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PRODUCT AND PROCESS FOR PREPARING SAME

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This invention relates to the prevention of cork stains, and in particular pertains to the treatment of pellicles of non-fibrous character, such as those made from regenerated cellulose, which are adapted for use as bottle caps and the like, in order to prevent staining of the caps when they are dried in contact with cork stoppers.

Cellulosic bottle caps, and in particular bottle caps of regenerated cellulose, are now used on a large commercial scale. These caps are applied to the bottles while they are still in a gel state, i. e. after coagulation and regeneration but before being dried, and are permitted to shrink in place by drying, thereby fitting tightly over and thus forming a seal for the bottle top. It has long been known, however, that when the gel caps are dried down over cork stoppers, the caps tend to become stained with spots ranging from brown to bluish black in color. This condition seriously impairs the utility and salability of the caps for this purpose, and this is particularly true of cellulosic caps containing opaquing material such as titanium oxide or other pigments.

It might be assumed that the problem could be easily solved by coating or otherwise treating the cork. I have found, however, that even a paraffin coating does not prevent such staining. Moreover, any treatment of the cork involves serious disadvantages. A manufacturer of a line of bottled preparations must necessarily carry a very large inventory of variously treated corks since it is obvious that certain liquids will attack the sizing on a given cork and impair the color, taste or other characteristics to the material being bottled. Finally, many treatments of corks have the disadvantage of making them slippery and not easily held in the bottle with its consequent difficulties. The result of such experiences has been that, lacking a suitable cellulosic cap such as one of regenerated cellulose which can be usefully employed in combination with corked bottles, the packaging industry has chosen to go on without the advantages of the sealing which such a closure would afford.

This invention has as an object diminution or prevention of cork stains. It is a further object of the invention to produce pellicles of cellulosic material, such as regenerated cellulose, which possess a high resistance to cork stains. Other objects of the invention will appear hereinafter.

In investigating the causes of the staining of cellulosic pellicles upon coming in contact with cork, it was found that by treatment of cork with hot water, an extract could be obtained consisting essentially of tannin, tannic acid, and other organic materials, and it was concluded that the staining of the cap was due to the absorption of these materials in one form or another by the caps.

I have discovered that cork stains can be greatly diminished and even completely prevented by using gel cellulosic pellicles which have been treated with a solution of a compound which is capable of forming a white or light colored precipitate in the presence of the tannins, tannic acids, and like materials present in corks, thereby preventing their absorption by the caps. In applying the principles of the invention, the gel pellicles are immersed in an aqueous solution of the stain-preventing compound and the immersion is continued until equilibrium is established between the solution and the pellicles. It is customary to ship gel regenerated cellulose bottle caps in a dilute aqueous glycerin solution, the glycerin acting as a softener. The caps may be placed in the shipping container and the treating solution, containing the desired amount of glycerin and of stain-inhibitor, then poured in until it covers the caps after which the container may be closed and shipped and the treated caps, whenever desired, placed on the bottles or like vessels, and permitted to dry and shrink over the tops of the bottles.

The compounds found to be effective in preventing cork-staining of pellicles of the character described herein may be classified as (1) protein material, and (2) salts of metals which are water-soluble and which form white or light colored water-insoluble precipitates with tannin, tannic acid and like materials present in cork.

As to the protein material mentioned under (1), the order of effectiveness is gelatin, casein and albumen, gelatin being by far the most effective of these three. Hydrolized gelatin may also be used. The gelatin may be hydrolyzed, for example, by dissolving in a 2% aqueous solution of acetic acid, heating for an hour at from 90 to 95° C., and then neutralizing with sodium hydroxide.

It is preferred, however, to use inorganic salts in aqueous solution as the impregnating medium. As to the solubility of these salts, they need only be soluble in water to the desired extent, that is to say, so as to form a concentration ordinarily of not appreciably less than about one-half per cent. These salts should in general be about neutral. Salts which would otherwise be suit-

able but which have either a too high or a too low pH, when dissolved in aqueous solution, may sometimes be used by adding certain buffer materials so that the final pH may be regulated within the desired limits, for example, to obtain a final pH corresponding to that of an aqueous solution of zinc acetate.

Among the inorganic salts which may be used in the practice of the invention, I have found a salt of a weak acid and a weak base to be particularly useful. Zinc acetate, aluminum acetate and cadmium acetate are examples of salts capable of precipitating the tannin, etc. to form light colored insoluble precipitates. It is to be understood, of course, that the invention generally contemplates other similar salts, for example, the corresponding salts of other lower fatty acids such as the formates, propionates, etc.

The following example illustrates one mode of applying the principles of the invention:

Example:—Regenerated cellulose pellicles obtained from viscose, adapted to be used as bottle caps, while still in the gel state, are placed in a shipping container. An aqueous solution containing glycerin and in which crystallized zinc acetate has been dissolved, is added to the container so as to cover the caps, the solution containing glycerin and zinc acetate in a concentration sufficient to produce an equilibrium solution containing about 6% glycerin and 4% zinc acetate. The container may then be sealed and shipped to the desired point, the caps being withdrawn whenever desired, the excess solution shaken off, the caps placed over the bottles, and shrunk in place. The dried caps show no substantial staining when shrunk over cork stoppers, even after long periods of time.

