

July 28, 1964

G. H. HOLOUBEK ETAL
 PROCESS FOR PRODUCING REGENERATED CELLULOSE PARTICLES
 WITH ENCAPSULATED OPACIFYING OR COLORED BODIES
 Original Filed April 4, 1960

3,142,580

FIG. 1

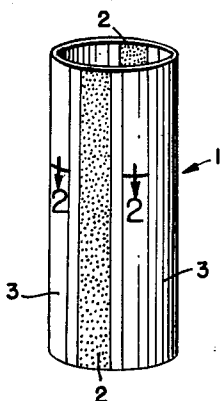


FIG. 2



FIG. 4

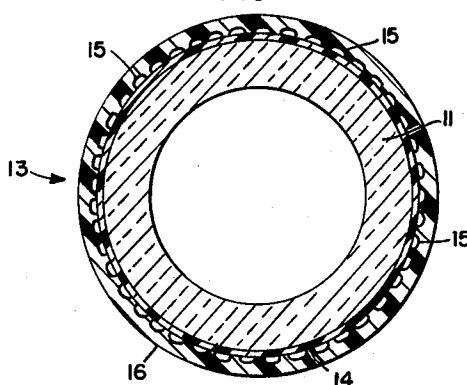


FIG. 3

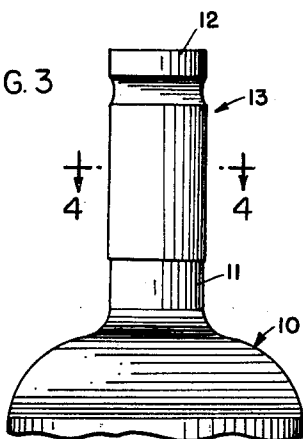


FIG. 5

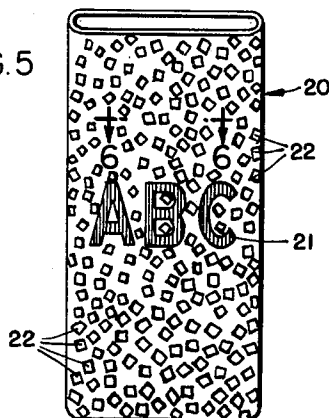


FIG. 7

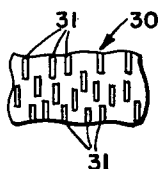


FIG. 8

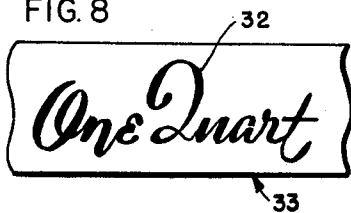
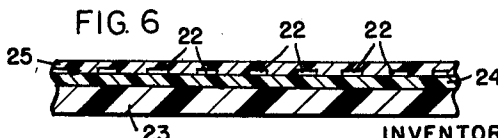


FIG. 6



INVENTORS:
 GEORGE H. HOLOUBEK
 HARLAND HARMS
 KENNETH E. GLIDDEN
 THEODORE SMITH

BY *Marjall Johnston, Cook & Root*
 ATT'YS

3,142,580
Patented July 28, 1964

2

PROCESS FOR PRODUCING REGENERATED CELLULOSE PARTICLES WITH ENCAPSULATED OPACIFYING OR COLORED BODIES

George H. Holoubek, Harland Harms, Kenneth E. Glidden, and Theodore Smith, all of Muscatine, Iowa, assignors to Thatcher Glass Manufacturing Company, Inc., New York, N.Y., a corporation of New York
Original application Apr. 4, 1960, Ser. No. 19,923.
Divided and this application July 19, 1960, Ser. No. 43,904

This invention, in general, relates to processes for producing regenerated cellulose pellicles, foils, tubes, bands and the like containing finely-divided, opaque bodies encapsulated on said pellicles, foils, tubes, bands and the like of regenerated cellulose by a covering film of regenerated cellulose. One aspect of the invention relates to processes to produce regenerated cellulose gel pellicles in tubular or band form which have a metallic luster when dry. Another aspect of the invention relates to the production of gel regenerated pellicles having a printed design, legend, or other indicia with a metallic luster. A still further aspect of the invention is the provision of processes for applying and encapsulating small, opaque bodies on gel regenerated cellulose films to enhance the appearance of dry cellulosic films.

