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2,807,584

MATERIAL FOR CLEANING SILVER

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1 Claim. (Cl. 252—91)

This invention relates to a new composition for cleaning silverware and especially to a cleaning cloth for removing the tarnish and other stains acquired by silver on exposure to air or by contact with foods containing corroding elements, including sulfur.

Cloths heretofore used to polish silver are generally effective only in removing very light stains and in brightening the surface. Some of these have a dry and dusty feel, and dust comes out of them when they are shaken, and even during the shaking incident to normal use of the cloth. Some have an oily feel and a disagreeable odor.

It is one object of this invention to provide a material containing a non-ionic liquid detergent and an inorganic powder free from hard grit, which mixture is capable of removing the stain and film from the surface of soft precious metals such as silver or gold; also, to incorporate this composition into cloth, unwoven fabric, paper or a wad of paper pulp, or cotton, to produce cleaning and polishing cloths or sheets or wads of fibrous material, thus producing a polishing medium which has an agreeable, moist feel, an appearance resembling chamois leather, and the solid ingredient does not dust out on shaking. It does not dry out and remains effective for a long time. It has no substantial odor, but if desired, a pleasant-smelling component can be added.

The applicant discovered, some years ago, that putty (linseed oil and whiting) is an effective silver polish. Other oils, such as lubricating oil and liquid petrolatum (white mineral oil), when mixed with whiting, were likewise effective. Such mixtures have the disadvantage, however, that they have an oily feel and tend to leave an oily film on silverware, which is difficult to remove except by washing with a detergent.

Within the past few years, a new type of detergent has come on the market which resembles oil in some of their physical characteristics. These are the non-ionic liquid detergents. Some of these are only slightly soluble in water, but from emulsions with it; others are completely soluble, and some of them form gels in the presence of certain proportions of water. Several of these liquids appear to be very strongly absorbed by cotton or paper.

It seemed probable that polishing creams made with these liquids would have some of the properties of oil-whiting mixtures but would not have the disadvantages involved in using oil. Mixtures of non-ionic liquid detergents with inorganic powders, with and without water added, were tested as silver polishes and were surprisingly effective. The addition of mineral oils or fatty oils to such mixtures is not necessary nor desirable.

An especially effective cleaning and polishing medium was produced when cotton cloth was dipped into slurries containing the non-ionic liquid detergent, whiting, and water, and then dried. This water can sometimes be omitted. The best cloth for this purpose appeared to be an absorbent napped fabric. Cotton outing is especially effective. When treated with the slurry, napped fabrics take on an appearance somewhat like moistened chamois leather, and have a moist and pleasant feel. A surpris-

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ingly large amount of the solid polishing agent can be incorporated in the slurry in this way.

The following liquid non-ionic detergents were mixed with whiting and cleaning cloths prepared from the mixture by dipping and squeezing out the excess:

(1) A condensation product of ethylene oxide with amyl phenol, produced by General Aniline and Film Corporation and retailed by B. T. Babbitt, Inc., as "Glim."

(2) Triethanolamine lauryl sulfate, sold by Procter and Gamble under the trade name "Joy."

(3) A fatty alkylolamine condensate sold by the Alrose Chemical Company (Providence, R. I.), as "Alrosol."

(4) An alkylated aryl polyether alcohol sold by Rohm and Haas Co. as "Triton X-45."

(5) Another alkylated aryl polyether alcohol sold by Rohm and Haas Co. as "Triton X-100."

(6) A dimeric alkylated aryl polyether alcohol sold by Rohm and Haas Co. as "Triton X-155."

