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2,768,944

COPPER COATING BY GALVANIC ACTION

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This invention relates to an improved method of applying a layer of metallic copper to a surface or base and, more particularly, to an improved galvanic method of applying a protective coating to the silvered reflecting surface of a mirror.

In my Patent #2,664,363, issued December 29, 1953, I explain how a copper coating may be deposited on a silvered surface by simultaneously flowing onto the surface a solution of copper sulphate and a water mixture of finely divided metal. In my Patent #2,720,487 I explain how the copper coating thus galvanically deposited may be hardened and otherwise improved by the addition of a small quantity of phosphoric acid to the copper sulphate solution.

It has been found that the copper coating deposited according to the method of the first named patent may be made harder and smoother also by the use of sulphuric acid instead of phosphoric acid as explained in the second named patent and that there are certain advantages in a copper coating thus applied. For instance, the coating will not be as hard as can be obtained with the use of phosphoric acid but it will overcome granulation, it will give a good sheen, it is thoroughly reliable if used as hereinafter explained, and the ingredients are both very economical to use and readily obtainable from the ordinary chemical supply house.

In experiments it was found that the principal disadvantage of the use of sulphuric acid resides in the fact that it will burn or damage the silvering unless thoroughly mixed with the copper or cupric sulphate or if, perchance, a slightly excess amount of acid is used. I have found that this disadvantage may be overcome by adding a small amount of alkali to the metallic dust and water mixture, as will be explained, so that it is now possible to use the sulphuric acid with full expectation of reliable results.

In carrying out the present process any accepted process for depositing the silver reflective coating may be used, however, since applicant contemplates high production procedure the glass plates or sheets should be placed vertically, angularly or flat on racks which are connected together to constitute a conveyor and the silvering applied to the sheets by spraying. After silvering the coating is then water rinsed and while the sheets are still in place on the racks and still wet from the rinse water, the copper coating is then applied.

A tank is provided containing a water solution of a copper salt such as copper sulphate, cupric sulphate or copper nitrate to which is added a small amount of sulphuric acid, the tank being above the level of the work, so that there will be a good flow from the tank through a hose and spray nozzle onto the work. A second tank is provided and filled with a very finely divided metallic dust suspended in the water, to which I add a small quantity of an alkali such as potassium in any form or sodium in any form, or a combination of the two such as Rochelle salts. Examples of alkalis which may be used are po-

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tassium hydroxide, sodium chloride, sodium carbonate, caustic soda and sodium oxide. Means must be provided in the second tank to maintain the contents under agitation sufficiently violent to keep the metallic dust in homogeneous suspension. Compressed air may be fed into the bottom of the tank for this purpose or motor driven paddles may be used, the paddles being located within the tank. Hoses or conduits lead from the second tank to a nozzle convenient to the work. In one method, compressed air is applied, supplied to a mixing nozzle where fluids from the two tanks are mixed and simultaneously sprayed upon the silvered surface. An advantage of this system is that it tends to maintain the violent agitation of the metallic particles within the mixing nozzle, thus preventing clogging of the nozzle and giving a more efficient reaction. Upon the mingling of the copper sulphate and sulphuric acid solution with the water-metallic dust-alkali mixture the more active metallic dust combines with the sulphate (SO_4) radical and free copper is immediately deposited. The sulphuric acid seems to prevent the copper from combining with the silver and the alkali seems to prevent the sulphuric acid from burning the silver. The alkali may be omitted if great care is used in measuring the amount of sulphuric acid added, but for ordinary factory production applicant strongly advises the use of the alkali as a safeguard against mistakes by workmen with consequent spoilage. And sulphuric and phosphoric acids may be mixed and used together in any proportion so long as they do not together exceed the limits herein recited.

The metallic dust which I use is preferably zinc because it is most readily and cheaply obtainable commercially and because it will not scratch the silvering. However, I may also use the dust or powder of iron, cadmium, nickel, cobalt, chromium, tungsten and molybdenum with the precaution that such dusts should have a fineness to be able to pass through a screen having 300 openings per square inch to avoid undue scratching of the silvered surface.