Shrinkable, hollow pellicle closures of regenerated cellulose, such as tubular bands and cup-shaped closures, have been used for a number of years as secondary container closures or bands about the necks of bottles. These closures or bands have both a decorative and utilitarian function. While providing an attractive decoration for the bottle, these closures or bands, when secured about the neck of the bottle and the stopper or closure therefor, serve as a deterrent to tampering with the bottle contents. By pigmentation and/or printing, these caps or bands can provide a wide variety of decorative designs or printed matter, as well as an attractively colored article.

When the shrinkable band or secondary closure of regenerated cellulose in gel form is placed over the bottle top with the primary closure, such as a stopper or cap, and is allowed to dry, the regenerated cellulose closure or band shrinks. The shrinkage provides a very firm fit about the bottle neck and primary closure—forming a tightly-stretched, tough seal.

The principal method in use today in the manufacture of regenerated cellulose bands of the type heretofore described, is by the extrusion of continuous lengths of cellulose tubing regenerated from viscose. The continuous lengths of cellulose tubing are then cut into short lengths to provide the bands. The bands are packaged and sold to the users in gel form.

Regenerated cellulose produced by the viscose process is usually made from wood as the primary raw material. In a typical viscose process, wood is shipped into small pieces, and the chips are treated with a bisulfite salt such as calcium bisulfite. The treated chips are then cooked with steam under pressure for about 14 hours. This treatment does not greatly affect the cellulose, but it decomposes and solubilizes the encrusting substances—thus purifying the cellulose. The purified pulp is then bleached with hypochlorite and converted into paperboard. After conditioning the paperboard under definite humidity and temperature conditions, the sheets are stacked in a press and soaked with a strong solution of caustic soda (about 18% strength) from one to four hours. This process is known as steeping or mercerizing. The hemicellulose is

After the excess alkali is pressed out of the alkali cellulose, the moist mass is put through a shredding machine where it is broken up into fine "crumbs." After shredding the "crumbs" are aged in contact with the atmosphere. Through oxidation by the atmospheric oxygen, degradative changes set in. Some depolymerization of the glucose residue in the cellulose molecule occurs, and the degree of polymerization falls from about 800 to 350 glucose residues per cellulose molecule. One process combines the shredding and aging steps by careful control of temperature and other physical conditions.

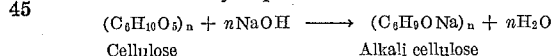
After aging, the alkali cellulose crumbs are introduced into rotating air-tight churns. About 10% of their weight of carbon disulfide is added, and the crumbs and disulfide are churned up together. A deep orange gelatinous mass of sodium cellulose xanthogenate is formed. Churning is continued for several hours, and thereafter the sodium cellulose xanthogenate is stirred with dilute caustic soda solution for several additional hours at low temperature. The xanthogenate dissolves to a viscous liquid similar in appearance to honey. This liquid is known as "viscose," but it must be treated further before it is ready for extruding. The viscose contains in the vicinity of 5.5–7.0% alkali and 6.5–8.5% cellulose.

The viscose then is agitated in a secondary mixer or blender. Any undissolved fibers from the original wood pulp are removed by filtering the viscose.

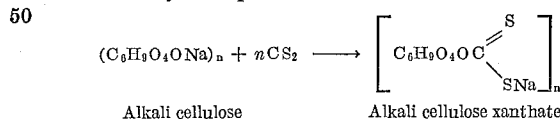
30 The viscose solution is next ripened for several days at low temperature. During the ripening, the viscosity first falls and then rises so that by the time the solution is ready for extruding the viscosity has risen almost to its original value. When the viscose solution is ripe all air
35 bubbles are removed by exposure of the solution to vacuum.

The viscose solution is extruded in tubular form into an acid bath wherein the cellulose in the viscose solution is regenerated. Sulfuric acid is the acid used primarily 40 for reasons of economics. The bath may also contain sodium sulfate, zinc sulfate and other known modifying agents.

