

Patented Sept. 15, 1931

1,823,402

UNITED STATES PATENT OFFICE

GRINNELL JONES AND DOROTHY WEED MARSHALL, OF CAMBRIDGE, MASSACHUSETTS,
SAID DOROTHY WEED MARSHALL, ASSIGNOR TO SAID JONES

SILVER CLEANING COMPOSITION

No Drawing.

Application filed January 21, 1930. Serial No. 422,479.

This invention relates to an improved method of inhibiting the formation of dark colored substances when polishing silver and other metals with abrasive polishes, and more particularly to an improved silver cleaning and polishing composition.

Hitherto, in the removal of tarnish from articles of silver and the imparting of a bright polish to the silver, it has been necessary to rub the articles with a cloth, or its equivalent, treated with a powder, paste, cream or suspension, containing an abrasive material, such as infusorial earth or whiting, admixed with a detergent, such as soap, and a dye and/or perfume, where desired. To secure a polished surface an abradant is necessary, as non-abrading cleaners leave a matt finish on the surface of the cleaned article. However, when such abrading polishing compositions are used on silverware or copperware, both the cloth and the polishing agent quickly become blackened. This blackening of the polishing agent and the polishing cloth tends to stain the hands and fingernails of the user and is objectionable to many people.

It has now been found that this objectionable blackening is due to the formation of minute particles of metal, such as silver, formed by the abrading action of the cleaner. Unless the silver or copper articles are tarnished to a very high degree, the greater part of the blackening is due to metallic particles instead of the metal sulphides. This blackening occurs with untarnished articles, and we have demonstrated by suitable chemical tests that the blackened polish contains, when silver is polished, metallic silver in finely divided form and that the silverware suffers a measurable loss of weight when rubbed with the polishing agent, the loss in weight amounting to as much as 3 milligrams from a single polishing of a teaspoon.

It is an object of this invention to provide an improved process for inhibiting the blackening of silver and other metallic articles occurring during cleaning.

It is a further object of this invention to provide an improved process for inhibiting blackening of metal polishes during use by

incorporating in the polishes compounds adapted to dissolve the abraded metal particles.

It is also an object of this invention to provide an improved process for inhibiting the blackening incident to the use of abrasive metal polishes by incorporating in the polishes compounds adapted to react with the abraded particles in the presence of air.

Yet another object of this invention is the provision of an improved metal cleaning polish containing a blackening inhibitor.

Still another object of this invention is the provision of an improved silver cleaning polish containing a blackening inhibitor.

Another object of this invention is the provision of an improved blackening inhibitor for abrasive polishes for cleaning silver and other metals.

These and other desirable objects and advantages of the present invention will be described in the accompanying specification, a certain preferred method of operation and a plurality of substances adapted to subserve the purposes of the invention being described hereinafter as illustrative of the concepts of the invention, but, since other specific compounds and process steps may be employed without departing from the spirit or the scope of this invention, it is not intended to be limited to the ones herein disclosed, except as such limitations are clearly imposed by the appended claims.

We accomplish the objects of our invention in a new and novel manner by incorporating in an abrasive polishing composition a substance which, when dissolved in water, is capable of dissolving finely divided metals, such as silver or copper or their alloys, in the presence of air. In the description which follows, the alloys of copper, as well as the metal itself, are to be considered as the equivalents of silver, as it has been found that they react in substantially the same manner, and the term silver will be used broadly to include the metals which, when abraded, are susceptible of being dissolved in the presence of air, by substances to be described further. Some of the substances which meet this condition are obviously unsuited for use in ma-

70

75

80

85

90

95

100

terials intended for domestic use, although entirely suitable from the standpoint of chemical reactivity and economy in price. Among these materials may be mentioned the 5 cyanides. Still other substances, such as ferric chloride and copper chloride, which aid in inhibiting blackening of the polishing agent used, have a tendency to stain the silverware, and are, therefore, unsuited for 10 this purpose.

As above intimated, we have found that soluble salts containing an anion which is capable of combining chemically with the silver ion to form complex ions, have a sufficient 15 solvent power on silver when it is in an extremely divided form, such as that resulting from the use of an abrading polishing compound, and in the presence of air, to prevent the blackening of the polish and cloth, 20 and yet do not damage the silver in the form of massive silver articles. Whether or not this theoretical explanation of the action is correct, we have found by experiment that the chlorides, bromides and iodides of sodium 25 and potassium and other alkali metals, which may collectively be called the halide salts of the alkali metals, are effective in preventing blackening of the polishing agent when added to abrasive polishes without any harmful 30 effects on the silver articles or on the hands of the user. The fluorides are excluded from further consideration, as are the cyanides, in view of their poisonous character. 35 The corresponding salts of the alkaline earths are useful and effective as blackening inhibitors in the improved combinations to be described, but they are not as suitable as the alkali halides for this purpose because 40 they interfere to some extent with the detergent effectiveness of soap as an ingredient of the polish when it is used.

In addition to the compounds included in the above classification, effective results have 45 also been secured with mercuric chloride and caustic soda as well as with a mixture of acetic acid and hydrogen peroxide. The first member of this group is, however, unsuited, because it deposits mercury and is poisonous. 50 Caustic soda is a strong lye and is unsuited because of its corrosive effect on the hands of the user. The mixture of acetic acid and hydrogen peroxide is unstable and preferably should be mixed immediately before use. 55 The alkali halides, above considered, and set forth as the preferred blackening inhibitors to be added to silver and other metal polishes now in use, meet substantially all of the following specifications:

60 1. They have a bleaching action which entirely prevents or substantially reduces the blackening during use.
2. They do not damage the silverware by scratching, staining or corrosion, or in any 65 other manner, even if the user is careless in

not rinsing off completely and promptly after using.

