Dec. 27, 1938. L. P. G. VAUTIER ET AL 2,141,776

CELLULOSIC STRUCTURE AND METHOD FOR PREPARING SAME

Filed Oct. 18, 1934 2 Sheets-Sheet 1

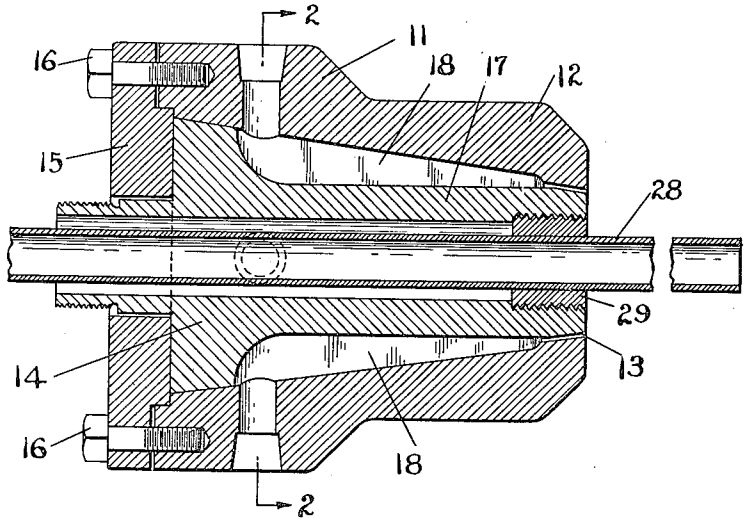

FIG. 1.

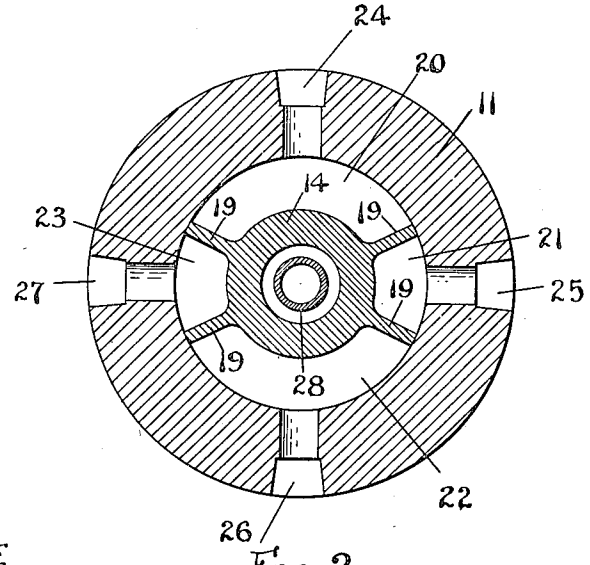

FIG. 2.

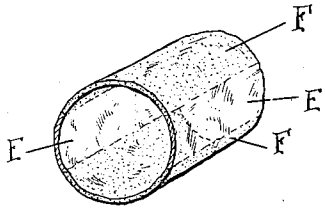

FIG. 3.

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CELLULOSIC STRUCTURE AND METHOD FOR PREPARING SAME

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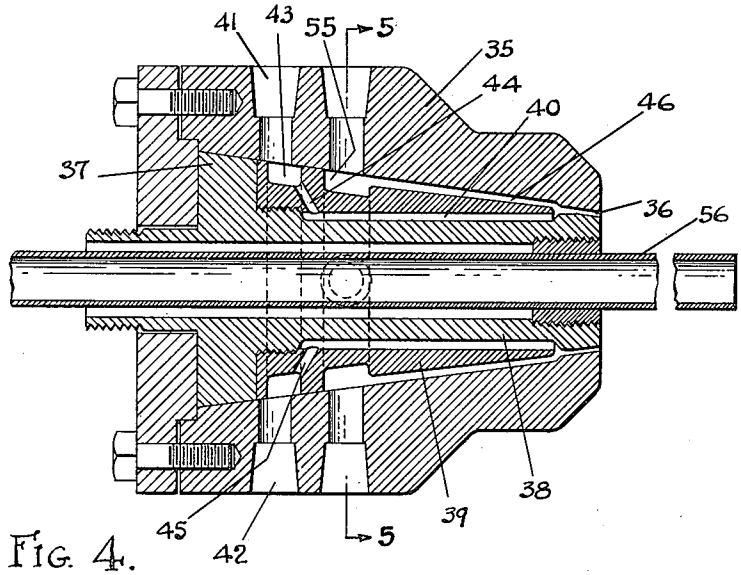

FIG. 4.

