Patented Jan. 12, 1943 2,307,760

UNITED STATES PATENT OFFICE

2,307,760

ARTICLE OF MANUFACTURE

John Conlyn Creadick, Kenmore, N. Y., assignor to E. I. du Pont de Nemours & Company, Wilmington, Del., a corporation of Delaware

No Drawing. Application July 26, 1940, Serial No. 347,785

18 Claims. (Cl. 106—164)

This invention relates to shrinkable container closures, especially caps and bands of regenerated cellulose, and the like. More particularly, it appertains to the production of gel pellicles which will have a metallic appearance when dry.

Shrinkable, non-fibrous, hollow pellicle closures, such as thimble-shaped caps, and tube-shaped bands have been used for years. These devices are sold to users in gel form. The user applies the gel pellicle and allows it to dry in position. During the drying it shrinks, and as a result snugly fits, and very firmly engages, the encompassed article.

The caps are usually produced by immersing a mandrel in viscose and, after withdrawing it, coagulating and regenerating the cellulose xanthate solution adhering thereto. The bands are conveniently prepared by cutting short sections from continuous tubing. In the case of regenerated cellulose, such tubing is manufactured by extruding viscose through an annular orifice into coagulating and regenerating baths.

The bands can be decorated by pigmentation, printing, dyeing, etc. One of the principal uses for these products is in the secondary closing or sealing of bottles containing alcoholic liquors. A demand in this field for caps and bands having a metallic appearance when dry has existed for a long time.

This invention had for an object the production of regenerated cellulose pellicles having a metallic appearance. Other particular objects were to produce caps and bands having a lustrous metallic gold appearance, and to produce caps and bands having the appearance of metallic silver. A general advance in the art, and other objects which will appear hereinafter, are also contemplated.

It has now been found that the regeneration of cellulose from viscose containing about 30% (based on the weight of the cellulose present) thin flat mica particles, of which about 60% have a size of 50 to 100 microns in their longest dimension, gives a pellicle of metallic appearance. This discovery was a great surprise to workers in the art, because ground mica had been used heretofore in viscose derivatives to secure opaqueness. That there is a critical size and shape of mica particles which will give a metallic luster instead of the usual dull, uninteresting effect, is almost unbelievable.

From the following description, in which is disclosed certain embodiments of the invention as well as details of what is believed to be the best mode for carrying out the invention, it will be apparent how the foregoing objects and related ends are accomplished. The parts are given by weight throughout the application unless otherwise specified.

The mica used must conform to very precise specifications. At least 30% must have a particle size of 50 to 100 microns (measured in the longest dimension), and at least 75% must have a particle size of 20 to 150 microns. Optimum results are obtained with a product ground as hereinafter described until 60% has a particle size of 50 to 100 microns.

Dry grinding will not produce a satisfactory product even though the mica so ground is of the aforementioned particle size. The mica must be wet ground to get the thin, flat plates which give the desired result.

Preferably a light colored, or colorless, mica is treated with a wetting agent or a dispersing agent, for example, a highly sulfonated oil, such as Turkey red oil, and then added to water in a pebble or similar grinding mill. After grinding to size, the mica slurry is dispersed in a small amount of viscose to produce a master batch. Portions of the master batch are added and mixed with the viscose casting solutions as needed.

For best results present experience indicates that 30% mica, based on the cellulose present (in the viscose or the pellicle) should be used. The range of 20% to 40% is useful.

The addition of finely divided (powdered) graphite along with the mica enhances the metallic appearance and makes it look like silver.

An amount of finely ground graphite within the range 0.1% to 0.5%, based on the amount of cellulose, and preferably 0.15%, produces the desired appearance.

The addition of finely divided, unreduced yellow vat dyes, such as those of Examples V and VI of U. S. A. Patents No. 1,705,023 to Lulek, with the mica, produces a metallic gold appearance. These dyes can be added to the viscose in the ground slurry form in which they appear on the market. The preferred amount of such pigments is 6%, based on the cellulose, but satisfactory results are obtained within the range 2% to 10%. A somewhat enhanced effect may be obtained by adding soluble dyes to the viscose.

In résumé, the mica particle size and the mode of production (wet grinding) are critical if a metallic effect is to be produced.

The metallic appearance is produced in a like manner in other non-fibrous pellicles, such as casein, gelatin, organic solvent soluble cellulose esters (cellulose acetate), organic solvent soluble cellulose ethers (ethyl cellulose), and the like. Similar results are also obtained with low (lowly) substituted (less than one mol per glucose unit) cellulose ethers, such as methyl cellulose, ethyl cellulose, glycol cellulose, etc. Cellulose regenerated from nitrocellulose and cuprammonium cellulose behaves in the same way.

Of the two specific (1':9'-isothiazolanthrone-2'-carbonyl)-amino-anthraquinones of the pat-

ent mentioned above, the 1-(1':9'-isothiazolanthrone - 2'-carbonyl)-amino-5-benzoylamino-anthraquinone (Example V) is preferred to the 1-(1':9'-isothiazolanthrone - 2' - carbonyl) - 6 - chloro-anthraquinone (Example VI).

Caps and bands having a very natural metallic appearance are produced by the present invention. The strength and smoothness of the dried pellicles are maintained, and the ability of the gel pellicle to shrink is not deleteriously affected. Industry has for many years produced pellicles of various colors and appearances, but has not heretofore been able to produce a product of a highly lustrous metallic appearance.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that this invention is not limited to the specific embodiments thereof except as defined in the appended claims.