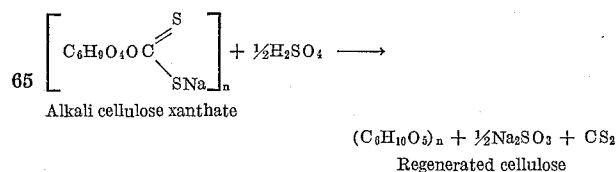
The reaction of cellulose and caustic to give alkali cellulose is usually expressed:



The reaction between the alkali cellulose and carbon disulfide may be represented:



55 During the ripening period, some of the alkali cellulose xanthate decomposes, regenerating cellulose which is maintained in emulsion form by the portion of alkali cellulose xanthate still undecomposed. The conversion of the remainder of alkali cellulose xanthate to cellulose
60 is accomplished in the acid bath. The latter reaction of the xanthate portion of the polymer may be represented:



70 One aspect of the invention relates to the production of metallic-appearing regenerated cellulose seals, such as the aforescribed bands or secondary closures, by the

application to said seals of metallic flake such as aluminum flake or bronze flake. The coating or casting of regenerated cellulose by conventional techniques cannot be used in processes where metallic flake is applied to the regenerated cellulose as the opacifying or pigmentary agent. The caustic used in the regenerated cellulose processes eventually attacks the aluminum flake to modify or destroy its metallic appearance or the sulfides present in the regenerated cellulose produced by the viscose process darkens bronze flake. Further, no known vehicle or adhesive has heretofore been available for adhering the metallic flake to the wet cellulose tubing. Also, no adhesive is available which swells and shrinks at the same rate as the regenerated cellulose seal shrinks upon drying.

To overcome the foregoing difficulties, we have developed a new process for the manufacture of tubular wet cellulose seals having a metallic appearance. In this process, wet cellulose tubing is coated with metallic flake, such as aluminum flake or bronze flake. The metallic flake coating is thereafter encapsulated by applying to the coated or printed wet cellulose tubing a continuous film of viscose, which is subsequently regenerated to form a regenerated cellulose, continuous, encapsulating outer film. This technique is also applicable to regenerated cellulose pellicle forms other than the tubular form.

To describe our process in greater detail, the regenerated cellulose pellicle prepared by a viscose process is washed, without drying, of all surface contaminants. The washed pellicle is then preferably, though not essentially, dipped for a short period in dilute caustic of a strength preferably in the range of 3% to 15%. After said dip, the surface moisture is completely removed from the pellicle. The metallic flake, as a dry powder or aqueous slurry or paste, is coated on the pellicle. The metallic powder coating may be printed as a design or a complete covering coating may be applied, as desired. A viscose solution is then sprayed, rolled or extruded on the pellicle—covering and encapsulating the metallic powder coating. Immediately following, the viscose-coated pellicle is immersed in an acid solution, such as sulfuric acid solution, to regenerate the viscose layer. When the viscose coating is regenerated it becomes tightly bonded to the metallic powder coated cellulose pellicle—presumably through a bond between the two cellulose layers. The acid from the regeneration bath is immediately washed out of the regenerated viscose layer with hot water, and the pellicle is trimmed and plasticized.

In the foregoing process the viscose used to form the gel pellicle has a content of 6.5–8.5% cellulose and 5.5–7% caustic. The acid regeneration bath will contain between 3–12% sulfuric acid or equivalent amount of other strong inorganic acid. The dipping of the tubing in the dilute, aqueous caustic solution need only be of short duration. A 3–30 second dip is ordinarily adequate.

The primary purpose of the dip treatment in aqueous caustic is to improve the bond between the viscose coating and the regenerated cellulose pellicle, between which the metallic flake is encapsulated.