In carrying the method into practice, each of the conduits from the two tanks are appropriately valved and the relative rate of supply of the fluids is carefully and critically controlled so as to properly form the deposit and the mixing nozzle is provided with a lever operated master valve so that the operator may cut the spray on and off at will.

In extensive tests it has been found that a copper solution having a proportion of 6 ounces per gallon of water to which has been added $\frac{1}{2}$ ounce of sulphuric acid per gallon of water, and a metallic suspension of $\frac{1}{2}$ ounce of metallic dust per gallon of water to which has been added $\frac{1}{2}$ ounce of an alkali is to be preferred and gives an excellent coating. It has been found possible, however, to vary the strength of the solution in the proportion of 6 to 40 ounces of a copper salt such as copper sulphate, copper nitrate or cupric sulphate to which has been added $\frac{1}{4}$ to 3 ounces of sulphuric acid per gallon of water. The metallic suspension mixture may be varied from $\frac{1}{2}$ to 3 ounces of metallic dust per gallon of water to which is preferably added from $\frac{1}{4}$ to 3 ounces of alkali per gallon of water. If the alkali is omitted the sulphuric acid in the foregoing formula should never exceed $\frac{1}{2}$ ounce per gallon of water. Also, since formaldehyde is a reducer of the copper, I have found that I can add $\frac{1}{4}$ to $\frac{1}{2}$ ounce of it per gallon of water in the metallic suspension and that I can reduce the amount of metal more or less in proportion. Thus, I can use $\frac{1}{2}$ to 3 ounces of metal dust and formaldehyde but I recommend that at least half of this mixture should be of metal dust.

While the herein described method describes the em-

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bodiments which I believe to be best, it is not contended that the proportions are critical but that they have been proved best under factory operating conditions and I therefore desire to be extended protection as defined by the scope of the appended claims.

What I claim is:

1. The method of copper plating a silvered surface by galvanic action which consists in simultaneously spraying onto the surface a solution composed of 6 to 40 ounces of a copper salt and $\frac{1}{4}$ to 3 ounces of sulphuric acid per gallon of water, and a mixture of water, metallic dust and an alkali, the dust being in a concentration of $\frac{1}{2}$ to 3 ounces per gallon of water and the alkali being in concentration of $\frac{1}{4}$ to 3 ounces per gallon of water, the dust being homogeneously suspended in the water and in the alkali and being selected from the group of metals consisting of zinc, iron, cadmium, nickel, cobalt and chromium.

2. The method of copper plating a silvered surface by galvanic action which consists in simultaneously spraying onto the surface a solution composed of 6 to 40 ounces of a copper salt and $\frac{1}{4}$ to 3 ounces of sulphuric acid per gallon of water, and a mixture of water, metallic dust, formaldehyde and an alkali, the dust and the form-

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aldehyde together being in a concentration of $\frac{1}{2}$ to 3 ounces per gallon of water and the alkali being in concentration of $\frac{1}{4}$ to 3 ounces per gallon of water, the dust being homogeneously suspended in the water and in the alkali and being selected from the group of metals consisting of zinc, iron, cadmium, nickel, cobalt and chromium, the powder having a fineness of the order of -300 mesh.

3. The method of copper plating a silvered surface by galvanic action which consists in simultaneously spraying onto said surface a solution composed of 6 ounces of copper sulphate and $\frac{1}{2}$ ounce of sulphuric acid per gallon of water, and a metallic suspension of $\frac{1}{2}$ ounce of metallic dust per gallon of water to which has been added $\frac{1}{2}$ ounce of an alkali, the dust having a fineness of the order of -300 mesh and selected from the group of metals consisting of zinc, iron, cadmium, nickel, cobalt and chromium.

References Cited in the file of this patent

UNITED STATES PATENTS

2,720,487 Meth Oct. 11, 1955