I claim:

1. Viscose containing 20% to 40% mica and 2% to 10% of 1-(1':9'-isothiazolanthrone-2'-carbonyl)-6-chloroanthraquinone, based on the cellulose, the said mica having been wet ground until at least 30% has a particle size of 50 to 100 microns (measured in the longest dimension), and at least 75% has a particle size of 20 to 150 microns.

2. Tubular regenerated cellulose pellicles containing 20% to 40% mica and 2% to 10% of 1-(1':9'-isothiazolanthrone-2'-carbonyl)-6-chloroanthraquinone, based on the cellulose, the said mica having been wet ground until at least 30% has a particle size of 50 to 100 microns (measured in the longest dimension) and at least 75% has a particle size of 20 to 150 microns.

3. Viscose containing 20% to 40% mica, based on the cellulose, the said mica having been wet ground until at least 60% has a particle size of 50 to 100 microns (measured in the longest dimension).

4. Tubular regenerated cellulose pellicles containing 20% to 40% mica, based on the cellulose, the said mica having been wet ground until at least 60% has a particle size of 50 to 100 microns (measured in the longest dimension).

5. Viscose containing 20% to 40% mica, based on the cellulose, the said mica having been wet ground until at least 30% has a particle size of 50 to 100 microns (measured in the longest dimension), and at least 75% has a particle size of 20 to 150 micons.

6. Tubular regenerated cellulose pellicles containing 20% to 40% mica, based on the cellulose, the said mica having been wet ground until at least 30% has a particle size of 50 to 100 microns (measured in the longest dimension), and at least 75% has a particle size of 20 to 150 microns.

7. Viscose containing 30% mica, based on the cellulose, the said mica having been wet ground until at least 30% has a particle size of 50 to 100 microns (measured in the longest dimension), and at least 75% has a particle size of 20 to 150 microns.

8. Tubular regenerated cellulose pellicles containing 30% mica, based on the cellulose, the said mica having been wet ground until at least 30% has a particle size of 50 to 100 microns (measured in the longest dimension), and at least 75% has a particle size of 20 to 150 microns.

9. Viscose containing 20% to 40% mica and 2% to 10% of 1-(1':9'-isothiazolanthrone-2'-carbonyl) - amino-5-benzoyl - amino - anthraquinone, based on the cellulose, the said mica having been wet ground until at least 30% has a particle size of 50 to 100 microns (measured in the longest dimension), and at least 75% has a particle size of 20 to 150 microns.

10. Tubular regenerated cellulose pellicles containing 20% to 40% mica and 2% to 10% of 1-(1':9'-isothiazolanthrone-2'-carbonyl)-amino-5-benzoyl-amino-anthraquinone, based on the cellulose, the said mica having been wet ground until at least 30% has a particle size of 50 to 100 microns (measured in the longest dimension), and at least 75% has a particle size of 20 to 150 microns.

11. Viscose containing 30% mica and 6% of 1-(1':9'-isothiazolanthrone-2'-carbonyl)-amino-5-benzoyl-amino-anthraquinone, based on the cellulose, the said mica having been wet ground until at least 30% has a particle size of 50 to 100 microns (measured in the longest dimension), and at least 75% has a particle size of 20 to 150 microns.

12. Tubular regenerated cellulose pellicles containing 30% mica and 6% of 1-(1':9'-isothiazolanthrone-2'-carbonyl)-amino-5-benzoyl-amino-anthraquinone, based on the cellulose, the said mica having been wet ground until at least 30% has a particle size of 50 to 100 microns (measured in the longest dimension), and at least 75% has a particle size of 20 to 150 microns.

13. Viscose containing 20% to 40% mica and 0.1% to 0.5% finely ground graphite, based on the cellulose, the said mica having been wet ground until at least 30% has a particle size of 50 to 100 microns (measured in the longest dimension), and at least 75% has a particle size of 20 to 150 microns.

14. Tubular regenerated cellulose pellicles containing 20% to 40% mica and 0.1% to 0.5% finely ground graphite, based on the cellulose, the said mica having been wet ground until at least 30% has a particle size of 50 to 100 microns (measured in the longest dimension), and at least 75% has a particle size of 20 to 150 microns.

15. Viscose containing 30% mica and 0.15% finely ground graphite, based on the cellulose, the said mica having been wet ground until at least 30% has a particle size of 50 to 100 microns (measured in the longest dimension), and at least 75% has a particle size of 20 to 150 microns.

16. Tubular regenerated cellulose pellicles containing 30% mica and 0.15% finely ground graphite, based on the cellulose, the said mica having been wet ground until at least 30% has a particle size of 50 to 100 microns (measured in the longest dimension), and at least 75% has a particle size of 20 to 150 microns.

17. Viscose containing 30% mica and 6% of 1-(1':9'-isothiazolanthrone-2'-carbonyl)-6-chloroanthraquinone, based on the cellulose, the said mica having been wet ground until at least 30% has a particle size of 50 to 100 microns (measured in the longest dimension), and at least 75% has a particle size of 20 to 150 microns.

18. Tubular regenerated cellulose pellicles containing 30% mica and 6% of 1-(1':9'-isothiazolanthrone-2'-carbonyl)-6-chloroanthraquinone, based on the cellulose, said mica having been wet ground until at least 30% has a particle size of 50 to 100 microns (measured in the longest dimension) and at least 75% has a particle size of 20 to 150 microns.

JOHN CONLYN CREADICK.