The fatty-acid alkylolamine condensate detergent referred to in (3) above is a non-ionic condensation product of a higher fatty acid with an alkylolamine in which the ratio of fatty acid to alkylolamine ranges from $\frac{1}{2}$ to 3 moles of the alkylolamine to 1 mole of fatty acid, the alkylol groups containing from about one to four carbon atoms and the fatty acid having from ten to eighteen carbon atoms. The fatty acid may be oleic, palmitic, stearic or lauric, etc. The product may contain a little of the free fatty acid and a little of the free amine used in the condensation process, but not enough to leave a film of free fatty acid on the silver cleaned by the cleaner. This non-ionic detergent is described in U. S. Patents Nos. 2,205,042 and 2,404,297.

The inorganic powders found to be especially effective in admixture with these liquid non-ionic detergents are whiting and precipitated chalk. Mineral whiting appears to have some advantage over the precipitated material. Highly purified whiting does not appear to have any advantage over the finely ground, chemically untreated mineral, provided it is free of coarse, abrasive particles i. e. free from hard grit.

There appears to be no appreciable advantage in heating the slurry above room temperature during the impregnation of the fabric.

To test the product, a method of artificially staining silver was devised; anhydrous potassium sulfide was placed in the bottom of a glass jar and pieces of flat silver placed on a platform above it. Hydrogen sulfide is evolved slowly by the reaction of the sulfide with atmospheric moisture and reacts with the surface portion of the silver to form silver sulfide. Dark brown, black, or dark purple stains are so formed in the course of a week.

Cheap, thinly plated silverware was used mostly in these tests, and was subjected, in the course of repeated tests, to staining and cleaning about once every two weeks for some five months. Although these stains were much darker (and more resistant to cleaning) than are usually seen on silverware, the silver on these thinly plated forks and spoons showed no sign of wearing through to the base metal during these tests.

The cloths produced by dipping were thoroughly tested on both plated and sterling silver, artificially and naturally stained, including some very darkly stained silver obtained from an antique shop. In all cases, they were found to be more effective, convenient, and time-saving than when using cleaning cloths now on the market. Cloths containing high proportions of the liquid detergent (relatively to the solid polishing ingredient) were effective on mildly stained, smooth silver without using any water; however, it seems best in most cases, to wet the silver with water, rub with the cloth, then rinse. The luster appears on rinsing.

The cloth is very convenient for the removal of food

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stains from silver when it is being washed. The polishing agent does not stick in depressions and grooves and is easily washed off. It is quite effective on heavily embossed silver.

For impregnating the fabric with the detergent mixture (non-ionic liquid detergent and whiting or the like, usually with some water added), it is convenient to cut the fabric into strips, to pass a strip A lengthwise through a vat or box containing the liquid mixture, under rollers therein, thence through a steel roll wringer, or iron roll wringer, and then to pass this with a similar strip B of such fabric through more squeeze rolls and to roll these up together and let stand for about ten minutes, more or less. Then the roll is unwound and strip A separated from strip B, the strip A is cut into the desired lengths (e. g. 1 foot) for packaging and sale, while the strip B, which has absorbed some of the liquid mixture and a little whiting from strip A, will be run through the vat, and wringer, and assembled with another dry strip to be similarly treated.

At any appropriate time, e. g. after separating the two strips, and before or after cutting into lengths, the fabric A can be subjected to a heat-drying step for removing a portion of the water therein. This drying step can often be omitted. Preferably I evaporate most of the water, in this step.

It is generally preferable, in making up the liquid slurry of the liquid non-ionic organic detergent, whiting and water, to use about equal weights of the said organic detergent and whiting, although the relative amounts of of these can vary between about 40:60 and 60:40.

The amount of water, if that is to be used in making the mixture for impregnation, should be enough to reduce the viscosity of the mixture, to give a slurry which will readily be absorbed by the fabric.

The best fabric to be used seems to be a cotton outing, i. e. a napped fabric having considerable body. A good grade is one weighing 3 to 4 ounces per square yard (i. e. $\frac{1}{4}$ to $\frac{1}{2}$ ounce per square foot). White is satisfactory and preferable, but colored goods could be used. Using cotton outing of this grade, the impregnated product somewhat resembles a moist chamois skin. A fabric heavier than here indicated is likely to be too stiff or too sticky, after impregnation.

