surface, substantially as hereinbefore described with reference to the example.

8. A copper or copper alloy surface treated by the method according to any one preceding claim.

K. G. JOHNSTON,
Chartered Patent Agent,
5, Mornington Road,
Woodford Green, Essex.
Agent for the Applicants.



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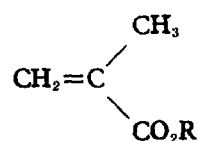
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