The viscose used to provide the outer, regenerated cellulose film will contain approximately 5–10% cellulose, approximately 5–12% caustic and has a salt index greater than 0.25. The period between application of the viscose to the cellulose pellicle and the immersion of the viscose-coated pellicle in the acidic regeneration bath should be only a few seconds to avoid attacking of the metallic flake—particularly when aluminum flake is employed—and preferably will not exceed 10 seconds in the case of aluminum flake. With metallic flakes which are not so quickly attacked by caustic, longer periods may be employed without detriment to the final results. The regenerating bath for the outer viscose film contains approximately 3–10% sulfuric acid and 15–30% sodium sulfate. Ammonium sulfate or potassium sulfate may be substituted for sodium sulfate, although the latter is preferred.

In a further aspect of our invention, the previously de-

scribed technique may be employed with opacifying or coloring particles other than metallic flake or powder. Instead of encapsulating the metallic flake or powder between the gel regenerated cellulose layer applied thereto, pigmentary or opacifying bodies such as organic or inorganic pigments may be so encapsulated to provide a protective cover or coating over said bodies and/or to securely adhere said bodies on the pellicle.

The foregoing process, wherein the metallic flake, metallic powder, organic pigment or inorganic pigment is applied to the original gel regenerated cellulose pellicle, may be modified to produce further new and novel embodiments of the gel regenerated cellulose articles herein described. In this modification, the gel regenerated cellulose pellicle is first coated or sprayed to give a thin film of transparent viscose of the type applied as the encapsulating coating in the previously described embodiments. The film thickness is approximately 0.0005"–0.002", optimally about 0.001". To this viscose film is applied, as by spraying or other technique, finely-divided opacifying or coloring bodies. This process is particularly useful in the application to the gel regenerated viscose pellicle of finely-divided flakes of metallic appearance, known in the trade as "glitters." Glitters are well known decorative articles in the packaging and printing industries and are small rectangular, usually square, flakes of plastic film, such as polyethylene terephthalate, with a metallized aluminum coating. The metallized aluminum surfaces are covered by a coating of clear or colored lacquer to provide "glitters" in a wide variety of colors. The dimensions of typical glitter flakes commercially marketed are 0.01" to 0.015" square with a thickness of 0.0005" to 0.001". This description of one type of glitter flakes is illustrative only because glitter flakes of other shapes and/or dimensions can be used in accordance with the process herein described.

Following the application of the thin, transparent film to the gel regenerated cellulose pellicle and the application on said film of pigmentary or opacifying bodies, a coating of clear viscose is applied, e.g., by spraying, over the opacifying or pigmentary bodies to encapsulate said bodies between two films of viscose. Thereafter, the viscose of both films is regenerated by a brief dip in a 3–10% sulfuric acid bath which may contain 15–30% of sodium, potassium or ammonium sulfate. With opacifying or pigmentary bodies which are not readily attacked by caustic in the viscose, the elapsed time between the application of said bodies on the first viscose film and the regeneration of the viscose of both films is not of critical magnitude. However, where the body is a material readily attacked by caustic, such as aluminum flake or powder, the elapsed time should not exceed about 10–15 seconds to minimize attack on the bodies by the caustic of the viscose. On the other hand, materials which are attacked readily by caustic, can be precoated with clear or colored lacquers or other protective coatings to render them harmless or more resistant to attack by caustic.

Another novel effect in the process wherein the pigmentary or opacifying bodies are encapsulated between two, thin viscose films is produced by printing, rather than spraying, on the gel regenerated cellulose pellicle the viscose film. The printed viscose film may cover all or only a portion of the gel pellicle. The glitters thereupon are sprayed on the viscose print and thereby adhered to the printed portion of the gel pellicle. Thereafter, a film of viscose is applied over the glitters and the viscose of both films is regenerated in the above-described manner.

A still further novel effect in the process where the pigmentary or opacifying bodies are encapsulated between two, thin viscose films on the gel regenerated cellulose pellicles is produced by applying to a die-printed gel regenerated cellulose pellicle a quantity sufficient only to give a light coverage over the viscose-coated area of glitters or other opaque, small bodies of the type hereto-

5

fore described, whereby a speckled appearance results. In this process, the gel regenerated cellulose pellicle is printed by the conventional azo process presently practiced with gel regenerated cellulose tubing or other pellicle form. The azo-printing may cover the entire pellicle surface to provide a completely opaque pellicle. Alternatively, the azo-printing may cover only a portion of the pellicle to give a design wherein some portions are colored and opaque whereas other portions remain clear and transparent. Words, designs, symbols and the like may be printed on the azo-printed portions and/or transparent portions.

