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METALLIC COATING FOR WIRE

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1 Claim. (Cl. 29—199)

This invention relates to coatings for electric conductors and more particularly to substitute coatings for tin on copper wire.

Because tin is a critical material in times of war or a period of extensive military preparedness, it is essential that its use be minimized as much as possible. A substantial saving on tin can be realized by replacing the tin coatings on copper wire with a non-critical material.

The substitute for the tin coating should possess approximately the same soldering properties as tin and also serve as an adequate barrier between the copper wire and the insulation. In addition, the coating should function satisfactorily in a wide temperature range. To enable the use of the coating in all types of climatic conditions, particularly in tropical exposures, high humidity resistance and resistance to fungal growth are important.

It is known by those skilled in the art that clean copper has excellent solderability. Hence, tinning would not be necessary if it were not for the formation of copper sulphide in those instances where no barrier layer is provided to prevent attack on the copper by the sulphur in rubber insulation and to prevent attack on the copper by atmospheric or other exposure. Therefore, a most necessary function of the barrier between the copper and the insulation is the prevention of attack by constituents in the insulating material, as, for example, the so called "copper" effect on rubber insulation. Here, the free sulphur in the rubber insulation attacks the copper and the compounds formed and the copper itself react with the rubber to deteriorate it. Where the insulation is of an organic chloride type, such as Vinylite, there is the possibility of attack on the copper by chlorine.

It is therefore a primary object of the present invention to provide a coating for copper wire, said coating possessing solderability equivalent to a standard tin coating, thus effecting a saving in tin.

A further object is to provide a coating for copper wire which will be resistant to high humidity corrosion.

A still further object is to provide a coating for copper wire which will be resistant to sulphur attack.

These and other objects and advantages of the present invention will be better understood as the detailed description thereof progresses.

In accordance with the present invention, there is provided a wire conductor having a duplex coating thereon, said coating comprising an electrodeposited lead barrier layer and an external coating of electrodeposited tin. A preferred embodiment is provided wherein the lead barrier layer has a thickness of from 0.00003 inch to 0.00006 inch and the external coating of tin has a thickness of from 0.000005 inch to 0.00002 inch.

Also, in accordance with the present invention, there is provided a method of electrodepositing a duplex coating consisting of an electrodeposited lead barrier layer and an external coating of electrodeposited tin comprising electroplating lead from an aqueous electrolyte containing lead fluoborate, free fluoboric acid and boric acid directly upon a wire conductor and thereafter electrodepositing tin from an alkaline aqueous electrolyte containing a stannate selected rom the group consisting of sodium, potassium and ammonium stannates, a hydroxide selected from the group consisting of sodium, potassium and ammonium hydroxides and hydrogen peroxide upon the lead. An electrolyte to be used in a preferred embodiment of the method of the present invention is provided, comprising 200 to 250 grams of lead fluoborate, 20 to 25 grams per liter of boric acid, 25 to 35 grams per liter of fluoboric acid and about 0.2 to 0.8 gram per liter of hide glue.

To enable the determination of the best substitute for a tin coating on copper wire it is necessary to understand the basic factors which determine the solderability of tinned copped wire using a rosin flux. The following hypothesis has been evolved as a result of the present invention concerning the behavior of tinned coatings when subjected to the soldering operation.

The coating on tinned copper wire is composed of one or all the following films or layers. The outermost surface consists of a film of tin oxide. This film varies in thickness depending upon the degree of porosity and roughness of the tin coating, the time, temperature, and atmosphere during aging and the preliminary cleaning treatment before soldering. Beneath this oxide film, there lies a layer of tin. The thickness of this layer depends primarily upon the original thickness of the tin deposit but is made thinner depending upon the greater the amount of formation of intermetallic compound. Beneath the tin film, there lies a compound layer probably consisting of Cu_6Sn_5 in contact with the tin and a layer Cu_3Sn in contact with the copper. This compound layer also varies in thickness being essentially non-existent in freshly electrotinned coatings, being extremely thin for wires aged even prolonged times at room temperature, and achieving appreciable thickness for wires held even for short times at temperatures exceeding the melting point of tin. Thus, the compound layer forms and grows in the soldering area during soldering operations on non fused electrotinned wires.

The relative as well as the absolute thickness of these layers determine the solderability of tinned copper wire. In the case of a thin oxide film with a little or no free tin beneath, the solderability is negligible. As the amount of free tin is increased (by means of thicker coatings), the solderability increases within practical limits of tin thickness. With the thicker tin coatings, the mechanism involved during the soldering operation is the breaking and washing away of the oxide film by the combined action of the molten tin beneath the film, the solder, and the rosin. The formation of intermetallic compounds of copper and tin reduce the quantity of free tin beneath the oxide film. Thus, for a critical thickness of free tin, solderability is greatly impaired by compound formation. If the oxide film and free-tin layers are virtually absent, the compound layer may decrease solderability owing to its apparent inherently poorer solderability than that of copper (about 20% less). Therefore, in order to achieve maximum solderability, both the formation of the oxide and the layer of intermetallic compounds must be eliminated.

