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(54) A METHOD OF POLISHING AND RESTORING A SILVER-PLATED ARTICLE AND A SOLID DRY FORMULATION FOR CARRYING OUT THE METHOD

(71) We, H.L.P. IMPORTS LIMITED, of 214 Bishopsgate, London, EC2, England, a British company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the polishing and restoring of silver-plated articles, in particular electroplated silver articles or antique Sheffield plate, i.e., plate obtained on hard metal such as nickel or copper, and to solid dry formulations for this purpose

The problem of the tarnishing of silver, particularly in large towns or where industrial atmospheres are prevalent, has been encountered for many years. In the case of atmospheres polluted by the presence of hydrogen sulphide, silver sulphide is formed on the surface of the silver-plated article as a result of the reaction which takes place in the presence of oxygen.

The various conventional polishing compositions, including powders, pastes, foams and liquids, all rely on the removal of the tarnish either by mechanical action due to abrasive components in the powders or pastes, or chemical action due to materials dissolved in the cleaning liquids which react with silver sulphide, the tarnish being dissolved from the surface of the plated article.

In either case, the polishing action involves the removal of minute amounts of silver. Repeated polishing carried out on a layer of silver which is only several microns thick at most must inevitably lead, after a period of time, to exposure of the underlying base metal. If the base metal is exposed over a sufficiently large area, the only satisfactory recourse has been for the article to be electroplated once again which is an expensive procedure.

On the other hand, it has been known for a considerable time that silver is deposited from a silver salt in the presence of a reducing agent. However, this procedure is only carried out on a commercial or industrial scale with the use of a cyanide such as potassium cyanide in order to give a coherent deposit. The use of cyanides makes the process dangerous and undesirable from the viewpoint of the operators who can only carry it out under strictly controlled conditions.

We have now discovered that the polishing of silver-plated, in particular electroplated silver or Sheffield plate articles, can be carried out satisfactorily in the home by the use of compositions which restore to the polished article at least as much silver as is removed in the polishing operation and which therefore can be carried out repeatedly over lengthy periods of time without the base metal being exposed, thereby obviating the need for the article to be replated under commercial conditions either by electroplating or commercial silver-plating involving the use of the dangerous cyanides as mentioned above.

According to one aspect of our invention, we provide a method of polishing a silver-plated article comprising the steps of a method of polishing and restoring a silver-plated article, comprising the steps of making up a paste by the addition of water to a dry powder free of any toxic component and therefore suitable for domestic useage, said powder comprising at least one silver generating component selected from silver oxide, silver nitrate, silver chloride, silver carbonate, silver acetate and silver phosphate, together with at least one reducing component for said silver-generating component, said reducing component being selected from