The printed pellicle is washed free of all contaminants before applying thereon, by spraying, printing, or the like, a film of clear viscose of a thickness of about 0.0005" to 0.003". Glitters or other opaque bodies are sprayed on the thin viscose film in a quantity sufficient to give a speckled appearance. A film of clear viscose is then applied over the speckled portion to cover and bond the speckles to the gel pellicle. The viscose of both films is regenerated in an acid bath by the previously described technique.

When the encapsulated opacifying bodies are particles of metallic flake such as aluminum flake, a good technique for producing a shiny, metallic foil-appearance on the regenerated cellulose pellicle is by applying on the gel regenerated cellulose either flattened metallic flake having essentially flat upper and lower surfaces or metallic flake particles which are in essentially parallel orientation. The orientation of the particles may be done during the process of transferring the metallic flake particles to the printing die, from which they are applied on the regenerated cellulose pellicle in essentially parallel orientation.

The previous description of the generic aspects and concepts of our invention as well as some embodiments thereof are further illustrated in the drawing wherein:

FIG. 1 is a perspective view of a gel regenerated cellulose pellicle in open-ended, flattened tubular form with two longitudinal stripes of opaque, finely-divided particles encapsulated on said pellicle by a regenerated cellulose film;

FIG. 2 is a magnified, cross-sectional view of the pellicle across one stripe, taken on section 2—2 of FIG. 1;

FIG. 3 is a broken, side elevation of the neck of a bottle with a dry, tubular regenerated cellulose pellicle with encapsulated metallic flakes and tightly shrunk on the neck and about a portion of the bottle closure;

FIG. 4 is an enlarged cross-sectional view of the bottle neck taken on section 4—4 of FIG. 3;

FIG. 5 is a perspective view of another embodiment of a printed gel regenerated cellulose pellicle in flattened, open-ended, tubular form with glitters thereon;

FIG. 6 is a magnified, cross-sectional view of a segment of the pellicle of FIG. 5, taken on section 6—6 thereof;

FIG. 7 is a greatly magnified view of a regenerated cellulose pellicle, in dry or gel form, with oriented particles of metallic flake encapsulated thereon by another film of regenerated viscose, and

FIG. 8 is a segmental view of a gel regenerated cellulose pellicle having bronze or aluminum flake printed on said pellicle and encapsulated by an outer film of regenerated viscose.

The open-ended, tubular pellicle of FIG. 1 comprises a tubular regenerated cellulose body 1 in gel form. The tubular pellicle may also be essentially flattened because this form permits easy transportation of the pellicle in its gel form. A portion of the clear, transparent pellicle 1 has on the outer surface two stripes 2 of metallic flake, e.g., aluminum flake or bronze flake, running longitudinally from edge to edge. These stripes are opaque and have a shiny, metallic appearance. The remaining portions 3 of the tubular pellicle are transparent.

The encapsulation of the metallic flake particles on the gel regenerated cellulose comprising the pellicles 1 is

6

shown in FIG. 2, wherein the outer surface of the gel regenerated cellulose film 4 is covered in part by a stripe of small particles 5 of aluminum or bronze flake. The metallic flake particles 5 are encapsulated between the gel regenerated cellulose film 4 and an overlying stripe, preferably of slightly wider dimension than the stripe 6 of the metallic flake, of regenerated viscose.

In FIG. 3, there is illustrated one use of the gel regenerated cellulose pellicles of the instant invention. A bottle 10 having neck 11 with stopper 12 inserted in the opening of said neck has a tubular, dry regenerated cellulose pellicle shrunk in tight fit about the neck 11 and a portion of the cap 12. The shiny appearance of the tubular pellicle 13 is provided by metallic flake encapsulated upon the entire outer surface of said pellicle.

