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SILVER TARNISH PREVENTION

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This invention relates to a method for the prevention of the tarnishing of metallic silver in any shape or form, such as silverware which may be in storage, on display in show cases, in ordinary boxes or buffet drawers for easy access in everyday home use, or under other conditions. The invention is also concerned with new compositions and products for use with the method.

The tendency for silver or silver plated articles to become tarnished on exposure to ordinary atmospheric conditions has long presented both the housewife and merchant with an undesirable cleaning problem. In ordinary table and cabinet drawers or other storage and display space, in the home or in the store, it is necessary to keep silverware easily accessible while protecting it from the wear of frequent cleaning and to keep it gleaming and bright ready for use or shown on instant notice without the expense of frequent polishing. A practical solution to this problem is very much needed, particularly a method adapted for general use and in which no technical knowledge or close supervision is necessary.

The problem of silver tarnishing has been partially overcome by compositions which remove tarnish producing agencies from the air. In these methods, the air must first contact the treating composition. In most cases, this is impractical because only a small fraction of the air is purified and a rather large bulk of composition is required to give partial protection for even a few months. Volatile amine solutions have been used, but there are many practical objections to their use, e. g., undesirable odors, high alkalinity, need for use of liquids and solutions which are easily spilled, need for having a relatively large container and need for frequent replacements of the product.

A principal object of this invention is the provision of a new method for the prevention of tarnishing of metallic silver. Further objects include

- (1) The provision of a new compound of low volatility for use in silver tarnish prevention
- (2) The provision of new reaction products of volatile amines and carbon dioxide
- (3) The provision of silver tarnish prevention products which may be easily handled and which may be used by the general public without recourse to special method or technical knowledge.
- (4) The provision of a silver tarnish prevention method adapted for use with metallic silver in any shape or form which is contained in a closed space.

Still further objects and the entire scope of

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applicability of the present invention will become apparent from the detailed description given hereinafter; it should be understood, however, that the detailed description and specific examples are given by way of illustration only and, while indicating preferred embodiments of the invention, are not given by way of limitation, since various changes and modifications within the spirit and scope of the invention will become apparent to those skilled in the art from this detailed description.

These objects are accomplished according to the present invention by placing a solid crystalline reaction product of a volatile amine and carbon dioxide in a closed space containing the silver which is to be protected from tarnishing, so as to permit the volatilized reaction product to contact the silver as it fills the air around it.

The success of this invention is dependent to a large extent upon the discovery that solid crystalline reaction products of volatile amines, e. g., morpholine and carbon dioxide prepared in substantially anhydrous media, e. g., ethers, aromatic or aliphatic hydrocarbons, chlorinated solvents, etc., are capable of preventing silver from tarnishing if the silver is stored in a closed space together with the reaction products, so as to permit the volatilized portions of the reaction products to come in contact with the silver. Since such reaction products possess extremely low vapor pressure but, nevertheless, are sublimable at ordinary temperatures, they are unusually well suited for prevention of silver tarnishing according to the present procedure.

Volatile amines which form solid salts with carbon dioxide and which are useful for this purpose include straight-chain and heterocyclic or cyclic amines, such as tetraethylene pentamine, diethylene triamine, mono-n-octyl amine, morpholine, and amino ethyl morpholine. Other amine salts of carbon dioxide, both liquid and solid may have varying degrees of usefulness and the method is not limited to the examples given or to solid, crystalline salts alone, although these have greatest practical value in ordinary handling and distribution.

The preparation of our new silver tarnish prevention products and our new tarnish prevention method will be more readily comprehended by reference to the following illustrative examples.

Example I

This example illustrates the preparation of a silver tarnish prevention composition from commercial morpholine and carbon dioxide.

One-hundred parts of morpholine is dissolved in 1000 parts of ethyl ether and carbon dioxide gas is bubbled through the solution until substantially all the morpholine is reacted. The reaction is fast and the temperature rises, but no trouble is caused except the evaporation of the ether. (Other ethers and other inert reaction media may be used, as will be appreciated by a chemist.)

The reaction product precipitates as it is formed and is filtered off. The precipitate is washed with more of the reaction medium, if a pure product is desired. No washing or little washing is needed for use in protecting silver from tarnish.

Example II

This example illustrates the preparation of a morpholine carbon dioxide reaction product of less purity than that produced in Example I.

Commercial morpholine is charged into a suitable reaction vessel or container. Solid carbon dioxide is then added portion wise to the morpholine until a gel or mushy crystalline mass is obtained.

The product may be used directly for the prevention of silver tarnish, according to our method or may be further compounded as in the following example.

Example III

A composition specially well suited for the prevention of silver tarnish is prepared by mixing together 90 parts by weight of the product of Example I or II and 10 parts by weight of a very low density, porous, precipitated silica (such as Santocel, manufactured by the Monsanto Chemical Company). The precipitated silica and reaction product are mixed together for a sufficient time to uniformly coat the product with the silica. Thereafter, a small percentage of suitable perfume is uniformly distributed throughout the mass.

The product as produced above may be used for the protection of silver by placing the material in a suitable container in a closed space with the silver or, it may be distributed upon the base of the silver storage unit in the fashion in which moth flakes or the like are used with clothing.

One-hundred parts of morpholine will produce 121 parts of crystalline reaction product which indicates a direct combination of 2 moles morpholine and 1 mole carbon dioxide. This ratio is further checked by hydrochloric acid titration of the pure salt compared to similar titration of morpholine. Since the reaction is carried out under anhydrous conditions, this ratio indicates that the final product contains no water in its structure and is different from those morpholine reaction products which may be formed by reaction of morpholine with CO_2 in presence of water.

The products of this invention have many advantages as a commercial silver anti-tarnish product. Their crystalline nature minimizes the danger of spills. Further, they are almost neutral

in reaction and can be brushed off harmlessly if spilled, their odor is mild as used and not unpleasant to most people, they are completely volatile when pure and they provide concentrated anti-tarnish products which occupy little space. No odor clings to silverware which is taken out for table use after being subjected to our anti-tarnish procedure.

Anti-tarnish products which comprise the reaction product of a volatile amine and carbon dioxide coated with or intimately admixed with precipitated silica of the aerogel type are particularly noteworthy. Thus, this combination seems to be especially effective possibly because the water adsorption properties of the silica modify the operation of the other ingredients apparently by coating the crystals of the amine salt, preventing too rapid absorption of water, and helping to maintain the product as a loose, free-flowing powder.

Ten grams of our products will easily protect a drawer full of silver for a year if the evaporation rate is suitably controlled. We have found that, for general use, this can be accomplished by placing a small amount of the product in a small glass bottle or jar and then placing the jar in a relatively confined space with the silverware. Most desirably, the cap of the container is perforated to allow a controlled evaporation rate which is effective, but not wasteful of the material, and also keeps down any noticeable odor. The cross sectional area of the lid perforations is of the order of .02 to .04 square inch for small spaces (less than 15 cubic feet) and .05 to .07 square inch for larger volumes in ordinary use (china closets or small display cases 20 to 40 cubic feet). These figures are only guides of course, because the conditions of use and the condition of the surrounding atmosphere will all exert some effect on overall efficiency.

We claim:

1. The method of preventing silverware from tarnishing which comprises exposing the silverware in a confined space to vapors of the anhydrous crystalline reaction product of morpholine and carbon dioxide in an anhydrous medium.

2. A process as claimed in claim 1, wherein said product is present as a free-flowing powder uniformly coated with granules of porous, fine silica.

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