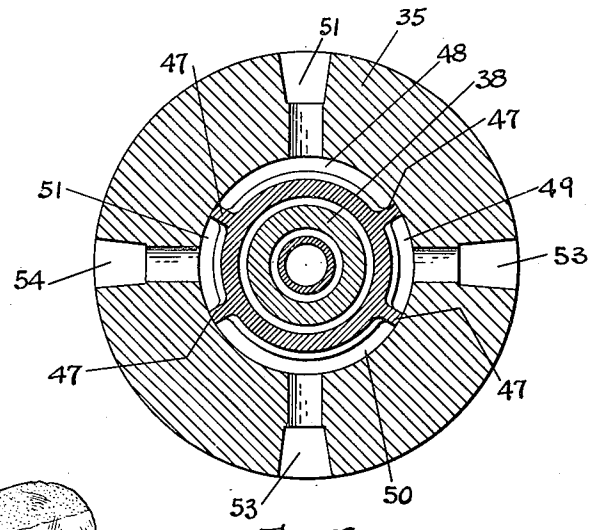

FIG. 5.

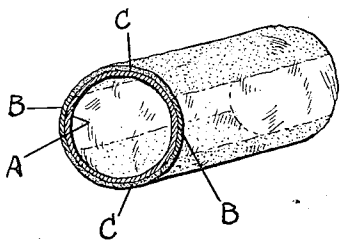

FIG. 6.

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2,141,776

CELLULOSIC STRUCTURE AND METHOD FOR PREPARING SAME

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Application October 18, 1934, Serial No. 748,880
In France November 3, 1933

10 Claims. (Cl. 18—57)

This invention relates to the continuous production of non-fibrous cellulosic sheet material. More particularly, it relates to the production of such materials having new and pleasing optical effects. The invention will be described in terms of seamless cellulose tubes regenerated from viscose although it is to be understood that it is equally applicable to non-fibrous sheet material generally and in practicular to non-fibrous cellulosic sheet materials in the form of tubes, strips and the like.

Recently seamless tubes of regenerated cellulose have come into extensive use as ornamental and decorative ribbons or strips for the manufacture of millinery and other purposes. Similar tubes of larger diameter have been in use as substitutes for animal casings on sausages. They have also been used as decorative and protective sleeves over various articles of manufacture, upon which they may be applied in a gel state and allowed to stand, whereupon they shrink down tightly over the articles as a result of the evaporation of their contained water.

It has been customary to impart various pleasing, ornamental effects to tubing of the type above mentioned, such as by incorporating various materials in the viscose from which the tubes are cast, and a tube so produced presents a homogeneous appearance which has been found suitable for many uses.

Heretofore, in the manufacture of these tubes a viscose solution has been introduced through an annular extrusion device into a coagulating bath, followed by suitable purification steps and, if desired, printing or other subsequent fashioning. The extrusion devices for cellulosic tubing used up to the present are only adapted to the use of a single-colored coagulable solution so that the finished tube must be of a single homogeneous optical appearance, such as entirely opaque or entirely metallic or entirely transparent, or a mixed coagulable solution may be used to produce a product having a mottled appearance.

An object of this invention is to continuously produce tubes of regenerated cellulose or other non-fibrous sheet materials exhibiting novel and pleasing color effects. Another object of the invention is the provision of an extrusion device useful in the manufacture of such novel tubes. A still further object is to produce seamless tubes exhibiting the aforesaid color effects. A still further object is the production of striped tubes in which the boundary lines between adjacent stripes are sharply defined. Still another object of this invention is the production of tubes having firmly united concentric layers of non-fibrous cellulosic materials.

The objects of this invention are accomplished in general by extruding viscose or other liquid from which non-fibrous sheet material may be coagulated through a novel extrusion device into a coagulating bath. This extrusion device consists of two or more chambers for introducing coagulable solutions capable of producing pellicles of different optical characteristics, for passing the solutions in parallel relationship, separated by dividing walls, towards an extrusion orifice, and for subsequently uniting the two coagulable solutions just prior to their extrusion into a coagulating bath. This device is adapted to produce a tube having parallel stripes or concentric layers which are sharply defined from one another, exhibiting a pleasing decorative effect and increased strength.

The solutions capable of producing pellicles of different optical characteristics may be differently colored or some of them may be colored, whereas others are transparent, or some of them may contain metallic particles, etc. It will be understood that a pellicle of different optical characteristics may be formed from a variety of solutions. For simplicity, reference will be made hereinafter to differently colored solutions.

It will be further understood that the cellulosic solutions will in all cases be sufficiently similar so that they will merge or unite to produce a unitary structure.

The details of the invention and the advantages thereof will become more clearly apparent by reference to the following description taken in connection with the accompanying illustrations of one specific embodiment thereof, and in which:

Fig. 1 is a vertical sectional view of an extrusion die for forming cellulosic tubing;

Fig. 2 is a sectional view taken along the line 2—2 of Fig. 1;

Fig. 3 is a perspective view of a tube, such as may be formed by the die shown in Figs. 1 and 2;

Fig. 4 is a vertical sectional view of a modified form of extrusion die for forming cellulosc tubing;

Fig. 5 is a sectional view taken along the line 5—5 of Fig. 4;

Fig. 6 is a perspective view of a tube, such as may be formed by the die shown in Figs. 4 and 5.

Inasmuch as innumerable modifications of this invention are possible, the detailed description and the accompanying illustrations will be confined to a method and apparatus for the production of striped tubing and tubing composed of

oncentric layers of differently colored sections, r having opaque and transparent sections. Obiously, this invention may be employed for the roduction of any system of stripes such as, for xample, stripes numbering from two to a dozen r more, or the stripes may be of different widths r they may be all of the same width.

Referring in detail to the drawings, reference haracter 11 designates the outer shell or housing f an extrusion die for forming cellulosic tubing. The die shell 11 has a hollow extension 12 which erminates in an orifice 13. A die insert or plug 4 is positioned within the die shell 11 and is aintained in spaced relationship therewith by ooperating surfaces of the insert 14 and shell 11. These surfaces are held in engagement with each ther by means of end plate 15 and bolts 16. The nsert 14 is provided with a cylindrical extension 7 which projects into the hollow portion of the xtension 12 and is substantially concentric herewith to provide an annular hollow chamber 8 between the internal surface of the extension 2 and the external surface of the cylindrical exension 17. The insert 14 is provided with a lurality of partitioning ribs 19 which project into he annular chamber 18 so as to divide the same nto separate arcuate chambers 20, 21, 22, and 23. lach of these arcuate chambers terminates at one nd in the common orifice 13 and at the other nd they are conneced to individual supply pasages, each of which is provided with its own upply of cellulosic solution. The chambers 20, 1, 22 and 23 are supplied with cellulosic solutions y means of conduits 24, 25, 26 and 27 respecively. A tubular member 28 is positioned within he insert or plug 14 and is adapted to project herefrom so as to be located within the tubing hich is extruded from the orifice 13. The member 28 may be concentrically spaced within the nsert 14 by means of a bushing 29 or the like. oagulating fluid is passed through the member 8 to the interior of the extruded tubing.

The ribs 19 terminate at the junction of the rcuate chambers 20—23 with the orifice 13 so nat the various cellulosic solutions may flow toether and firmly unite to each other within the xtrusion nozzle slightly before the solutions are ontacted with a coagulating medium.

The striped tubing is produced by means of the bove mentioned apparatus in the following maner:

Referring to the drawings, two or more differntly colored cellulosic solutions may be introuced by means of the conduits 24, 25, 26 and 27 o their respective chambers. The cellulosic solulons are passed from the respective chambers to he common outlet orifice 13 at which point they ow together and unite just prior to coagulation f the same. The extruded tubing is passed into coagulating bath which is adapted to coagulate he exterior thereof, whereas the interior surface f the tubing is coagulated by passing a cogulating liquid through the member 28. Fig. 3 lustrates a tube such as may be produced from he extrusion die shown in Figs. 1 and 2 when, or example, an opaque cellulosic solution is introuced to opposite channels and a transparent, ellulosic solution is introduced in alternate oposing slots. Reference character F designates he opaque portions of the tube and reference haracter E designates the transparent portions f the tube.

By reference to the drawings, it will be seen hat the viscose solutions contact each other only or a comparatively short distance before striking the coagulating bath. It will also be seen that the viscoses, at the point at which they meet, are flowing practically parallel to each other. These two features are necessary in order to be certain that the two viscoses do not appreciably intermingle before striking the coagulating bath. The ribs 19 are preferably beveled or rounded at the ends thereof which abut the orifice 13 to prevent the formation of eddy currents or variations in the pressure on the solutions, and thereby prevent blurring and waviness in the dividing line. If the distance from the coagulating bath to the point at which the two viscoses meet is greater than a certain maximum, there will likewise be intermingling and blurring. On the other hand, this distance should be sufficiently great so that a firm and lasting bond is formed between the viscoses before they are coagulated.

The modified form of extrusion apparatus illustrated in Figs. 4 and 5 comprises an outer shell or housing 35, terminating in an orifice 36. A die insert 37 is positioned within the die shell 35 and maintained in spaced relationship therewith in the manner set forth above in Fig. 1. The die insert 37 comprises a cylindrical extension 38 and an annular division ring 39. The division ring 39 is spaced from the cylindrical extension 38 so as to provide an annular channel 40. The annular channel 40 terminates at one end at the orifice 36. The other end of the channel is connected to supply conduits 41 and 42 by means of the annular groove 43 and the openings 44 and 45 in the division ring. The division ring is also spaced from the internal surface of the housing 35 to provide a second annular channel 46 which terminates at one end in the annular groove 55 and at the other end in the orifice 36. A plurality of radially extending partitioning ribs 47 are formed on the external surface of the division ring to divide the annular channel 46 into arcuate channels 48, 49, 50 and 51. These arcuate channels are individually supplied with cellulosic material by supply conduits 51, 52, 53 and 54 respectively. The division ring 39 separates the annular channels 40 and 46 up to a point closely adjacent the entrance to the orifice 36 at which point the two channels converge so that the solutions of cellulosic materials may flow together and securely unite before being coagulated. The radial ribs 47 extend throughout the length of the channel 46 and across the groove 55. The ends of the ribs 47 and the division ring 39 are beveled or rounded to maintain a uniform pressure between the separated portions of the cellulosic materials which are flowing together and simultaneously entering the orifice. A tubular member 56 for supplying coagulating fluid to the internal portions of the extruded tubing is arranged within the cylindrical extension 38 in the manner set forth above with reference to Figs. 1 and 2.

Fig. 6 illustrates a small section of tubing such as will be produced by the extrusion die of Figs. 4 and 5 when a substance for producing a transparent pellicle is passed through the inner channel 40 and the arcuate channels 49 and 51, which pellicles are designated in the tubing by A and B, and a solution for producing an opaqued pellicle is passed through the arcuate channels 48 and 50, which pellicle is designated by C.

The modification of the extrusion die illustrated in Figs. 4 and 5 is obviously operated in the same manner as above defined with reference to the extrusion die illustrated in Figs. 1 and 2.

After issuing from the extrusion orifice, the material is led through the necessary coagulating

and/or regenerating baths and thence through successive purifying baths and is finally wound up into reels and/or cut into short sections. The finished tubing shows parallel stripes in which the dividing lines between stripes are extremely sharp and of pleasing appearance. Subsequently, the tubing may be printed with suitable indicia and/or submitted to other finishing operations.

In order to produce viscoses capable of yielding pellicles of optical characteristics different from those of colorless transparent pellicles formed from the ordinary viscose, it has been customary to add materials to the viscose before precipitation. These materials may be added to one or more of the viscoses used in the practice of this invention. Examples of materials which have been found suitable are pigments, particularly titanium oxide, to form opaque stripes; dyes, to form colored stripes; scintillating particles such as mica, to form stripes of metallic appearance; and others. Any desired combination of one or more of these materials may be added to any viscose, when it is desired to alter the optical characteristics of the film produced therefrom. For example, a pigment alone, a pigment and a dye, or any other combination may be used. In addition, the optical characteristics of a tube may be further altered in subsequent steps, for example, by dyeing after coagulation. These materials may be incorporated in the viscose, adding to the mixer water before the sodium cellulose xanthate is dispersed therein, or dispersing or dissolving in water and then adding to the viscose.

The following are examples of compositions and the products obtained thereby useful in the practice of this invention. In all the following examples, where percentages are mentioned, it is to be understood that the percentage is based on the weight of the cellulose in the viscose.

Example I.—Three portions of viscose are made up as follows:

To portion A is added 15% of titanium oxide and 1% of the red dyestuff known under the trade name "Pontamine Fast Scarlet 4–BS" (Color Index No. 326); to portion B is added 15% of titanium oxide and 0.5% of the blue dyestuff known under the trade name "Pontamine Sky Blue 5–BX" (Color Index No. 520); to portion C is added 15% of titanium oxide. An extrustion device such as that illustrated by the drawings is used having a plurality of partitions forming twelve arcuate channels. Viscose from portions A, B and C is passed through alternate channels of the extrusion device. A tube is produced having a beautiful red, white and blue appearance, suitable as protective or decorative covering on golf club handles, stacks of poker chips or for any other purpose in which a protective or decorative covering is desired.