The present invention is based upon the discovery that a very thin coating of tin overlaying a layer of lead upon copper wire will eliminate diffusion of tin into copper thus reducing the quantity of tin required to coat the copper wire to a small fraction of the usual amount required and the resulting duplex coating will have solderability equal or superior to a coating wholly consisting of tin. Inasmuch as the usual thickness of a standard tin coating is 0.00006 inch and the present invention requires an overlay of tin only 0.00001 inch thick, it is apparent that the savings in tin can be quite appreciable.

The lead barrier layer is electrodeposited upon the copper wire from an electrolytic bath containing lead fluoborate, free fluorboric acid, free boric acid and a little hide glue. The concentration of these constituents in the bath and the necessary steps in the plating procedure are described hereunder.

The wire plate consists of 33 inch lengths of 16 gauge copper wire (0.05082 inch diameter) stretched to 36 inches by means of a vise and a pair of pliers. The cathodes consist of 5 lengths of straightened wire six inches in active cathode length. The wires are so racked that they lie in a vertical plane with axes 0.75 inch apart. During the plating, the cathode assembly is agitated in the direction of the plane of the wires.

Prior to the plating of the copper wire specimens, they are subjected to a preliminary treatment to insure maximum purity and cleanliness. The steps in this treatment are as follows.

The copper wire specimens are vapor degreased. They are then electromechanically cleaned by making them one of the electrodes in a bath composition consisting of 75 grams of "Anodex" per liter, the bath being kept at 200° F. throughout the cleaning and a current density of 90 amperes per square foot being applied. The specimens are electromechanically cleaned as a cathode for 45 seconds and as an anode for 15 seconds. The next step is to cold rinse them and then they are dipped for one minute in an acid bath, the bath consisting of a solution of ammonium chloride in a 0.5 normal hydrochloric acid, the concentration of the ammonium chloride being 150 grams per liter. The acid bath is kept at 130° F. during the dipping. The specimens are again cold rinsed and then placed as a cathode in an electrolytic solution consisting of 22.5 grams per liter of cuprous cyanide, 30.0 grams per liter of sodium cyanide, 60.0 grams per liter of Rochelle salts, 25.0 grams per liter of sodium carbonate and 6.0 grams per liter of sodium hydroxide. The solution is adjusted to a pH of 12.7 and a current with a density of 30 amperes per square foot is passed through the solution for 3 minutes. The temperature during this process is maintained at 150° F.

To plate the copper wire with lead, an electrolyte bath consisting of 220 grams per liter of lead fluoborate as Pb, 31 grams per liter of free fluoboric acid, 22 grams per liter of free boric acid and 0.4 gram per liter of hide glue is used. The bath is maintained at a temperature of 75° F. to 100° F. during the plating. The electroplating process consists of passing a current with a density of 10 amperes per square foot through this bath, the prepared copper wire specimen being made the cathode while lead plates are used as anodes. After 2 minutes of plating, the plated specimens are rinsed.

To plate the lead coated copper wire with tin, an electrolytic bath consisting of 120 grams per liter of sodium stannate, 7.5 grams per liter of sodium hydroxide, 15 grams per liter of sodium acetate, 0.5 milliliter per liter of hydrogen peroxide and 12 grams per liter of free sodium hydroxide is used. The bath is heated to a temperature of 170° F. and a current density of 15 degrees per square foot is passed through the solution. The lead coated copper specimens are made the cathode and two nickel anodes are used. A plating time of 10 seconds gives a tin coating thickness of 2.5×10^{-6} inches, 20 seconds gives a tin coating thickness of 5×10^{-6} inches, etc. After the plating, the specimens are cold rinsed, rinsed in a 95% alcohol solution and dried wtih cleaning tissue.

The duplex coating consisting of a lead barrier layer, 0.000045 inch thick and an overlay of tin 0.00001 inch thick was tested with respect to solderability, sulphur resistence continuity of coating, solderability after againg, high humidity coating resistance and adhesion to the underlying copper.

To test solderability, a pair of 16 gauge coated wire specimens were clamped in a vise at the ends and twisted together (7 complete turns for 7 inch long specimens). The twisted wires were cut to a 6 inch length. The twisted wires were suspended in a solution of 40 grams of wood rosin in 100 cc. of ethyl alcohol and their fluxed ends were then suspended with a 0.4 inch immersion in a 50 lead–50 tin solder bath for 30 seconds at 312° C. The wood rosin was removed with xylene and the capillary rise of the solder above the point of contact with the solder bath was measured to the nearest 64th of an inch. The height of the capillary rise of the solder was recorded in multiples of 64th of an inch. A coating of tin only 0.00001 inch thick over a lead underlay 0.000045 inch thick showed a solderability which compared quite favorably with that of a standard tin coating 0.00006 inch thick.