Non-ionic liquid detergents which are substantially harmless to the human skin are selected. Among these, those of low viscosity are chosen with the purpose of avoiding thick and heavy slurries.

The effect of the nature of the whiting on the viscosity of the pastes was also studied. Materials of small particle size, such as precipitated calcium carbonate, formed slurries of high viscosity at low concentrations of the powder. Purified mineral whiting, from which the coloring material had been removed by air separation, also gave rather thick slurries. Commercial whiting, containing impurities which gave it a brownish color (probably due to compounds of iron) produced slurries which were less viscous than those made from the purer materials. It appears probable that the impurities, or some of them, acted as dispersants.

It was also found that the addition of substances known to act as dispersants for solid particles in aqueous suspensions decreased the viscosity. Those tried were derivatives of lignosulfonic acid produced by the Marathon Chemical Corporation from paper mill waste and sold under the trade name "Marasperse." These impart a brown color to the cleaning cloth which is pleasing and increases its resemblance to chamois leather.

Attempts were made to produce cleaning cloths from anhydrous slurries (liquid non-ionic detergent and powder only), but the cloths so produced were mostly too wet, too thick, and too heavy, probably because the slurries were too thick. So far, the addition of sufficient whiting to give the required ratio of powder to detergent has resulted in slurries which in most cases were too thick for satisfactory operation with the equipment used.

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However, little or no water should be present in the finished cloth, except perhaps as hygroscopic moisture. Any water added to the slurry must be mostly squeezed out or evaporated. It is therefore desirable to keep the quantity of water in the slurry at a minimum. On the other hand, the addition of water appears usually to be necessary to obtain a cleaning cloth of the desired characteristics.

The following examples are given for illustration:

Example 1

"Alrosol" (a fatty alkylolamine), as sold, contains 13% of water. Solutions of "Alrosol" in water have a minimum viscosity range between 40 and 60% concentrations of "Alrosol." Mixtures within this range can be produced by adding one volume of water to about 2 volumes of "Alrosol." To 3 parts by weight of this solution, some three parts or more by weight of commercial whiting can be added without increasing the viscosity of the slurry beyond the optimum value.

Slurries containing 2 parts "Alrosol," 1 part water, and 3 parts of whiting, all by weight, have been used with cotton outing for the production of cleaning cloths, and excellent results secured. A possible disadvantage is caused by the tendency of this material to take up moisture from the atmosphere when the humidity is high, especially in summer. This difficulty does not appear in winter, when the atmosphere is usually dry. If the cloths become too wet, they can be dried out in the sunshine or by artificial heat.

Example 2

"Alrosol C" is an alkylol fatty acid amide containing 100% active organic ingredient and is miscible in water in all proportions. It does not have a strong tendency to form gels. Slurries containing "Alrosol C," water and whiting (preferably in the proportions of 2:1:3), were found to be less viscous than when "Alrosol" is used in the same proportion. However, cloths so produced were about as hygroscopic as those produced from "Alrosol." Both commercial and refined whiting were used with "Alrosol C."

Further examples of making the polishing cloths are given, as follows:

Example 3

100 parts of "Triton X-100" were mixed with 240 parts of fine ground whiting and 400 parts of water, to give a slurry. Cotton outing fabric air dry (weighing about 3.5 oz. per square yard) was dipped in this, and passed through a wringer under strong pressure, leaving a wet cloth then weighing about 38 oz. per square yard. This fabric was then subjected to drying in a current of warm air until most of the water had been evaporated. The fabric then weighed about 18 oz. per square yard. Pieces of this were found to be very suitable for polishing stained silverware.

Example 4

A slurry was made of 2 parts "Alrosol," 1 part water and 3 parts of very fine whiting, all by weight. This slurry was rather stiff and to this I added about $\frac{1}{2}$ % of powdered "Marasperse C," which increased its fluidity. This mixture was used for impregnating fabrics, and gave good silver polishing cloths.

