It has now been found that a regenerated cellulose secondary closure having the desired degree of shrinkage, metallic luster and opacity can be manufactured by incorporating into viscose from which the closure is to be manufactured from 3 to 65%, based on the weight of the cellulose in the viscose, of a nacreous micaceous flake pigment and regenerating the viscose to a gel cellulose structure of the desired shape.

By "nacreous micaceous flake pigment" is meant a pigment composition consisting essentially of translucent micaceous flakes having on the surface thereof a translucent layer, about 20–250 millimicrons thick, of metal oxide particles of at least one of the group consisting of titanium dioxide, zirconium dioxide, hydrous titanium dioxide, and hydrous zirconium dioxide particles. The major dimension, usually the diameter, of substantially all of the metal oxide particles is less than 0.1 microns. It is also contemplated that a second layer of metal oxides, preferably chromic oxide or antimony trioxide, may be deposited on or intermingled with the titanium dioxide or zirconium dioxide layer. These novel pigments are the subject of a pending application Serial Number 120,157, filed June 28, 1961, and now U.S. Patent 3,087,828, and assigned to the assignee of this application, the disclosure of which is incorporated herein by reference.

Although the nacreous micaceous flake pigment may be added directly to the viscose, it is preferably dispersed in soft water before addition to the viscose. The pigmented viscose is mixed under vacuum until it reaches the desired casting index, generally 6 to 24 hours and is then cast in the normal manner. The resulting closure when dry exhibits a beautiful lustrous appearance, much like a metallic foil.

Bands having a metallic appearance can be made with as little as about 3% and as much as about 65% of a nacreous micaceous flake pigment, based on the weight of cellulose. The preferred amount of the pigment is about 12 to 20%.

Metallic bands having any given colored metallic effect may be made in different ways. For example, bands having the appearance of golden foils may be made by any one of several methods. They may be made by using a golden nacreous flake pigment. They may also be made by incorporating yellow dyes into viscose along with a silver-colored nacreous flake pigment. Alternatively, the yellow dye may be incorporated in a transparent overlay on a cellulose layer containing a silver-colored nacreous flake pigment. Metallic bands in a wide variety of colors may be made by proper choice of pigments and dyes.

This invention is not limited to the production of gel regenerated cellulose secondary closures, but is equally applicable to the production of regenerated cellulose fibers and pellets having a metallic appearance. Articles regenerated from cuprammonium cellulose and nitrocellulose also fall within the scope of this invention. Similarly, articles with a superior metallic appearance can be manufactured from casein, gelatin, organic solvent-soluble cellulose esters such as cellulose acetate, organic solvent-soluble cellulose ethers such as ethyl cellulose, methyl cellulose, hydroxyethyl cellulose, and the like.

The following examples will serve to illustrate the practice of this invention. Parts and percentages are given by weight unless otherwise designated.

**Example 1**

Twelve parts of a pigment composition consisting essentially of translucent micaceous flakes having on its surface a layer of titanium dioxide particles and hydrous titanium dioxide particles, the layer having a thickness of about 20–50 millimicrons and 40 parts of soft water were mixed and the slurry was added to 1000 parts of transparent vis-
The viscose and pigment slurry were mixed under vacuum for approximately 8 hours. The pigmented viscose was then cast in tubular form onto the conventional aqueous acid coagulating and regenerating baths. A shrinkable gel tubing was obtained which when dry exhibited a beautiful light silver metallic appearance. During drying, the bands of this example shrunk in size by 42%.

In controls, bands loaded with sufficient conventional mica and opacifier to give an acceptable metallic effect shrunk only about 10 to 16%. Standard transparent bands containing no micaceous pigment shrunk about 38 to 44%.

Various shades of silver, steel, and other: white and gray metallic shades are also possible by the addition of gray and black pigments to the above formula.

Example 2

A pigmented cellulose tubing was prepared as described in Example 1 except that the metal oxide particles on the flake pigment were zirconium oxide and hydrous zirconium oxide. The appearance of the finished band was substantially the same as in Example 1.

Example 3

Example 1 was repeated employing a pigment wherein the thickness of the layer of titanium dioxide and hydrous titanium dioxide particles was about 120–135 millimicrons. The finished band possessed a lustrous metallic blue color.

With coatings of other thicknesses, other colors, such as silver (20–40 millimicrons), gold (40–90 millimicrons), red (90–110 millimicrons), violet (110–120 millimicrons), and green (135–155 millimicrons) were obtained.

Example 4

To 36 parts of soft water were added 2.81 parts of a yellow pigment (A.A.T.C.C. Colour Index No. C.I. 61,725) and 0.82 part of Pigment Brown E.I.D. No. 1, and the mixture was passed through a 100 mesh screen. To this was added 12 parts of the micaceous flake pigment of Example 1 and this mixture was added to 1000 parts of transparent viscose. The entire mass was mixed under vacuum for approximately 10 hours, and then cast into a conventional aqueous acid coagulating and regenerating bath. A shrinkable gel tubing was obtained which when dry exhibited a beautiful metallic golden appearance. These bands shrank 40% in size during drying.

By proper choice of pigments and dyes it is possible to prepare bands having the appearance of gold, bronze, copper and other colored metals.

Example 5

To 60 parts of soft water were added 2.29 parts of a yellow pigment (A.A.T.C.C. Colour Index No. C.I. 61,725) and 0.20 part of a blue pigment (A.A.T.C.C. Colour Index No. C.I. 69,810). After thorough mixing, the resulting slurry was passed through a 100 mesh screen and added to 17 parts of the micaceous flake pigment of Example 1. Again after thorough mixing, this slurry was added to 1000 parts of transparent viscose and the entire mass was mixed under vacuum for approximately 6 hours. This viscose was cast as the underlay together with a transparent viscose as the overlay through a duplex dye as described in U.S. Patent 1,918,383 with a thickness ratio of the 2 layers of about 40 to 60%. The shrinkable gel tubing which was obtained exhibited when dry a highly lustrous golden metallic appearance of a shade different from that obtained in Example 4. These bands shrank 39% in size during drying.

Example 6

Example 1 was repeated using a pigment having a surface layer consisting mainly of titanium dioxide but containing a small amount of chromic oxide, said layer having a thickness of about 30–90 millimicrons. The finished bands possessed a metallic gold appearance different from that of both Examples 4 and 5 but its shrinkage was similar.

Example 7

To 80 parts of soft water was added 17.6 parts of the micaceous flake pigment of Example 1, and after thorough mixing the slurry was added to 100 parts of transparent viscose. The entire mass was agitated for approximately 12 hours under vacuum. This viscose was employed as the underlay of a duplex band.

To 10 parts of soft water was added 10.5 parts of a scarlet pigment (A.A.T.C.C. Colour Index No. C.I. 71,135), and after thorough mixing the slurry was passed through a 320 mesh screen and added to 1000 parts of viscose. The entire mass was mixed under vacuum for 2 hours. To the pigmented viscose the following solution was added at a rate not to exceed 10 parts per minute:

<table>
<thead>
<tr>
<th>Parts</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium hydrosulphite concentrate</td>
</tr>
<tr>
<td>Sodium hydroxide 26% solution</td>
</tr>
<tr>
<td>Soft water</td>
</tr>
</tbody>
</table>

Mixing was continued under vacuum for an additional 8 hours. This viscose was employed as the overlay of a duplex band.

The two above-described viscoses were cast through a duplex die as described in Example 3 at a thickness ratio of about 50%, while maintaining the sodium sulfide content of the desulfuring bath at 0.85% and the temperature at 92° C. A shrinkable gel cellulose tubing resulted which when dry exhibited a highly lustrous, brilliant red metallic appearance. During drying these bands shrank 37% in size.

By proper selection of the vat dyes it is possible to obtain similar brilliant blue, green, violet and other colored metallic effects. It is also possible to prepare by this method colored metallic tubings in light pastel shades such as pink, blue, orchid, etc. The novel, vivid, metallic color effects produced in the method of this example employing reduced vat dyes are possible because of the high transparency of the colored transparent overlay or outer panel which results from this method of coloring as described in my U.S. Patent 3,005,723.

The viscoses of this invention illustrated in the foregoing examples may be used in making other known types of bands. They may be used to make striped window type bands, like those described by Vautier et al. in U.S. Patent 2,141,776, and in making the outer layer in bands as described by Haft et al. in U.S. Patent 2,331,974.