Marked benefits are obtained from the use of much smaller amounts of zinc acetate, even as low as one-half per cent in an equilibrium solution. With corks of exceptionally good quality, complete protection may be obtained with only 1% to 2% zinc acetate in the treating solution, but with poor quality corks, a higher percentage is desirable.

The concentration of the stain-inhibiting compound in the treating solution may be varied, depending on the conditions of use, for example, upon whether good quality or poor quality corks are used in the bottles over which the caps are to be applied. The concentration may vary between a fraction of a per cent in the treating solution up to the limit of solubility of the stain-inhibiting compound in the solution. Ordinarily, the concentration of the stain-inhibiting compound will be within the range of a fraction of a per cent to five per cent in the equilibrium solution.

While it is believed that the prevention of cork stains is due to the formation of insoluble tannates and the like by interaction with the stain-inhibiting agent, the invention in its broader aspects, includes the use of compounds which react with the tannins to produce insoluble precipitates, whether these precipitates be tannates or insoluble compounds containing a negative radical other than tannate.

The invention is of particular utility when applied to the treatment of regenerated cellulose bottle caps and bands, especially prepared from viscose. Similar treatment, however, may be applied to pellicles of regenerated cellulose obtained from cuprammonium solution, to pellicles of cellulose esters such as cellulose acetate, or of cellulose ethers such as glycol cellulose or ethyl cellulose, which are cast in aqueous soution. The invention may be applied wherever any such pellicles come in contact with cork or with other materials which stain in a similar manner.

While the invention is preferably applied to gel pellicles, it will be understood that the scope of the invention includes the treatment of pellicles which have been dried and then rewetted prior to treatment. Moreover, it is to be understood that instead of shipping pellicles submerged in a shipping solution, they may of course be removed from a shipping solution which has attained equilibrium and shipped in a moist condition to the point of use.

Any variation or modification of the above procedure which conforms to the spirit of the invention is intended to be included within the scope of the claims.

I claim:

1. A regenerated cellulose bottle cap adapted to be placed in contact with cork having incorporated therein a colorless, water-soluble compound which will form a substantially colorless, or light colored, precipitate with tannin, tannic acid, and like materials contained in cork.

2. A regenerated cellulose bottle cap adapted to be placed in contact with cork having incorporated therein a colorless, water-soluble salt which will form a substantially colorless, or light colored, precipitate with tannin, tannic acid, and like materials contained in cork.

3. A regenerated cellulose bottle cap adapted to be placed in contact with cork having incorporated therein a colorless, water-soluble, substantially neutral salt which will form a substantially colorless, or light colored, precipitate with tannin, tannic acid, and like materials contained in cork.

4. A regenerated cellulose bottle cap adapted to be placed in contact with cork having incorporated therein a colorless, water-soluble protein which will form a substantially colorless, or light colored, precipitate with tannin, tannic acid, and like materials contained in cork.

5. A regenerated cellulose cap adapted to be placed in contact with cork having incorporated therein zinc acetate.

6. A regenerated cellulose cap adapted to be placed in contact with cork having incorporated therein aluminum acetate.

7. A regenerated cellulose cap adapted to be placed in contact with cork having gelatin incorporated therein.

8. The method which comprises treating nonfibrous cellulosic pellicles, which are subject to shrinking by loss of water and which are subject to staining when shrunk in contact with cork, with an aqueous solution of a material which will inhibit cork staining, said material being substantially colorless and capable of forming substantially colorless or light colored precipitates with tannin, tannic acid and like materials contained in cork.

9. The method which comprises treating nonfibrous cellulosic pellicles, which are subject to shrinking by loss of water and which are subject to staining when shrunk in contact with cork, with an aqueous solution of zinc acetate.

10. The method which comprises treating nonfibrous cellulosic pellicles, which are subject to shrinking by loss of water and which are subject to staining when shrunk in contact with cork, with an aqueous solution of aluminum acetate.

11. A cellulosic pellicle which is subject to shrinking by loss of water and which is subject

to staining when shrunk in contact with cork having associated therewith a colorless water-soluble compound which will form a substantially colorless or light-colored precipitate with tannin, tannic acid and like materials contained in cork.

12. A cellulosic pellicle which is subject to shrinking by loss of water and which is subject to staining when shrunk in contact with cork having associated therewith a colorless water-soluble, substantially neutral salt which will form a substantially colorless, or light-colored precipitate with tannin, tannic acid and like materials contained in cork.

13. A cellulosic pellicle which is subject to shrinking by loss of water and which is subject to staining when shrunk in contact with cork having associated therewith zinc acetate.

14. A cellulosic pellicle which is subject to shrinking by loss of water and which is subject to staining when shrunk in contact with cork having associated therewith aluminum acetate.

15. A cellulosic pellicle which is subject to shrinking by loss of water and which is subject to staining when shrunk in contact with cork having associated therewith gelatin.

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