The "Marasperse C" appears to be a dry powder consisting largely of calcium lignosulfonate, made by partial precipitation and drying of sulfite waste liquor from bisulfite pulp mills. Another similar product is "Marasperse CB" which appears to be a partly desulfonated sodium lignosulfonate. This is also suitable as a dispersing agent in the present invention.

The amount of these "Marasperse" products if used, can be small, e. g. 0.4% to 1.2% (based on the amount of the slurry). They are used, particularly when the slurry is very thick and viscous.

Example 5

50 parts of "Glim" were heated to drive off about 27.5 parts of water. Then 225 parts of water were added, and 100 parts of commercial whiting. A cotton outing fabric (1 square foot) weighing about 11.7 grams, was immersed in this slurry, drained, squeezed by the pressure of the hand, then hung up to dry, in a warm atmosphere. After drying the fabric (carrying the detergent and whiting) weighed 50.6 grams. It made a good silver polishing cloth.

Here the 11.7 grams (1 square foot) of dry fabric takes up detergent-water-whiting mixture or slurry, which after drying contains 38.9 grams of a substantially dry mixture of the liquid non-ionic detergent and whiting in the proportions of 1 part of the detergent to about 4.4 parts of whiting. This square foot accordingly contains about 7.16 grams of the detergent and about 31.54 grams of whiting (both in a substantially dry state).

It is to be understood that various other kinds of fabric, felt, paper, etc., can be used instead of the cotton outing. I prefer the latter, as it has a soft feel and looks well. The fabrics can, of course, have trademarks etc., printed thereupon, if desired.

It will be understood that the proportions as given in the examples are for illustration, and not given by way of limitation.

Various other liquid non-ionic synthetic detergents (especially those from the above list) can be used in the same manner as indicated in the above examples.

The quantity of the polishing agent (detergent plus whiting plus any water therein) taken up by the cloth can be varied widely by varying the composition of the slurry and changing its consistency; also by changing the pressure on the wringing rolls. A variation in the amount of polishing agent of from 1 to 4 ounces per square foot of cloth has been observed, while still getting satisfactory polishing cloths.

Silver polishing creams are sold in jars containing 8 ounces of cream, but about 75% of this is water. They therefore contain only about 2 ounces of active polishing material. The cloths prepared as described therefore contain (in a square foot) about as much polishing material as the jar of cream, in addition to about one-half ounce of cloth. The cloths are much more convenient to use than are the creams.

To summarize: Mixtures containing non-ionic liquid

detergents and inorganic powders which are mild abrasives, preferably finely divided whiting, with or without water, are effective polishes for soft precious metals such as silver and gold. These mixtures, as I have found, are especially effective and convenient when impregnated into napped fabrics. The quantity taken up by one square foot of fabric is about equivalent to the weight of actual polishing agent (e. g. about 2 ounces) in an eight-ounce jar of silver polishing cream. The cloths are effective and much more convenient than cream.

The whiting which I prefer to use is the commercial (putty grade) without chemical purification. This should be ground to substantially all pass a 200 mesh screen. The purified, air-floated grade (which substantially all passes a 300 mesh screen), and "precipitated chalk," which also passes a 300 or 325 mesh screen, preferably are not used, since they give slurries which are too viscous to impregnate the fabric well and uniformly.

I claim:

A polishing cloth suitable for polishing and cleaning silverware which comprises a fabric base impregnated with a non-ionic fatty-acid alkylolamide detergent admixed with an abrasive selected from the group consisting of whiting and precipitated chalk, said detergent being a condensation product of a higher fatty acid with an alkylolamine in which the ratio of fatty acid to alkylolamine ranges from $\frac{1}{2}$ to 3 moles of the alkylolamine to 1 mole of fatty acid, the alkylol groups containing from about one to four carbon atoms and the fatty acid having from ten to eighteen carbon atoms.

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