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	potassium hydrogen tartrate, sodium potassium tartrate, sodium sulfite, sodium metabisulfate and sodium thiosulfate, said silver generating component and said reducing component being in powdered form; applying said paste to at least part of	
5	the surface of the silver-plated article; allowing the paste to remain on the surface to which it has been applied; and, thereafter, removing the paste by the application to the coated article of a fabric, the removal of the paste being accompanied by the rubbing of the coated portions of the surface with said fabric. According to another aspect of our invention, we provide a solid, dry	5
10	formulation free of any toxic components and therefore suitable for the silver polishing and restoration of silver-plated articles under conditions of domestic use, said formulation comprising, in powdered form, at least one silver generating component selected from silver oxide, silver nitrate, silver chloride, silver carbonate, silver acetate and silver phosphate; and at least one reducing component for said silver generating component, said reducing component being	10
15	selected from potassium hydrogen tartrate, sodium potassium tartrate, sodium sulfite, sodium metabisulfate and sodium thiosulfate; said silver generating component, and said reducing component being in powdered form and constituting a homogeneous mixture.	15
20	Additionally, at least one specific polishing agent selected from conventional abrasives may be included in the powder, which may also additionally include at least one anti-caking or drying agent. Contrary to what would have been expected from the prior art, our experiments have shown that various mixtures of silver salts and/or silver oxide with suitable reducing agents function as satisfactory polishing compositions with	20
25	the considerable advantage that the application of such pastes and subsequent removal by rubbing or polishing as indicated above leads to the addition or replacement of silver on the surface and therefore avoids the danger of conventional polishing compositions which is the exposure of the base metal after repeated polishing operations.	25
30	Our experiments have also shown that if either conventional polishing agents are omitted altogether or very mild agents such as Bentonite or Fullers Earth are used, then a surface with a patina corresponding to that of antique plate can be obtained which is advantageous in certain circumstances. On the other hand, if a so-called bright finish is needed, then it is necessary to	30
35	include varying amounts of conventional polishing agents such as the diatomaceous earths, e.g., Kieselguhr, often obtained as Celite (trade mark), rouge (red ferric oxide) or calcium carbonate, e.g., in the form of whiting or Newburg chalk. Although we have found that silver oxide is a perfectly satisfactory source of silver, we have also obtained good results by using silver nitrate, silver chloride,	35
40	silver carbonate, silver acetate and silver phosphate, all of which are readily available in commerce. Various forms of reducing agent may be used but a preferred material is so-called cream of tartar or potassium hydrogen tartrate. We may, however, also use sodium potassium tartrate, sodium sulphite, sodium metabisulphate or sodium thiosulphate. Sodium thiosulphate is less practicable	40
45	because of the strong smell of sulphur dioxide which would be evolved. We have also found in many cases that the composition is improved by the presence of a chloride such as sodium chloride or an ammonium chloride. The precise effect of the sodium chloride is not entirely clear but it is believed to function as a source of chloride ions. It is also possible that in compositions which	45
50	do not contain conventional polishing agents the sodium chloride acts to some extent as a polishing agent until it has been fully absorbed by the chemical reactions which take place on the surface of the article being polished. Minor amounts of other ingredients may also be present such as hydroxyethyl activities and improved alcohol.	50
55	cellulose and isopropyl alcohol. Hydroxyethyl cellulose increases the viscosity, whilst isopropyl alcohol increases the wetting power of our mixture. When we use silver oxide we can also make a small addition of ammonia which improves the wetting power. Improved wetting power may be necessary if the surface is very dirty or greasy. It is part of our invention to prepare either powders or pastes involving the	55
60	various ingredients needed to polish the silver plated article whilst restoring to the article being polished at least as much silver as is being removed by the polishing operation. Our preferred composition includes either silver nitrate or silver oxide together with a sufficient amount of potassium hydrogen tartrate to reduce the nitrate or oxide to silver when water has been added to the powder and the paste is	60

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	applied to the surface of the silver, together with small amounts of sodium chloride and of Kieselguhr as a conventional polishing agent. The present invention is further illustrated by the following examples.	
5	Example 1 A powder was prepared from the following components, all parts quoted being by weight:	5
10	Silver nitrate 2 Potassium hydrogen tartrate 10 Sodium chloride 2 Kieselguhr 1.85.	10
15	The ingredients were finely powdered and then mixed together. When the powdered mixture was to be used, water was added to successive amounts of the powder in sufficient quantities to form a paste in each case. The paste was applied to the article to be polished by means of a cloth or brush and after a very short period of not more than about one minute, coated portions were rubbed with a polishing cloth to remove the paste coating. The result was found to be a fine polish	15
	on the treated part of the article and extensive repetitions of this operation were found to reproduce the same result without any indication of thinning of the silver coating of the electroplated article or any appearance of the underlying base metal.	
20	Example 2 The following components and parts by weight were used:	20
25	Silver oxide 6 Potassium hydrogen tartrate 12 Sodium chloride 2 Kieselguhr 1.5.	25
30	These ingredients were again finely powdered and mixed as in example 1. Portions of the powder were made into pastes with water and applied to an electroplated silver article as in the case of example 1; this led to a good polish on the treated parts without any indication of any removal of silver, even after a very large number of applications.	30
35	Example 3 The polishes of examples 1 and 2 were used on small portions of the surface of an electroplated article, where previous repeated polishings with conventional polishing agents had led to a sufficient thinning or removal of the silver layer for the underlying base metal to be exposed. Repeated applications of paste formed from the powders of examples 1 and 2 were able, after some time, to cover the exposed portions of base metal sufficiently for the latter to be no longer visible.	35
	Example 4 This powder comprised (in parts by weight) the following components:	
40	Silver nitrate 2 Sodium chloride 2 Potassium hydrogen tartrate 14 Iron Oxide 0.5	40
45	The silver nitrate and ammonium chloride were finely ground and mixed together and thereafter mixed with powdered potassium hydrogen tartrate and finely ground iron oxide. Water was added to the resulting mixture to form a paste. This was used on exposed base portions of a silver-plated copper surface as in example 3, and in each case the copper was eventually covered by a continuous bright film of silver.	45
50	Example 5 The following ingredients and proportions were employed:	50
	Silver oxide 4.5 Sodium chloride 15 Potassium hydrogen tartrate 12	

4	1,603,875	4
	These ingredients finely powdered were mixed together, formed into a paste with a sufficient amount of water and used to polish an electroplated silver article as in examples 1 and 2 above. A so-called antique or matt finish was obtained which was less bright than that obtained in examples 1 to 4.	
5	Example 6 The same ingredients were powdered and mixed together as in example 5, together with the addition of 1% of Celite (trade mark), a proprietary form of Kieselguhr sold by Johns Manville Company, U.S.A. The results obtained with this paste both on unworn portions of an	5
10	electroplated silver article and on worn or exposed portions were similar to those of example 5, i.e., a so-called antique finish was obtained.	10
	Example 7 The following components and parts by weight were used:	
15	Silver nitrate 4.0 Potassium hydrogen tartrate 28.0 Sodium chloride 4.0 Kieselguhr 1.0 Hydroxyethyl cellulose 0.1 Water 10.0	15
20	Water 10.0 Isopropyl alcohol 2.0	20
25	The solid components were first finely ground and mixed together and thereafter made into a paste form with the 10 parts of water and 2 parts of isopropylalcohol. The paste obtained was found to be as effective as those obtained by means of the powders of examples 1 to 6 above, a bright finish being obtained in this case both on unworn and on exposed portions of electroplated silver articles.	25
	Examples 8 and 9 The following two compositions were obtained, all parts given being by weight.	
	Example 8 Example 9	
30	Silver nitrate 2 —	30
	Silver oxide — 6 Cream of tartar 14 16	
	Common salt 2 2	
	Celite 1.5 2	
35	The ingredients in both cases (8 and 9) were finely ground together and made into a powder. The powder was made into a paste with water and rubbed either on unworn or exposed portions of electroplated silver articles; the resulting products were found to have an attractive antique finish at the treated parts. The following is an additional example which has been found to be	35
40	satisfactory. All parts are by weight:	40
	Example 10	
	Silver nitrate Ammonium chloride	
	Kieselguhr 0.5	45
45	Sodium sulphite (Na ₂ SO ₃ . 7H ₂ O) 5 Hydroxy ethyl cellulose 0.1	43
	Example 11 Silver nitrate 2 A mmonium chloride 2	
	Ammonam omorae	50
50	Kieselguhr 0.3 Sodium metabisulphate 5	50
	Example 12	
	Silver nitrate 2	
55	Sodium chloride 2 Iron oxide (of fine particle size) 0.5 Sodium thiosulphate 5	55

10. A solid, dry formulation free of any toxic components and therefore suitable for the silver polishing and restoration of silver-plated articles under

conditions of domestic use, said formulation comprising, in powdered form, at least one silver generating component selected from silver oxide, silver nitrate, silver chloride, silver carbonate, silver acetate and silver phosphate; and at least one reducing component for said silver generating component, said reducing component being selected from potassium hydrogen tartrate, sodium potassium

tartrate, sodium sulfite, sodium metabisulfate and sodium thiosulfate; said silver generating component, and said reducing component being in powdered form and

constituting a homogeneous mixture.

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11. A dry formulation as claimed in claim 10 which additionally comprises at least one specific polishing component selected from conventional abrasives.
12. A dry formulation according to claim 10 or 11, which additionally comprises at least one anti-caking or drying component.

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