As shown in the cross-sectional view of FIG. 4, the neck 11 of the bottle 10 has tightly shrunk thereabout the tubular pellicle 13 comprising a body of dry, regenerated cellulose 14 whose outer surface is covered with small particles 15 of metallic flake. The particles 15 of metallic flake are encapsulated on the film 14 by an overlying layer 15 of regenerated viscose having a thickness in the order of 0.0005–0.002 inch.

Another novel effect of the instant invention is shown in FIG. 5 wherein a gel regenerated cellulose pellicle 20, illustrated in flattened tubular form, has printed thereon a legend 21 by the azo printing process. The outer surface of the tubular pellicle 20 is covered with small glitters 22, previously described, in a speckled arrangement.

From FIG. 6 it is seen that the outer surface of the gel regenerated cellulose film 23 of the pellicle 20 has adhered thereon a thin film of regenerated viscose 24, to which, in turn, are adhered the glitters 22. These glitters are then encapsulated by an overlying film of regenerated viscose 25 which is bonded and probably is an integral part of the regenerated film 24.

FIG. 7 is a highly magnified view of a regenerated cellulose pellicle 30, shown only in segment thereof, wherein metallic flake is encapsulated thereon by any of the previously described techniques. In this embodiment, the metallic flake particles 31 are arranged in essentially parallel orientation.

In FIG. 8, a legend 32 is printed with bronze or aluminum flake on the gel regenerated pellicle 33. The legend is encapsulated by a covering film of gel regenerated viscose.

The gel regenerated cellulose pellicles heretofore described contain at least 50% by weight of water. They are maintained in this moist state until they are applied over a bottle neck or the like. Upon drying, the pellicles shrink to yield the tight fitting closures of the type previously described. In general, these gel regenerated cellulose pellicles contain about 65–80% water.

Example 1

In one specific, illustrative embodiment of our invention, a tubular gel regenerated cellulose pellicle containing about 75% by weight water is drawn from the end of an extrusion machine and is washed with water to remove all water-soluble contaminants. This washing step may be done by submerging the tubing in a washing tank or by spraying the tubular pellicle.

The washed tubing is then dipped for approximately 5 seconds in an aqueous solution of 10% by weight sodium hydroxide. The surface moisture on the tubing is then removed and dry, aluminum flake powder is applied to the outer surface of the tubing with a printing die. The printing may cover either the entire outer surface of the pellicle to give a complete coating of metallic flake, or a design legend or other indicia may be printed on only a portion thereof. The gel regenerated viscose tube may be clear or may have a complete or partial coating of pigmentary coloring bodies applied by the conventional azo process. Instead of applying the aluminum or bronze flake of the dry powder by a printing die the metallic

flake may be slurried in water and sprayed or cast on the outer surface of the gel regenerated cellulose tubing.

Immediately following the coating of the gel regenerated cellulose tubing with the metallic flake, a thin viscose layer in the order of 0.001" is sprayed on the tubing to cover and encapsulate the metallic flake thereon. The sprayed tubing is thereafter immediately submerged in sulfuric acid solution where the sprayed viscose layer is regenerated and bonded to the tubing. The acid is removed from the tubing by washing in hot water. It is important in the case of aluminum flake, which is readily attacked by caustic, to quickly neutralize the caustic in the thin, sprayed viscose film before a reaction between the aluminum flake and the caustic is initiated.

The viscose used to form the encapsulating film contains about 7.5% cellulose, 6.5% caustic and has a salt index of about 0.35. The acid regenerating bath for regenerating the viscose film contains approximately 5% sulfuric acid and 20% sodium sulfate. The elapsed time between spraying of the viscose on a given point of the tubing and the submergence of that point of the tubing in the regenerating bath is approximately 5 seconds.

Example 2

In another illustrative, specific embodiment of our invention, the regenerated cellulose tubing in gel form, as previously described, is first coated with a thin layer of approximately 0.001" of viscose containing 7.5% cellulose, 6.5% caustic and having a salt index of about 0.35 by spraying said viscose on said tubing. Glitters are then sprayed on the wet viscose film to give a speckled pattern like that illustrated in FIG. 5. The glitters are small flakes which are approximately 0.01 to 0.15" square and having thicknesses in the range of about 0.005 to 0.001". These flakes are a plastic film of polyethylene terephthalate having a metallized aluminum coating. The metallized aluminum surface is covered by a clear lacquer when a silvery appearance is desired or by colored lacquers to produce the desired color.

