March 29, 1955 A. O. RUSSELL 2,704,860

METHOD AND APPARATUS FOR PRODUCING PELLICLES

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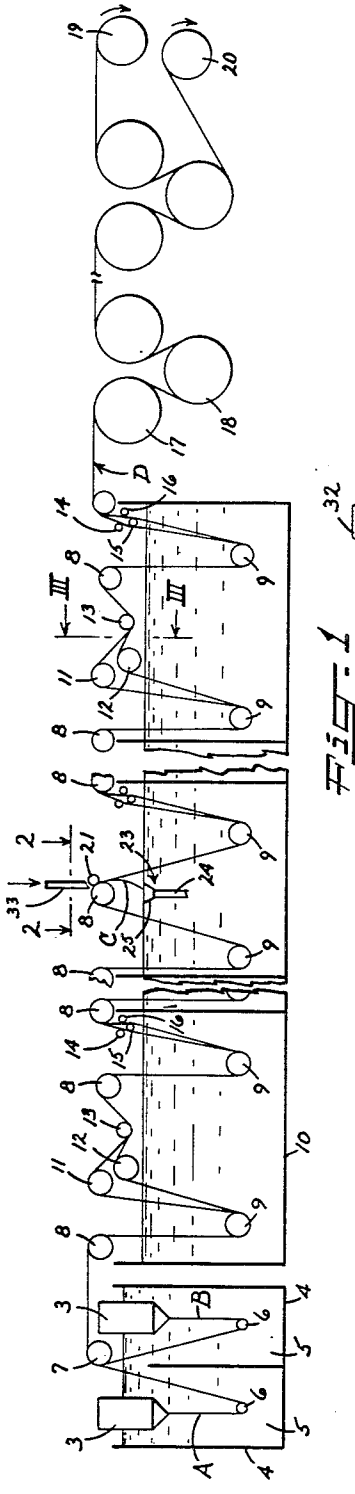


Fig. 1

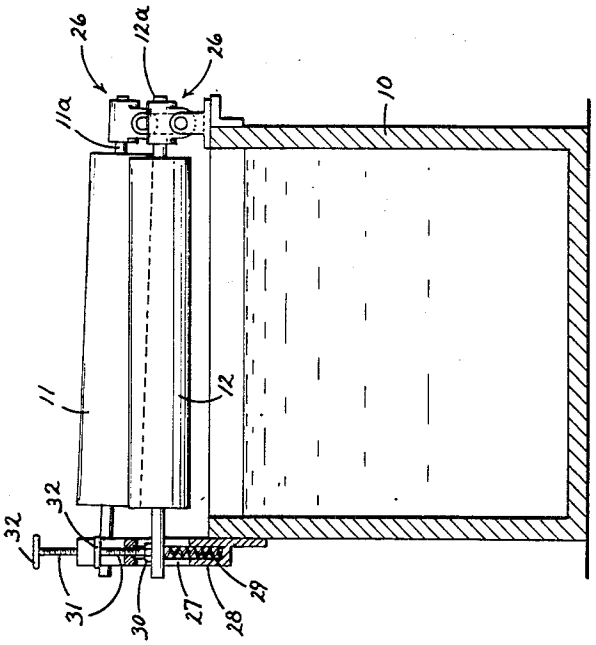


Fig. 3

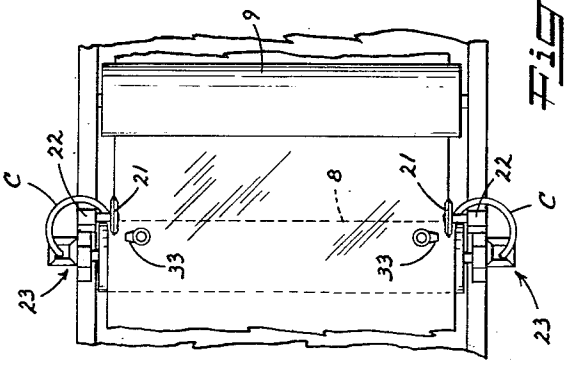


Fig. 2

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METHOD AND APPARATUS FOR PRODUCING PELLICLES

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Application March 20, 1953, Serial No. 343,629

6 Claims. (Cl. 18—15)

This invention relates to the production of non-fibrous polymeric films, foils, sheets and pellicles and is particularly concerned with the production of pellicles of this type having improved characteristics, especially those of strength, swelling, and shrinkage, both transversely and longitudinally, as well as substantial uniformity in thickness, and freedom from striations.

In the conventional system for the production of pellicles, such as regenerated cellulose from viscose or other cellulosic solution, such as cuprammonium cellulose, the film-forming solution is extruded into a coagulating and/or regenerating bath through a narrow slot, the width of which in commercial practice is frequently tapered down to an even narrower width at each end in order to substantially reduce the formation of thickened longitudinal edges on the pellicle, commonly referred to as a "bead." The film is drawn from the extrusion slot through a series of treating liquids, generally by the use of suitably disposed guiding rolls, at least some of which are positively driven to draw the pellicle through the system. Some of the rollers are disposed above the baths for transferring the film from one to another of the baths and some are disposed in the baths to provide a zig-zag path of travel for the film through the baths thereby enabling the film to pass a considerable distance through such baths while economizing on space. The nature of the baths depends upon the particular type of film-forming solution used. For example, when it is of viscose, the pellicle may pass from the coagulating and/or regenerating bath into a regenerating bath to substantially complete the regeneration, then to suitable washing, desulfurizing, bleaching, neutralizing, and softening baths as well as intervening washing or rinsing baths which follow one another in sequence in conventional manner. Because of the force exerted upon the film by the driving rollers, the film is tensioned in the machine direction, that is longitudinally, and depending upon the rate of speed through the baths, the number of rollers, the length of travel through the baths, and the particular disposition of the rollers therein, more or less stretching may be effected upon the film. The amount of stretch thus inherently imparted to the film in a longitudinal direction may vary from as low as 5% to as high as 50% or more elongation relative to the initial length of the film. After passing through the liquid treatment baths, the film proceeds in a sinuous path about a series of drying rolls which may be heated internally and/or may be disposed in a closed chamber through which a heated fluid medium is circulated. At least some of these rolls are driven and the tension produced longitudinally in the film prevents any shrinkage thereof longitudinally. One serious disadvantage of the use of a slot with tapered ends is the fact that the edges are weakened and tear easily. When a tear starts from the edge, it progresses almost instantly across the entire pellicle interrupting the operation of the machine.

The product obtained at the completion of the drying step is frequently found to have distinct irregularities both transversely and longitudinally. For example, the marginal areas, especially the outer 3- to 5-inch width, do not lie perfectly flat relative to the central area when a sheet thereof is laid or allowed to rest upon a flat table. Instead, they have a slight wavy disposition. Also, the edges frequently are not straight and parallel but have an irregular wavy form. It has also been found that frequent longitudinal ridges or striations are formed in the marginal areas of the pellicle. Consequently, in spite of

the precautions used in providing tapered ends of the extrusion slot, it has frequently been the practice to slit off from 3 to 5 inches or more of the edges of the dried pellicles thus produced.

It is an object of the present invention to provide improved methods and apparatus for producing non-fibrous pellicles having substantially uniform properties, especially in respect to thickness, planarity (that is flatness throughout its area), freedom from striations, and straightness of edges.

According to the present invention, it has been discovered that a narrow marginal edge may be removed from each side of the pellicle while the pellicle is still in a wet gel condition or state and thereby there is produced a product which after drying is substantially free of the disadvantages and non-uniformities of pellicles which have been dried without the removal of the narrow marginal edge. Whereas a width of 3 to 5 inches from each marginal edge would have to be removed from dried films in order to leave the remaining central portion of the pellicle having substantially true planarity (that is flatness throughout its extent), the removal of as little as ½ to 1 inch of the marginal edges while in the wet gel state is adequate to substantially reduce and practicably prevent the development of waviness and irregularities in the marginal edges of the dried product. Furthermore, this procedure of the invention is applicable to pellicles which have been produced either from slots having uniform thickness throughout their length or through those having tapered ends. Because of the fact that far less marginal area is removed when operating in accordance with the invention as compared to prior practices, the invention provides the additional advantage of reduction of material wastage.