3. They will not injure the hands of the user by staining, corrosion or astringency, cause no pain, and do not leave odor on the 70 hands.

4. They are chemically stable and are not subject to decomposition or deterioration by putrefaction, fermentation or chemical instability, or by chemical reaction with any 75 ingredient in the polish.

5. They do not react chemically with soap in such a way as to destroy its value as a detergent.

6. They are non-poisonous.

7. They are non-inflammable and non-explosive.

8. They do not have an unpleasant odor.

9. They are not volatile, and, thus, are not liable to be lost by evaporation before the 85 polish is consumed.

10. They are not injured by freezing nor by the highest temperature likely to be encountered in transportation and use.

11. They are soluble in water, which permits their use in solution, instead of as a solid.

Among the various substances which can be used, and which meet the above qualifications, we prefer to use sodium chloride. In addition to its effectiveness as a blackening inhibitor, it is non-poisonous, non-corrosive to silverware or to the hands of the user, and is non-volatile, non-odorous, and readily available at a low price, which permits the desirable 95 improvements of the present invention to be incorporated readily in abrasive polishes generally without any substantial increase in their costs.

The sodium chloride may be incorporated 105 in an abrasive cleaner in substantial amounts, and, preferably, in an amount sufficient to give a saturated solution. A suitable range may include from 5 to 15 per cent, although, it will, of course, be understood, that wide 110 variations from these limits may be permitted without departing from the spirit and scope of the invention. Sodium bromide is effective in amounts from 4 per cent upwards, as is sodium iodide.

The following is given as an example of 115 compositions of matter suitable for use in polishing silver and other metals and which contain an alkali halide as a blackening inhibitor:

	Per cent
Infusorial earth	20
Sodium oleate	20
Sodium chloride	10
Water	50

The proportions of the ingredients may, however, as above intimated, be varied over a wide range, without departing from the spirit and scope of the invention, and other 130

alkali halides or other substances capable of dissolving finely divided silver may be substituted for the sodium chloride.

This particular function of the halides and analogous compounds in preventing blackening due to abraded silver or other metallic particles, is novel in the combination herein set forth, although the solvent action, as such, of such substances on silver has been known 10 for over seventy years without any practical application of such knowledge being disclosed to the public to its benefit.

In a comprehensive treatise on "Inorganic and Theoretical Chemistry" by Mellor 15 (Longmans Green: London 1923), Vol. III, at page 347, we read:

"According to G. Wetzlar, when silver is subjected to an aqueous solution of sodium chloride with access of atmospheric air, silver 20 chloride is formed, and the solution acquires an alkaline reaction. H. St. C. Deville made a similar observation in 1859, for he found that silver dissolves with extreme rapidity though in small quantity in a concentrated 25 aqueous solution of sodium chloride and the solution turns red litmus blue, owing to the formation of sodium hydroxide."

Again, at page 348, Mellor says:

"According to A. Ditte, silver is attacked 30 by an aqueous solution of potassium iodide, forming a layer of silver iodide on the metal: with a concentrated solution of potassium iodide a double salt KI , AgI , $1/2H_2O$, may be formed." * * * "Analogous results are 35 obtained with potassium bromide." * * * "C. J. B. Karsten and J. Percy found that at a temperature between 12 and 20° C., a solution of cuprous chloride alone reacts very slowly on silver * * * but the reaction is 40 very rapid in the presence of sodium chloride. * * * According to G. Wetzlar, metallic silver slowly reduces an aqueous solution of ferric chloride."

The formation by silver of negative complexes ions in strong solutions of soluble chlorides, is now, for the first time, made use of 45 in silver polishes, with highly efficient results, and substantially without additional cost. In the reactions involved, silver chloride is 50 appreciably soluble in strong solutions of sodium chloride or other soluble chlorides. Sodium bromide, sodium iodide, potassium bromide and potassium iodide act similarly. The tendency of the bromides and iodides to 55 form complexes is even greater than that of the chlorides. Sodium bromide and sodium iodide have the advantage over the chloride of being more soluble, but the overwhelming disadvantage of being much more expensive, 60 especially in the case of the iodide.

It will now be appreciated that there has been provided an improved process of inhibiting the blackening of abrasive silver and metal polishes and cleaning compositions, as 65 well as a plurality of such compositions in-

cluding a variety of inhibitors, which, for the purpose of this invention are designated generally as halides, and more particularly as the alkali halides.

What is claimed is:

1. A silver cleaning composition of the abrasive type, containing from 5 to 15 per cent. of an alkali metal halide.

2. A silver cleaning composition of the abrasive type, containing infusorial earth 75 substantially 20%, sodium oleate substantially 20%, an alkali metal halide 5 to 15%, balance water.

3. A silver cleaning composition of the abrasive type, containing substantially 20% 80 infusorial earth, substantially 20% sodium oleate, 5 to 15% sodium chloride, balance water.

4. A silver cleaning composition of the abrasive type, containing substantially 4% 85 of sodium iodide.

5. A silver cleaning composition of the abrasive type, containing substantially 4% of sodium bromide.

GRINNELL JONES.

DOROTHY WEED MARSHALL.

70

90

95

100

105

110

115

120

125

130