

# UNITED STATES PATENT OFFICE

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## METHOD OF FORMING SILVER SULFIDE COATINGS

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This invention relates to the method of forming silver sulphide coatings on articles having a silver surface, and more particularly to the formation of a uniform, black silver sulphide deposit upon solid silver or silver plate.

There are certain applications where a uniform deposit of silver sulphide upon silver or silver plate is very desirable. For example, in the case of certain types of electrical apparatus employing silver or silver surfaced conductors through which high frequency currents are passed, it has been found advantageous to provide on such conductors a surface layer of silver sulphide for the purpose of controlling such currents in desired manner. In such cases, it is quite essential that the surface deposit or layer of silver sulphide be even and uniform. The production of an even, uniform deposit of silver sulphide on silver has usually been found to be very difficult, if not even impossible, according to prior art methods.

The primary object of my present invention is to provide an improved method of forming a coating or deposit of silver sulphide upon articles having silver surfaces, which method will not be subject to the limitation of conventional, prior art methods.

More particularly, it is an object of the present invention to provide an improved method of forming a uniform, even film or deposit of silver sulphide on solid silver or on silver plate regardless of what the silver may be deposited upon in the latter case.

Another object of my present invention is to provide an improved method of forming silver sulphide deposits on silver as aforesaid which can be very easily and accurately controlled between wide limits for the purpose of varying the color and density of the deposit.

Still another object of my present invention is to provide an improved method of forming silver sulphide deposits on silver whereby black deposits of silver sulphide can be applied quickly and easily, the resulting deposits not being harmful to the silver and affecting it only by turning the surface thereof black.

A further object of my present invention is to provide an improved method of forming silver sulphide coatings as aforesaid which will not require complicated equipment such as has been required by prior art methods and which is very inexpensive to carry out in practice.

Still a further object of my present invention is to provide an improved method of forming deposits of silver sulphide on silver surfaces which

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can be readily practiced even by one not skilled in the art.

It is also an object of my present invention to provide an improved method of forming silver sulphide deposits or coatings on silver which is highly efficient in use.

In accordance with my present invention, the article having a silver surface is first treated with a water solution or water emulsion of a film-forming hydrophilic substance to which may be added a wetting agent. The film-forming hydrophilic substance may be a water soluble wax-like derivative of a polyhydric alcohol, or a film-forming hydrophilic colloid. This forms a film on the surface of the silver. The water present in the film is allowed to evaporate, and, when the film is dry, the treated article is placed in an atmosphere containing from about 90 percent to 100 percent humidity and a suitable concentration of free hydrogen sulphide. The operation may be performed at room temperature. The speed of formation of the film is increased by increase in humidity, temperature, concentration of the hydrogen sulphide and the time of exposure. The silver sulphide deposits which are formed are an integral part of the surface and cannot be rubbed off easily.

The novel features that I consider characteristic of my invention are set forth with particularity in the appended claims. The invention itself, however, together with additional objects and advantages thereof, will best be understood from the following description of one embodiment thereof:

A solution or emulsion is prepared by dispersing a film-forming water soluble, wax-like derivative of polyhydric alcohols, or a film-forming hydrophilic colloid in water with the aid of a wetting agent. Among the wax-like derivatives of polyhydric alcohols which I have found satisfactory is one sold under the trade name "Carbowax 4000." This is a hard, translucent solid composed of polyethylene glycols having an average molecular weight of around 4000 and a melting point of from about 50° C. to about 55° C. Gelatine, agar, etc., may be mentioned as representative of film-forming hydrophilic colloids which are suitable for use according to my present invention. Any one of a number of well known wetting agents, such as triethanolamine, Triton NE Special (a non-ionic wetting agent consisting of an alkylated phenoxy polyethoxy ethanol in which the alkylating groups may contain from 5 to 16 carbon atoms), or the like may also be used, if desired. A typical formula which is representa-

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tive but which is not to be taken as limiting, since the particular ingredients may be varied and since various concentrations thereof may be employed, is as follows:

	Parts
Carbowax 4000.....	10
Triton NE Special.....	2
Triethanolamine .....	2
Water .....	100

A typical, representative formula employing one of the film-forming hydrophilic colloids is the following:

	Parts
Gelatine .....	5
Triton NE Special.....	2
Triethanolamine .....	2
Water .....	100

The ingredients set forth above are prepared in solution or in an emulsion. The silverware or silver surfaced article on which the silver sulphide deposit is to be formed is treated with this solution or emulsion, as by dipping, spraying, or the like, to form a film of the solution or the emulsion thereon, as the case may be. The excess liquid is allowed to drain off from the article and the water in the film is permitted to evaporate until the surface is air dried. The treated silver article is then hung or otherwise suitably placed in an enclosure in which is present from about 90 percent to about 100 percent humidity and sufficient hydrogen sulphide to cause blackening. A very easy and satisfactory method of accomplishing this atmosphere is to place in the enclosure an open jar (preferably of glass) containing about 500 ml. of water for every cubic foot of air present in the enclosure, the water being saturated with hydrogen sulphide. The humid hydrogen sulphide fumes emanating from the hydrogen sulphide solution will react chemically with the silver sulphide surface to produce a firm, adherent, uniform, even silver sulphide deposit thereon. The reaction may be carried out at room temperatures, that is, between approximately 70° F. and 90° F., the higher the temperature, the more speedy being the reaction. The density of the deposit of silver sulphide and the blackness of the color thereof which is desired determine the time of exposure, which may vary from about one hour to several hours.

From the foregoing description, it will be apparent to those skilled in the art that I have provided a novel and simple, yet highly effective method of providing a uniform, adherent coating of silver sulphide upon a silver surface. Although I have specified certain particular materials which may be employed in treating the silver article according to my present invention, it will be obvious that other equivalent materials, in varying concentrations, may be employed. I therefore desire that my invention shall not be limited ex-

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cept insofar as is made necessary by the prior art and by the spirit of the appended claims.

I claim as my invention:

1. The method of forming a coating of silver sulphide on a silver surface which comprises first treating said silver surface with a film-forming hydrophilic substance, then drying said treated surface, and then exposing said treated surface to a humid atmosphere saturated with hydrogen sulphide and containing from about 90 percent to about 100 percent humidity until a desired coating of silver sulphide has formed on said treated surface.

2. The method of forming a coating of silver sulphide on a silver surface which comprises first treating said silver surface with a solution of a water soluble wax-like derivative of a polyhydric alcohol, then drying said treated surface, and then exposing said treated surface to a humid atmosphere saturated with hydrogen sulphide and containing from about 90 percent to about 100 percent humidity until a desired coating of silver sulphide has formed on said treated surface.

3. The method of forming a coating of silver sulphide on a silver surface which comprises first treating said silver surface with a water emulsion of a film-forming hydrophilic colloid, then drying said treated surface, and then exposing said treated surface to a humid atmosphere saturated with hydrogen sulphide and containing from about 90 percent to about 100 percent humidity until a desired coating of silver sulphide has formed on said treated surface.

4. The method of forming a coating of silver sulphide on an article having a silver surface which comprises first treating said silver surface with a water emulsion of a film-forming hydrophilic substance, then drying the treated surface, and then placing said article in an enclosure containing a solution of approximately 500 ml. of water for every cubic foot of air in said enclosure and saturated with hydrogen sulphide whereby to subject said treated surface to humid hydrogen sulphide fumes emanating from said solution, and retaining said article in said enclosure until a desired coating of silver sulphide has formed on said surface.

5. The invention set forth in claim 4 wherein the contents of said enclosure are maintained at temperatures of between about 70° F. and 90° F.

CLIFFORD W. MELL.

#### REFERENCES CITED

The following references are of record in the file of this patent:

#### UNITED STATES PATENTS

Number	Name	Date
2,079,690	Grisdale .....	May 11, 1937
2,339,200	Sowa .....	Jan. 11, 1944