Example II.—The same procedure is followed as in Example I, except that 50% of mica is substituted for the titanium oxide in each portion of viscose. A tube of beautiful vari-colored metallic appearance is obtained.

When a die of the form illustrated by Figs. 4 and 5 is used the inner concentric channel is preferably provided with a cellulosic solution which will produce a transparent pellicle whereby the finished tubing will have greatly increased strength than would be the case where an entire cross-section of the tubing contains an opaquing agent or similar material incorporated therein.

Many other variations are possible within the scope of this invention. Any number of differently colored or otherwise differently appearing stripes may be produced from two up to a dozen or more. They may be opaque, metallic in appearance or transparent or any desired combination of these, together with various colors in combination. It will be evident that the number, type and location of the different stripes will depend upon the use to which the tubes are to be put.

Our invention has enabled us to produce tubes of regenerated cellulose or other non-fibrous sheet material of novel and interesting appearance having stripes with sharp dividing lines therebetween. It has furthermore enabled us to produce tubing of novel appearance having concentric layers and stripes of different optical characteristics. Tubing may be produced having novel striped appearance without sacrificing the desired strength thereof by providing the same with an inner layer of transparent material. Tubes produced in the manner described above may be used in the flat, collapsed form as ribbons or strips to be used in producing ornamental effects on packages tied therewith.

Since it is obvious that various changes and modifications may be made in the above description without departing from the nature and spirit thereof, it is to be understood that the invention is not to be limited thereto except as set forth in the appended claims.

We claim:

1. The method of forming tubular articles from freely flowing solutions which are instantly coagulable in a coagulating medium which comprises passing a plurality of such solutions, while maintaining them separated from each other, to a point closely adjacent said coagulating medium joining said solutions in an annular stream of substantially uniform cross section to form a bond therebetween and maintaining a sharp line of division at the joint between said solutions by causing them to flow in parallel relationship to each other prior to coagulation of the same, and immediately thereafter passing said stream into said coagulating medium.

2. The method of forming tubular articles from freely flowing viscose solutions which comprise passing a plurality of viscose solutions, while maintaining them separated from each other, to a point closely adjacent said coagulating medium joining said solutions in an annular stream of substantially uniform cross section to form a bond therebetween and maintaining a sharp line of division at the joint between said solutions by causing them to flow in parallel relationship to each other prior to coagulation of the same, and immediately thereafter passing said stream into said coagulating medium.

3. The method of forming tubular articles from freely flowing cellulosic solutions which are instantly coagulable in a coagulating medium which comprises passing a plurality of said solutions through substantially parallel passages, while maintaining them separated from each other, to a point closely adjacent said coagulating medium joining said solutions in an annular stream of substantially uniform cross section to form a bond therebetween and maintaining a sharp line of division at the joint between said solutions by causing them to flow in parallel relationship to each other prior to coagulation of the same, and immediately thereafter passing said stream into said coagulating medium.

4. The method of forming tubular articles from freely flowing cellulosic solutions which are in

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nprises passing a plurality of said solutions of different optical characteristics, while maintaining them separated from each other, to a point closely adjacent said coagulating medium, joining said solutions in an annular stream of substantially uniform cross section to form a bond therebetween and maintaining a sharp line of division at the joint between said solutions by causing them to flow in parallel relationship to each other prior to coagulation of the same, and immediately thereafter passing said stream into said coagulating medium.

8. A new article of manufacture comprising a thin, flexible, seamless tubing of regenerated cellulose having integrant, longitudinally parallel, circumferential sections, at least one of said sections being transparent, the remaining section or sections having a pigment uniformly distributed within the body of said section or sections to render the same non-transparent, the said tubing exhibiting sharp and distinct lines of demarcation between the said integrant sections.

9. A new article of manufacture comprising a thin, flexible, seamless tubing of regenerated cellulose having integrant, longitudinally parallel, circumferential and concentric sections, at least one of said circumferential sections being transparent, the remaining circumferential section or sections having a pigment uniformly distributed within the body of said section or sections to render the same non-transparent, the said tubing exhibiting sharp and distinct lines of demarcation between the said integrant sections.

10. The new article of manufacture comprising a thin, flexible, seamless tubing of regenerated cellulose having integrant, longitudinally parallel, circumferential sections, at least one of said sections being transparent, the remaining section or sections having a pigment uniformly distributed within the body of said section or sections to render the same non-transparent, the said tubing exhibiting sharp and distinct lines of demarcation between the said integrant sections, and a further section of regenerated cellulose in said tubing concentric with said integrant sections for reinforcing the latter.

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