In order to determine the resistance of the coating to attack by free sulphur in rubber, the coated wires were vulcanized in a sheet of rubber. A normal and an accelerated (high sulphur rubber) test were employed. The normal rubber was compounded according to a standard formula for cable covering while the high sulphur rubber contained five times as much sulphur as the normal rubber. The specimens were placed between two sheets of rubber and vulcanized at 290° F. (143° C.) under pressure, for 30 minutes for the normal test and 45 minutes for the accelerated test. The results of this test showed that the duplex coating did not show any blackening by the sulphur and its solderability remained good after this test.

To determine continuity of coating, the testing procedure required the following special solutions, the preparation thereof being described below.

A hydrochloric acid solution of 1.088 specific gravity was required for this test and was prepared as follows. Commercial hydrochloric acid (specific gravity 1.12) was diluted with distilled water to a specific gravity of 1.088 measured at 15.5° C. (60° F.). A 180 milliliter test portion of the dilute acid was considered to be exhausted when ten test specimens of 16 gauge wires had been immersed in it for two cycles.

A second solution required for this test was a sodium polysulphide solution of specific gravity 1.142. This was prepared in the following manner. A concentrated solution was prepared by dissolving sodium sulphide crystals in distilled water until the solution was saturated at about 21° C. (70° F.), adding about 250 grams per liter of flowers of sulphur and allowing the resulting solution to stand for at least 24 hours. The test solution was made by diluting a portion of the concentrated solution with distilled water to a specific gravity of 1.142 at 15.5° C. (60° F.). The sodium polysulphide test solution had to have sufficient strength to blacken thoroughly a piece of clean, untinned copper wire in 5 seconds. A portion of the test solution used for testing samples was considered to be exhausted when it failed to blacken a piece of clean copper.

The procedure for testing coating continuity consisted of the following steps. A length of at least 4½ inches of clean coated wire specimen was immersed in accordance with the following cycles in test solutions maintained at temperatures between 15.5° C. and 21° C. (60° F. and 70° F.). The specimen was immersed in the hydrochloric acid solution described above, washed, and wiped dry. The specimen was then immersed for 30 seconds in the sodium polysulphide solution described above, washed, and wiped dry. After each immersion, the specimens were immediately and thoroughly washed in clean water and wiped dry with a clean soft cloth. After the operations described above, the specimens were examined to ascertain if any copper was exposed through openings in the coating as revealed by blackening action of the sodium polysulphide. Such blackening of exposed copper indicated failure of the coating.

The duplex coating of tin on a lead underlay when subjected to this test showed satisfactory continuity and no blackening was observed.

To test for solderability after aging, the wire specimens were placed in a helium atmosphere at 200° C. for 30 hours. At the end of this period the appearance and adhesion of the coating was noted and then the specimen was again tested for solderability. The duplex coating of tin over lead showed satisfactory results after being subjected to this test, having good solderability.

To test resistance to high humidity corrosion, coated wire specimens were exposed to a high humidity atmosphere for 100 hours at a temperature of 105° C. in a corrosion testing box. At the end of this period, the solderability of the specimens remained high.

The test for adhesion of the coating consisted of bending the wire around a rod having a diameter equal to four times the diameter and dipping the bent portion of the wire in a sodium polysulphide solution (as described hereinabove in the "Continuity of Coating" test) for 30 seconds. Any cracking or parting of the coating shown by blackening of the copper would have been indicative of failure. The coating which is the present invention gave no indication of cracking or parting when subjected to this test.

In summary, this invention teaches that a duplex coating consisting of a thin tin coating over a lead barrier layer upon copper wire is a very effective substitute for a standard tin coating on copper wire, being equivalent to the latter with respect to solderability, sulphur resistance, coating continuity, adhesion, and resistance to corrosion caused by high humidity. Thus, with this coating, great savings in tin can be realized.

While there have been described what at present are considered to be preferred embodiments of the invention, it will be understood by those skilled in the art that various changes and modifications may be made herein without departing from the invention and it is therefore aimed in the appended claims to cover all such modifications as fall within the spirit and scope of the invention.

What is claimed is:

A solderable copper wire conductor of high resistance to humidity and fungal growth comprising a first coating of an electrodeposited lead film of a thickness from 0.00003 inch to 0.00006 inch and a second coating of electrodeposited tin having a thickness from 0.000005 inch to 0.00002 inch.

References Cited in the file of this patent

UNITED STATES PATENTS

534,209	Edison	Feb. 12, 1895
1,405,535	Merritt	Feb. 7, 1922
1,475,973	Summers	Dec. 4. 1923
1,509,101	Dang	Sept. 23, 1924
1,509,102	Dang	Sept. 23, 1924
1,876,745	Potter	Sept. 13, 1932
1,886,997	Wilkins	Nov. 8, 1932
2,039,068	Domm	Apr. 28, 1936
2,176,066	Domm	Oct. 17, 1939
2,283,868	Fowle	May 19, 1942
2,307,801	Pierce	Jan. 12, 1943
2,386,951	Howe	Oct. 16, 1945
2,472,296	Hartnell	June 7, 1949
2,474,092	Liger	June 21, 1949

OTHER REFERENCES

Transactions Electrochemical Society, vol. 36, pp. 243–265, 1919, vol. 80, pp. 617–629, 1941.