

1

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GALVANIC PLATING OF HARDENED COPPER

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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 copper coating to the silvered reflecting surface of a mirror in such manner that the copper will be hardened with resultant improved protective and appearance qualities.

While the method disclosed herein is particularly adapted for use in the mirror manufacturing industry and the disclosure is primarily so directed, it is to be understood that the method is not to be restricted thereto and that there is a broader application. This method may be used whenever it is desired to deposit a layer of copper on any conducting surface or base.

While I am aware that copper plating by galvanic action is known, the copper coating heretofore deposited has been soft and readily oxidizable. A principal object of this invention is to teach the galvanic deposition of a hardened copper. As will be hereinafter more fully described, I accomplish this by adding a hardening agent which becomes effective at the time of deposition. The result is a coating having greater protective quality and better appearance.

In the manufacture of silvered mirrors it has been the standard practice to place the transparent sheet on a perfectly horizontal surface and then pour a mirroring solution over the top surface of the sheets. The solution usually comprises a silver salt such as silver nitrate (AgNO_3) or a complex silver salt such as silver ammonium nitrate ($\text{AgNO}_3\text{NH}_4\text{NO}_3$) which has freshly mixed therewith a reducing agent such as Rochelle salt ($\text{KNaC}_4\text{H}_4\text{O}_6\text{H}_2\text{O}$), a sugar, formaldehyde (HCHO) or the like. The silver is precipitated in a thin layer of free metal to form the reflecting method of spraying the silvering solution on the plate, the silver salt and reducing agent being mixed and sprayed on the surface. The silver layer must then be washed and dried and the mirror handled and manipulated to transfer it to a copper electroplating bath, where the reflective coating becomes an electrode and has deposited thereon a protective layer of copper. The copper layer is then covered by spraying, brushing or rolling with a paint well known to the industry.

The handling of the freshly silvered mirror without injury to the thin reflective surface becomes a serious practical problem. The layer is easily scratched and rubbed off, and the supporting of the plate in the bath and establishment of electrical connections is difficult, time consuming and costly. It has also been found that in the electroplating there is some reaction between the layers of silver and copper, with a serious impairment in the quality of the mirror.

In using the electroplating processes (as distinguished from the galvanic process), due to the difficulties just mentioned, manufacturers now experience a reject loss of from 5% to 20% of the total volume and there is a high material wastage, all this combining to undesirably increase unit cost. Applicant, by the process herein dis-

2

closed, has reduced rejections to a fraction of 1% of total volume and has materially reduced manufacturing costs.

It is an object of the present invention to provide a simple and economical method of depositing a hard, durable layer of metallic copper on a surface or base by galvanic action, the copper being hardened as it is deposited.

Still another object of the invention is to provide a method of forming a copper layer wherein the layer may be applied to the work wherever it may be supported and without the use of special vats or the like.

A further object of the invention is to provide a method of applying a protective copper coating to the silvered surface of the mirror which eliminates costly electroplating steps, reduces the percentage of rejects to a negligible amount, and prevents reactions between silver and copper coatings which impair the quality of the mirror.

Still another object of the invention is to provide a method of forming a copper protected silvered mirror wherein the transparent plate may be placed on a rack, the silver reflective layer applied and the copper protective layer immediately applied thereafter while the reflective layer is still wet and without moving or handling the plate, thus materially simplifying manufacturing procedure, shortening manufacturing time, and substantially eliminating injury to the reflective layer due to handling.

A further object of the invention is to provide a method of coating a base or surface of readily oxidizable metal, wherein the coating may be applied so quickly after cleaning that a minimum of oxide is permitted to form and the copper layer deposited thereon may serve as a base for further electroplating or painting of finish metals.

A still further object is to teach the addition of phosphoric acid to the copper sulphate solution, the phosphoric acid thus intermingling simultaneously with the copper sulphate and the water mixture of metal dust whereby the copper coating is hardened as formed.

With the above and other objects in view as will be presently apparent, the invention consists in general of certain novel details hereinafter fully described and particularly claimed.

In carrying out the present method any known process for depositing the silver reflective coating may be used. The transparent plate may be placed horizontally and the flow method used, but in connection with the present disclosure it is preferable that the spray method be used and the plates racked up substantially vertical or at a sharply acute angle to the vertical.

A tank is provided containing a water solution of copper sulphate (CuSO_4) to which has been added a small amount of phosphoric acid, which tank is substantially above the level of the work to establish flow, and is provided with a lower outlet aperture. A second tank is also used, which tank contains a very finely divided metallic dust suspended in water. It is highly necessary and a very important part of the present improved method that this suspension be kept violently agitated. Any desired means may be used to maintain a homogeneous suspension, such as compressed air or vibration of the container, but agitation by a motor driven screw or paddles has been found to be very efficient. Hoses or conduits are used to conduct the solution and suspension from the tanks to a mixing nozzle. In one method, compressed air is supplied to the nozzle and the two fluids simultaneously mixed and sprayed upon the silvered reflective surface. It may be noted that the use of compressed air has been found effective since the air tends to maintain the violent agitation of the zinc particles within the mixing nozzle which gives a more efficient reaction. Upon the mingling of the CuSO_4 and phosphoric acid solution with the metal suspension, the more active metallic dust tends to combine with the sulphate (SO_4) radical and free metallic copper is immediately deposited. The sub-

3

stantially simultaneous mixing of the solution and suspension and application to the reflective surface insures that the metallic copper will be deposited in a firmly adhering coat at the maximum rate and without loss of efficiency due to partial reaction and deposition as might occur in a mixing chamber. The homogeneous metal suspension, due to violent agitation, provides maximum reaction efficiency and an even coating of the free hard copper, and is absolutely necessary to the practical success of the method.

