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ARTICLES HAVING TARNISH-RESISTING SURFACE AND PROCESS OF MAKING SAME

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This invention relates to articles having tarnish-resisting exterior strata of metal and to processes of making such articles.

Although the invention, in its broadest aspects, is not to be limited to an article in which such a stratum includes silver as an ingredient and is a separate and distinct entity, as to composition, from the rest of the article, yet the invention has been developed with especial reference to, and will therefore be described in connection with, such an article.

It has long been well known that silver and silver plated articles were readily tarnishable and required frequent cleaning in order to look well. Such cleaning is not only a great inconvenience to the user and dealer but there is great danger that it will result in abrasion of and therefore marring of the surface of the article, which is annoying to the user and dealer and also a source of expense to the latter because he is compelled to dispose of such marred articles as damaged or shopworn and therefore at a loss, more or less, of profit.

This very serious difficulty is overcome according to the present invention by the provision in such articles of an exterior stratum or surface layer consisting of a complete mixture of metals, including silver and a metal, such as chromium, whose shielding properties will protect the stratum or layer against tarnishing under the usual conditions of use or exposure to the atmosphere; the stratum or layer being continuous so that at no point therein is there any tendency to tarnish and of such a depth that when worn down by grinding, polishing, or the like, its tarnish-resisting quality will be preserved.

In the preferred embodiment of the invention, the said surface layer or exterior stratum is obtained by electrodeposition.

In carrying out the invention according to this preferred embodiment of it, the article to be coated, which may be of any material suitable for the purpose, and which usually is of electrically conductive material, is immersed to the required extent in a solution capable of delivering the silver, and the necessary shielding metal, such as chromium, in a completely mixed condition and in a continuous coating to the surface of the article to be coated when such surface is included as a cathode in the plating circuit. While many metals are capable of being used as a shielding metal, in practice it has been found that chromium is eminently satisfactory for the purpose, since when thus electrodeposited with the silver, the electrodeposited coating acts as if it were an alloy of the two metals, viz: chromium and silver. Such a coating, when finished by the usual methods of polishing, burnishing and buffing and the like, will maintain its color and lustre against the action of the atmosphere. Such a tarnish-resisting coating when produced by the use of chromium has the further advantage that it is harder than the electrodeposited silver surface and hence less easily marred or worn. Also, the coating so deposited in a completely mixed condition and in a continuous layer has no tarnishable spots or islands.

It would be useless and it is also unnecessary to attempt to state any theory as to the action of the chromium in this mixture. It is sufficient to state that whatever be the explanation the fact is that the shielding properties of the chromium, however exerted, result in the production of a surface which is, as a whole, tarnish-resisting.

A few examples will now be given of the methods of carrying out the invention.

In making the bath, chromium sulphate is dissolved by boiling in sufficient water. As soon as this has been accomplished, chromic acid is added. Then silver chromate is mixed with the solution and sufficient water added to make up to volume. It is advisable to maintain the solution at the boiling point for say 15 or 20 minutes after the silver chromate has been added, and at all times during the making of the bath the temperature of the solution should not be allowed to fall below the temperature at which the bath is to be used in plating. This will be generally about 65 to 70 degrees C.

In practice it has been found that the range of percentage will be about as follows: chromium sulphate, not over 4%. The best results are obtained with about 1%. Chromic acid not above 30%.

The term per cent as used assumes that 1 per cent equals 10 grams of chromium sulphate or chromic acid, respectively, per liter of solution.

Silver chromate, in sufficient amount to form a saturated solution and supply an excess. The excess serves to maintain the strength of the bath during the plating operation, because as silver and chromium are removed from the bath, a corresponding amount of the excess silver chromate goes into the solution.

In practice, the invention has been carried out with a direct current generator giving a difference of potential between poles of 8 to 10 volts.

The current density or amperes per square inch of cathode surface will range between about ½ and 3 amperes.

In general the percentage of silver in the deposit and the character of the deposit, (particularly as to its size of crystals), will be determined by the density of the current, the percentage of chromic acid, the percentage of the chromium sulphate, the relation of area of anode surface to area of cathode surface, the distance between the anode and cathode, and the temperature of the bath.

The following examples will illustrate the manner of carrying out the invention:

Example I.—To plate a deposit containing about 50% silver and 50% chromium:

(*a*) *Bath*

The plating bath is proportioned as follows:

Chromic acid (CrO_3)	30 grams
Chromic sulfate ($Cr_2(SO_4)_3$)	5 grams
Silver chromate (Ag_2CrO_4)	An excess
Water sufficient to make one liter.	

The bath is made as follows: Place the chromic acid and chromium sulfate in a glass beaker or other suitable container. Add about 800 gms. of water. Heat to boiling. Now add silver chromate in a quantity sufficient to give an excess forming a layer on the bottom of the container. After the addition of silver chromate add enough water to bring the volume up to one liter. Boil for a few minutes. The bath is now ready for plating.

(*b*) *Plating process*

1. The circuit.—The current may be generated by any suitable means, such as a dynamo or battery. It is necessary to have a rheostat suitable for closely controlling the current and an ammeter for reading its strength. The difference in potential between anodes and cathodes of course must be sufficient to deposit chromium. This is about 4 volts.

2. Anodes and cathodes.—The anodes may be of some insoluble metal. Lead has been used satisfactorily. The anode surface may well be approximately twice that of the cathode.

3. Actual plating.—Allow the solution to cool to 50° C. It should be maintained at this temperature as nearly as possible. Immerse the anodes. Immerse the cathode (the article to be plated) before turning on the current. The current should be turned on to give a density at the cathode of about one ampere per sq. inch. Plating for five minutes gives a good deposit, sufficient for buffing, but for heavier deposits a longer time is necessary. The anodes may be from ½ to 2 inches from the cathode.

Sometimes the anode will coat over with a deposit. In this case it is advisable to remove such deposit so as to maintain a clean anode. Frequently when starting a bath, it may be found to be sluggish in action. Under this condition, it is often convenient to plate a blank before attempting to plate the regular work. Usually a few minutes of use "activates" the plating system. If for any reason the bath is allowed to cool below the plating temperature, it should be re-heated at least 20° C. above the plating temperature before further plating is done.

Example II.—To plate a deposit containing about 70% silver and 30% chromium:

(*a*)

30 gm. chromic acid.
10 gm. chromic sulfate.
Excess silver chromate.

(*b*)

(1) Circuit—same as for Example I.
(2) Anodes and cathodes—same as for Example I.
(3) Plating temperature 75° to 73° C.
Current density (¾ to 1) ampere per sq. inch.

By the use of the term "complete mixture" and "continuous" in this specification and claims as describing the coating, it is not intended to limit the coating to one having at all points the same percentage composition of the tarnishable metal, but merely to make clear the fact that there is such an intimate molecular association of the two metals at all points that the surface is throughout tarnish-resisting.

What is claimed is:

1. The process of providing an article with a tarnish-resisting coating comprising a mixture of silver and chromium, which consists in preparing an aqueous bath containing at least 3 per cent chromic acid, and a compound of the silver, using the article to be coated as a cathode, passing a plating current through the solution by means of a suitable anode, and maintaining an excess of said silver salt in contact with the bath.

2. The process of providing an article

with a tarnish-resisting coating comprising a mixture of silver and chromium, which consists in preparing an aqueous bath containing at least 3 per cent chromic acid, chromium sulphate and a compound of the silver, using the article to be coated as a cathode, passing a plating current through the solution by the use of a suitable anode, and maintaining an excess of said silver salt in contact with the bath.

In testimony whereof, we have hereunto set our hands.

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