Whereas conventional cellulose bands loaded with sufficient mica and opacifier for acceptable metallic appearance exhibit shrinkages of at best about 50% that of standard transparent bands, the bands of this invention exhibit shrinkages between about 90 to 100% that of transparent bands. They also exhibit brilliant and novel metallic effects not heretofore possible.

What is claimed is:

1. A shrinkable, cellulosic article having incorporated therein from 3 to 65%, based on the weight of cellulose, of a pigment composition consisting essentially of translucent micaceous flakes having on the surface thereof a translucent layer of metal oxide particles of at least one of the group consisting of titanium dioxide, zirconium dioxide, hydrous titanium dioxide, and hydrous zirconium dioxide particles.

2. A shrinkable, cellulosic band secondary closure having incorporated therein from 3 to 65%, based on the weight of cellulose, a pigment composition consisting essentially of translucent micaceous flakes having on the surface thereof a translucent layer of metal oxide par-
3. A shrinkable, regenerated cellulose band secondary closure having incorporated therein from 3 to 65%, based on the weight of cellulose, of a pigment composition consisting essentially of translucent micaceous flakes having on the surface thereof a translucent layer of metal oxide particles, of at least one of the group consisting of titanium dioxide, zirconium dioxide, hydrous titanium dioxide, and hydrous zirconium dioxide particles.

4. A shrinkable, regenerated cellulose band secondary closure as in claim 3 wherein the thickness of said translucent layer is 20–250 millimicrons.

5. A shrinkable, regenerated cellulose band secondary closure as in claim 3 wherein the thickness of said translucent layer is 20–40 millimicrons and the band is silver.

6. A shrinkable, regenerated cellulose band secondary closure as in claim 3 wherein the thickness of said translucent layer is 40–90 millimicrons and the band is gold.

7. A shrinkable, regenerated cellulose band secondary closure as in claim 3 wherein the thickness of said translucent layer is 90–110 millimicrons and the band is red.

8. A shrinkable, regenerated cellulose band secondary closure as in claim 3 wherein the thickness of said translucent layer is 110–120 millimicrons and the band is violet.

9. A shrinkable, regenerated cellulose band secondary closure as in claim 3 wherein the thickness of said translucent layer is 120–135 millimicrons and the band is blue.

10. A shrinkable, regenerated cellulose band secondary closure as in claim 3 wherein the thickness of said translucent layer is 135–155 millimicrons and the band is green.

11. A shrinkable, regenerated cellulose band secondary closure as in claim 3 wherein said translucent layer is of titanium dioxide particles.

12. A shrinkable, regenerated cellulose band secondary closure as in claim 3 wherein said translucent layer is of zirconium dioxide particles.

13. A regenerated cellulose secondary band closure for bottles and the like having incorporated therein from 3 to 65%, based on the weight of cellulose, of a pigment composition consisting essentially of translucent micaceous flakes having on the surface thereof a translucent layer of metal oxide particles of at least one of the group consisting of titanium dioxide, zirconium dioxide, hydrous titanium dioxide, and hydrous zirconium dioxide particles.

14. A process which comprises uniformly dispersing translucent micaceous flakes having on the surface thereof a translucent layer of metal oxide particles of at least one of the group consisting of titanium dioxide, zirconium dioxide, hydrous titanium dioxide, and hydrous zirconium dioxide particles in viscose; casting said viscose in tubular form into an aqueous acid bath to produce a shrinkable gel regenerated cellulose film.

15. A process which comprises uniformly dispersing translucent micaceous flakes having on the surface thereof a translucent layer of metal oxide particles of at least one of the group consisting of titanium dioxide, zirconium dioxide, hydrous titanium dioxide, and hydrous zirconium dioxide particles in soft water to form a dispersion; adding said dispersion to viscose; casting said viscose in tubular form into an aqueous acid bath to produce a shrinkable gel regenerated cellulose film.

References Cited by the Examiner

UNITED STATES PATENTS
2,691,600 10/1954 Warren et al. 106—168 X
3,087,828 4/1963 Linton et al. 106—291

ALEXANDER H. BRODMERKEL, Primary Examiner.
J. H. WOO, Assistant Examiner.