After spraying the glitters on the viscose film, to which the glitters adhere, a second or covering coating of viscose of the same chemical character as the first applied layer of viscose is applied as by spraying over the glitters. The applied viscose films then are regenerated in the manner previously described in Example 1. If desired, the first coating of viscose applied to the gel regenerated cellulose tubing may be printed rather than sprayed on said tubing. In this case the glitters adhere essentially only to the viscose printed surface of the cellulose tubing. The outer viscose layer, however, is preferably sprayed over the area covered by the glitters in order to assure encapsulation of the glitters.

The foregoing description and specific embodiments of our invention illustrate the wide varieties of processes for producing various patterns and appearances with gel regenerated cellulose pellicles. Many new and novel effects are producible in accordance with the principles herein disclosed, and our invention contemplates many embodi-

ments in addition to the specific embodiments herein disclosed.

The invention is hereby claimed as follows:

1. A process for producing an attractive gel regenerated cellulose article which comprises applying on a side of a gel regenerated cellulose pellicle finely-divided, opaque particles, covering the area of said pellicle on which said particles are applied with a viscose film and covering said particle with said viscose film, and then regenerating said viscose film covering said particles in an acid bath to thereby encapsulate said particles on said pellicle under the regenerated viscose film.

2. A process for producing an attractive gel regenerated cellulose article which comprises applying directly on a surface of a gel regenerated cellulose pellicle finely-divided, metallic particles, covering the area of said pellicle on which said particles are applied with a viscose film and covering said particles with said viscose film, and immediately regenerating said viscose film covering said particles in an acid regenerating bath to thereby encapsulate said particles on said pellicle under the regenerated viscose film.

3. The process of claim 2 wherein said metallic particles are aluminum flakes.

4. The process of claim 2 wherein said metallic particles are bronze flakes.

5. The process of claim 2 wherein said metallic particles are aluminum flakes, and said aluminum flakes are arranged in essentially parallel orientation when they are applied to said pellicle.

6. The process of claim 5 wherein said aluminum flakes are flattened aluminum particles which have essentially flat upper and lower surfaces.

7. The process of claim 1 wherein said pellicle is dipped in 3-15% caustic prior to applying said particles.

8. A process for producing an attractive gel regenerated cellulose article which comprises applying directly on a surface of a gel regenerated cellulose pellicle a film of viscose, applying finely-divided opaque particles on said film of viscose, applying on said film of viscose and over said particles a second film of viscose, and then regenerating said films of viscose in an acid regeneration bath to encapsulate thereby said particles on said pellicle between the regenerated viscose films.

9. The process of claim 8 wherein said particles are small, aluminum metallized flakes coated with a lacquer.

10. The process of claim 9 wherein said flakes are applied to said film of viscose by depositing said flakes on said film of viscose in a speckled pattern.

References Cited in the file of this patent

UNITED STATES PATENTS

2,087,094	McBurney et al.	July 13, 1937
2,125,341	Hall	Aug. 2, 1938
2,182,188	Walter	Dec. 5, 1939
2,273,677	Wallach	Feb. 17, 1942

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,142,580

July 28, 1964

George H. Holoubek et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 2, line 67, for " $(C_6H_{10}O_5)_n + \frac{1}{2}Na_2SO_3 + CS_2$ " read
-- $(C_6H_{10}O_5)_n + \frac{1}{2}Na_2SO_4 + CS_2$ --; column 3, line 29, for "through"
read -- though --; column 5, line 32, after "the" insert
-- gel --; column 7, line 32, for "0.15" read -- 0.015 --;
line 33, for "0.005" read -- 0.0005 --.

Signed and sealed this 8th day of December 1964.

(SEAL)

Attest:

ERNEST W. SWIDER
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents