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ANTITARNISH WRAPPERS

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This invention relates to protecting silver against tarnishing and more particularly to cloth, paper, or other suitable covering or wrapping material impregnated with sulfur-reacting chemicals and adapted to be used to wrap silverware to protect it from tarnishing.

In the past many different chemicals have been employed as impregnants for cloth, paper, etc. used for wrapping or storing articles of silver, including both solid silver and silverplate. All of such treated cloths have to date had disadvantages. Some of the proposed impregnants release strong acids upon reaction, some become dark upon exposure to sulfur containing compounds, some do not remain in the cloth, and others are insufficiently reactive, or are too toxic for use.

It is an object of this invention to prepare a non-corroding antitarnish wrapper for articles of silver having an exceptionally high sulfur-combining property.

A further object is to prepare an antitarnish wrapper which does not alter in color after extended use.

A still further object is to prepare an antitarnish wrapper containing relatively insoluble salts which are thoroughly incorporated in material suitable for wrapping silverware.

A still further object is to prepare an antitarnish wrapper having a high stoichiometric ratio of impregnant to sulfur.

These objects may be accomplished by impregnating a wrapping material with an aqueous solution of a zinc salt of a weak acid such as zinc acetate. The excess solution is removed and the zinc is precipitated as a zinc carbonate or a zinc borate by means of a solution of sodium carbonate or sodium borate, the excess alkali salt squeezed out, the wrapping material dried, and any excess powder is removed.

The zinc salt may be used in any desired concentration, but I have found that 8 to 16 ounces of salt for each gallon of water yields a very satisfactory product. The alkali metal carbonate or borate may also be present in any desired concentration though I have found that from 1.5 to 2.5 ounces of salt per gallon of water is preferred. It is evident that the concentration of the salts in the solutions governs the final weight of metal precipitated in the wrapping material. I have found that from 0.5 to 5% by weight of zinc on the total weight of material is required, and I prefer to precipitate from 1% to 3.5% zinc by weight. The solution concentrations given above will yield my preferred degree of deposition of zinc when excess of the solutions is removed. It is to be understood that when wrappers are to be constantly exposed to deleterious gases, higher concentrations are required for long life than when the silver is semi-protected as is the case when it is in a chest. If the amount of zinc is below 0.5% by weight, the protection is often not sufficient for long periods of time; if the amount of zinc exceeds 5%, difficulty with dusting is encountered.

In the above description the order of treatment consists in first impregnating the wrapper with the solution of the zinc salt of a weak acid, followed by the alkali dip. This is the preferred order. If the reverse order is carried out, i. e. the wrapper first immersed in the alkali carbonate or borate, followed by immersion in the solution of the zinc salt, the wrapper contains much less zinc carbonate or zinc borate than when treated by the preferred method. The reason for this is believed to be due to incomplete precipitation and therefore lack of proper concentration of insoluble zinc in the interior of the wrapper. In any case it has been ascertained that the order of treatment is important to obtain maximum effectiveness.

The effect of such a treatment is to impregnate the fabric with a relatively insoluble salt of zinc, the anion of which is very weakly acid, together with a small amount of residual sodium carbonate or sodium borate and sodium acetate. Upon attack of the zinc compound by a sulfur-containing compound such as H_2S, the sulfide of zinc is formed together with an innocuous acid. The acid is immediately neutralized by the basic sodium salt of the weak acid present in the wrapper. If the fabric has been impregnated with zinc acetate followed by sodium carbonate, a carbonate is formed; if the wrapper has been impregnated with zinc acetate followed by sodium borate, a borate is formed. The carbonate or borate may or may not be the normal carbonate or borate but is believed to be a basic compound. In any case, the compound formed reacts readily with hydrogen sulfide to form a white zinc sulfide salt which will not alter the color of the cloth. Carbon dioxide formed will escape without damage to the silver present and boric acid is not damaging. While sodium bicarbonate may be used in place of sodium carbonate, it is not preferred.

Both zinc carbonate and zinc borate are white and relatively insoluble. Thus the wrapping material containing either of these salts may be washed without substantial loss of antitarnish activity, although the pH of the wrapping material may drop below the optimum point if the material is washed frequently, which is not ordinarily the case. The wrapping material may be any one of the usual materials adapted for the purpose of wrapping silverware.

The pH of the resulting salts impregnated in the cloth should be in excess of 7 and below about 10. It has been found that H_2S reacts most readily with this salt mixture when the pH of the latter is between about 7.5 and 9.0 and as such a pH range is safe for both the wrapping material and the enclosed silver, and may be readily obtained by adjusting the amount of the residual sodium carbonate (or borate) and sodium acetate in the wrapper. It is my preferred range.

While other salts of zinc than zinc acetate may be employed in the first bath, it is important that they be salts of weak acids which do not react appreciably with silver, for otherwise the salt formed from the reaction in the second bath will not be alkaline and hence will not be useful in adjusting the pH of the salt mixture in the wrapper.

Cadmium salts as impregnants are to be avoided because of their relatively high toxicity.

A most surprising result of my invention is that the zinc present as zinc carbonate or zinc borate has a sulfur combining power in the order of three times that of the corresponding soluble zinc salt from which it was prepared. This high combining power is of considerable importance since it serves to extend the life of the wrapper as well as enhancing its effectiveness during its life.

In order to illustrate my invention the following examples are given:

Example I

Double napped duvetyn was thoroughly wet in a zinc acetate solution containing 12 ounces of salt per gallon. The excess solution was wrung out, then dipped in sodium carbonate solution containing 12 ounces per gallon, crushed to near dryness as possible, and dried. The pH of the material was about 10. Silver wrapped in this cloth for several months was free from white spots attributable to acid, and from sulfur tarnish.

Example II

The following was carried out to determine the weight of sulfur which various treated cloths were capable of picking up. Identical pieces of cloth were treated with zinc acetate and with zinc acetate and sodium carbonate. The procedure described in Example I was followed except that one of the zinc acetate pieces was not dipped in sodium carbonate.

	Untreated	Treated with zinc acetate	Treated with zinc acetate and sodium carbonate
Percentage by weight of zinc after treatment	0	5.0	3.1
Percentage of sulfur by weight picked up by exposure to hydrogen sulfide	0.05	3.06	5.50

It is evident that although there was less zinc present in the cloth treated in accordance with my invention than in the zinc acetate treated material, the amount of sulfur picked up was considerably in excess of that picked up by the zinc acetate treated material.

Example III

Pieces of gray double napped cotton duvetyn heavyweight cotton cloth were treated in the following manner:

One piece was used as a control. A second piece was dipped in and thoroughly wet in zinc acetate solution containing 12 ounces per gallon, crushed as near to dryness as possible and air dried. A third piece was thoroughly wet in the zinc acetate solution, the excess solution wrung out, then dipped in sodium tetraborate, pentahydrate solution containing 9.2 ounces per gallon, crushed as near to dryness and dried.

The pH of the control was 7.7, the zinc acetate treated material 6.7 and the zinc acetate-sodium tetraborate material 8.75. The three pieces were placed in a desiccator containing an atmosphere saturated with hydrogen sulfide. The cloth remained in the desiccator 20 hours. The pH of the untreated cloth was 4.8, the zinc acetate treated material 4.6, and the zinc acetate-sodium tetraborate material 8.0. It is evident that the material made in accordance with my invention stays alkaline while untreated and zinc acetate treated cloth becomes acid upon exposure to H_2S.

Silver articles wrapped in cloth treated in accordance with my invention as described in this example are preserved for long periods of time against tarnish.

While I do not wish to be bound by my theory of the reasons for the particular usefulness of the zinc salts of this invention, the following is given as an explanation.

Zinc salts, as do nearly all inorganic salts, enter into a reaction in the presence of moisture, and therefore a salt having at least some solubility is required since an extremely insoluble compound is rather unreactive. Zinc oxide, for instance, is reported in the "Handbook of Chemistry and Physics" 28th ed. to be soluble to the extent of only 0.00016 gram per 100 mol. of water, and is not suitable.

Hydrated zinc acetate, on the other hand, is readily soluble in water and may be easily removed by washing. Although the presence of moisture normally present in the air will cause sufficient ionization for a reaction, hygroscopic salts are neither necessary nor desirable. Added ingredients such a glycerine serve only to cause unnecessary dampness in the wrapper.

Thus the ideal salt is one that is readily reactive with sulfur containing compounds, is white, forms an insoluble white sulfide, is non-hygroscopic, and is soluble only to a limited extent. Other requirements such as lack of toxic qualities, a high stoichiometric ratio of sulfur to weight of compound employed and, upon reaction with hydrogen sulfide, the release of a non-injurious acid, are also of importance. Finally the pH of the resulting salt is important as an aid to rapid and complete reaction with sulfur compounds.

I have found that the zinc carbonates or zinc borates formed by adding an alkali metal carbonate or borate to a zinc salt of a weak acid are ideal when impregnated into a wrapper or the like in the presence of sufficient alkaline salts to raise the pH above about 7 and below 10, and preferably between 7.5 and 9.5.

The presence of some sodium carbonate or borate and sodium acetate in the antitarnish wrapper serves to neutralize any acid gases present such as sulfur dioxide. The life of the wrapper is thereby extended, and made more effective, sinc zinc sulfide is relatively unstable towards strong acids and if no basic salts were present in the wrapper, active acid gases would cause zinc sulfide to react and form hydrogen sulfide.

While my invention is particularly applicable to wrapping materials such as cotton cloth which may be laundered, other wrapping materials such as tissue paper, kraft paper and boxboard may advantageously be treated by the process of my invention.

This is a continuation-in-part of my application Ser. No. 473 filed January 3, 1948, now abandoned.

I claim:

1. An article of manufacture for protecting silverware from tarnish comprising a fabric impregnated with a salt of zinc, the anion of which is a member of the group consisting of a carbonate and a borate and containing sodium acetate, said impregnated fabric when moistened having a pH from 7.0 to 10.0.

2. An article of manufacture according to claim 1 wherein the zinc salt is a zinc borate.

3. An article of manufacture for protecting silverware from tarnish comprising a fabric impregnated with a tarnish-proofing composition consisting essentially of a salt of zinc, the anion of which is a member of the group consisting of a carbonate and a borate, together with sodium acetate and an alkali metal salt of said ion, the pH of said impregnated fabric when moistened being between 7.0 and 10.0.

4. An article of manufacture for protecting a silverware from tarnish comprising a fabric impregnated with a tarnish-proofing composition consisting essentially of a zinc carbonate, sodium acetate, and sodium carbonate, the pH of said salts when moistened being between 7.5 and 9.0.

5. An article of manufacture for protecting silverware from tarnish comprising a fabric impregnated with a tarnish-proofing composition consisting essentially of a zinc borate, sodium acetate, and sodium borate, the pH of said salts when moistened being between 7.5 and 9.0.

6. A process for protecting articles having a silver surface which comprises impregnating a wrapping material with an aqueous solution of a zinc salt of acetic acid, precipitating a zinc carbonate in said wrapping material by impregnating said material with an aqueous solution of an alkali metal carbonate, in an amount in excess of that required to react with said zinc salt and sufficient to provide an alkaline condition in said wrapping material when the same is moistened subsequent to its manufacture, drying said wrapping material, and wrapping an article having a silver surface with said material.

7. A process for protecting articles having a silver

surface which comprises impregnating a wrapping material with an aqueous solution of a zinc salt of acetic acid, precipitating a zinc borate in said wrapping material by impregnating said material with an aqueous solution of an alkali metal borate, in an amount in excess of that required to react with said zinc salt and sufficient to provide an alkaline condition in said wrapping material when the same is moistened subsequent to its manufacture, drying said wrapping material and wrapping an article having a silver surface with said material.

8. A process for protecting articles having a silver surface which comprises impregnating a wrapping material with an aqueous solution of zinc acetate, said zinc acetate solution having a concentration of from 8 to 16 ounces of salt per gallon, precipitating a zinc carbonate in said wrapping material by impregnating said material with an aqueous solution of sodium carbonate, said sodium carbonate solution having a concentration of from 1.5 to 2.5 ounces per gallon, drying said wrapping material, and wrapping an article having a silver surface with said material.

9. The process in accordance with claim 8 wherein the wrapping material is cotton cloth.

10. The process in accordance with claim 8 wherein the wrapping material is paper.

11. A process for protecting articles having a silver surface which comprises impregnating a wrapping material with an aqueous solution of zinc acetate, said zinc acetate solution having a concentration of from 8 to 16 ounces of salt per gallon, precipitating a zinc borate in said wrapping material by impregnating said material with an aqueous solution of sodium tetraborate solution having a concentration of from 1.5 to 2.5 ounces per gallon, drying said wrapping material, and wrapping an article having a silver surface with said material.

12. The process in accordance with claim 11 wherein the wrapping material is cotton cloth.

13. The process in accordance with claim 11 wherein the wrapping material is paper.

14. A process for protecting articles having a silver surface which comprises impregnating a wrapping material with an aqueous solution of zinc acetate, precipitating a zinc salt in said wrapping material by impregnating said material with an aqueous solution of an alkali metal salt of a member of the group consisting of carbonate and borate, in an amount in excess of that required to react with said zinc acetate and sufficient to provide an alkaline condition in said wrapping material when the same is moistened subsequent to its manufacture, drying said wrapping material and wrapping an article having a silver surface with said material.

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