The method is not limited to the use of any one metal dust. Zinc is preferred because it is the most easily obtained and is the cheapest of all metallic dusts commercially available. Also it acts instantaneously to precipitate the copper from the copper sulphate and causes the most nearly complete reaction of the copper sulphate thus wasting a minimum amount. However, dusts of iron, cadmium, nickel, cobalt, chromium, tungsten and molybdenum are all adaptable and commercially preferable more or less in the recited order.

In carrying out the method, each of the conduits carrying the copper sulphate solution and phosphoric acid, the metal suspension and the compressed air supply 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 nozzle is provided with a lever operated master valve so that the operator may cut the spray on or off at will.

In extensive tests with this method it has been found that a copper sulphate solution having a proportion of 16 ounces CuSO_4 and $1\frac{1}{2}$ ounces of phosphoric acid to the gallon of water and a metal suspension of 3.2 ounces to the gallon of water is to be preferred and gives a coating of maximum quality. It has been found possible, however, to vary the strength of the solution in the proportion of 6 to 40 ounces of CuSO_4 per gallon of water with a variation of the acid from $\frac{1}{4}$ ounce to 2 ounces per gallon of water, and to vary the density of the suspension in the range of 1 to 6 ounces of metal per gallon of water.

It has been found that the copper layer deposited by this method completely seals and protects the silver reflecting layer, the copper is harder and of better appearance and that there is no interaction between the coats which might spot or impair the reflecting quality of the mirror.

While there is herein shown and described the preferred embodiments of the invention, it is nevertheless to be understood that minor changes may be made therein without departing from the spirit and scope of the invention as claimed.

What I claim is:

1. The method of copper plating a silvered surface by galvanic action which consists in simultaneously spraying a solution composed of 6 to 40 ounces of copper sulphate and $\frac{1}{4}$ to 2 ounces phosphoric acid per gallon of water, and a mixture of water and metallic dust onto said surface, the dust being in a concentration of 1 to 6 ounces per gallon of water and homogeneously suspended in the water, said dust 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 providing a solution composed of 6 to 40 ounces of copper sulphate and $\frac{1}{4}$ to 2 ounces of phosphoric acid per gallon of water in

4

providing a container of water having 1 to 6 ounces per gallon of metallic dust therein, said dust being selected from the group of metals which consists of zinc, iron, cadmium, nickel, cobalt and chromium in vigorously and continuously agitating said metallic dust and water to the point of causing said dust to be suspended homogeneously in said water and in then spraying said solution and said water mixture simultaneously onto said silvered surface.

3. The method of copper plating a silvered surface which consists in providing a solution composed of 6 to 40 ounces of copper sulphate and $\frac{1}{4}$ to 2 ounces of phosphoric acid per gallon of water, in providing a container of water having 1 to 6 ounces per gallon of metallic dust therein, said dust being selected from the group of metals consisting of zinc, iron, cadmium, nickel, cobalt and chromium in mechanically agitating said water and metallic dust by a mechanical stirring means to the extent that said dust is homogeneously suspended in said water, and in then simultaneously spraying said solution and the water mixture onto said silvered surface.

4. The method of copper plating a silvered surface by galvanic action which consists in simultaneously spraying onto said surface a solution composed of 16 ounces of copper sulphate and $1\frac{1}{2}$ ounces of phosphoric acid per gallon of water, and water having 3.2 ounces per gallon of a metallic dust homogeneously suspended therein, said metallic dust being selected from the group of metals consisting of zinc, iron, cadmium, nickel, cobalt and chromium.

5. The method of making a mirror which consists in supporting a transparent plate on a rack, in applying silvering solutions thereto whereby the plate is silver coated, in immediately water rinsing said coating, and while the coating is still wet from rinse water immediately applying thereto a spray of 6 to 40 ounces of copper sulphate and $\frac{1}{4}$ to 2 ounces of phosphoric acid per gallon of water and simultaneously applying thereto a mixture composed of 1 to 6 ounces of finely divided metal dust per gallon of water, said metallic dust being homogeneously suspended in the water, said metallic dust being selected from the group of metals consisting of zinc, iron, cadmium, nickel, cobalt and chromium.

6. The method of making a mirror which consists in supporting a transparent plate on a rack, in applying silvering solution thereto whereby one surface of said plate is silver coated, in immediately water rinsing said coating and while the coating is still wet from rinse water immediately spraying thereon a solution composed of 16 ounces of copper sulphate and $1\frac{1}{2}$ ounces of phosphoric acid per gallon of water and simultaneously spraying thereon water having 3.2 ounces of metallic dust per gallon suspended therein, said dust and water being under substantial agitation and said dust being homogeneously suspended in the water at the moment of spraying onto said surface, said dust being selected from the group of metals consisting of zinc, iron and cadmium.

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