It appears that the presence of a bead at the edges of the pellicle as they pass over the internally heated drying rolls affects not only that portion of the margin immediately adjacent the bead having increased thickness relative to the central portion of the sheet but also an additional inwardly disposed longitudinal area, the width of which may be 4 to 10 or more times that of the width of the thickened edge or margin of the pellicle. By trimming off the thickened edge portion or bead before the drying of the pellicle, its influence in producing distortions in the inwardly extending adjacent longitudinal area of the pellicle is completely overcome. The full width of the sheet passing over the drying rolls is of substantially the same thickness throughout clear up to the very edge so that there is no tendency (such as that which occurs with thickened edges) to lift the adjacent longitudinal area of the pellicle up out of contact with the drying rolls as it proceeds about them.

The invention is applicable to systems in which a single pellicle is produced and also to those in which a plurality of pellicles are produced simultaneously. In the latter system, two or more pellicles may be extruded from adjacent slotted orifices and passed through liquid treatment baths together and finally through the drying system, such as over heated rolls, during most of which passage through the liquid treatment baths and the drying, the pellicles are maintained in contact. The removal of the beaded edges from the pellicle before drying has additional advantages when the plural pellicle system is employed. It sometimes happens that the edges of the superposed sheets are displaced out of alignment as they proceed through the treating processes. When this occurs on the drying rolls, the beaded edge of one pellicle tends to produce a pressure line on the surface of the other pellicle as it proceeds about the circumference of the drier roll, both when it is on the outside and when it is on the inside relative to the other pellicles. Along the other edge of the system, the beaded edge of the other pellicle will impress itself into the surface of the former pellicle, assuming both pellicles are of the same width at the particular time involved. This impression is greatly reduced by the elimination of the bead.

A further feature of the invention is to provide for the alignment of the plurality of pellicles when more than one is being produced at one time prior to the entry of the pellicles into the common drying system. Preferably, this alignment is effected not only through the

drying but through the liquid-treating stages. It results in the avoiding of any streaks near the edges caused by pressure of an edge of one sheet against the marginal surface of the other sheet. It also assures uniform drying of all areas of both sheets and drying substantially at the same rate so that there will be no tendency for a projecting marginal area of one sheet to dry faster and shrink before the remainder of such sheet which is in contact with the other pellicle. By maintaining the sheets in superposition with their edges in alignment throughout the liquid treatment, such treatment is effected more uniformly on the pellices; and the absence of the bead, which tends to vary somewhat in thickness along the length of the pellicle, avoids the irregular entrance of the liquids between the pellicles along their lateral margins which would cause variations in the rate of set-up and purification with possible distortions adjacent the edges.

In the drawing, which is illustrative of preferred embodiments of the invention,

Figure 1 is a diagrammatic side elevation with parts removed of an apparatus for carrying out the invention,

Figure 2 is a plan view of that portion of the wet end of the machine shown in Figure 1 where the slitters are located,

Figure 3 is an end view taken on line III—III of Figure 1 to show the means for aligning the pellicles as they proceed through the system.

As shown, a pair of extrusion hoppers **3** are provided in one or more coagulating bath containers, such as in adjacent containers **4**. The film-forming material, such as a viscose solution, is extruded through slits at the bottom of the hoppers and passes downwardly through the liquid coagulating baths **5** about guide rods or rolls **6** which may be of the arcuate spreader type. The pellicles A and B proceed then about an upper roll **7** to a series of liquid treating stages which, of course, depend upon the character of the pellicles A and B. Each stage comprises a plurality of upper rolls **8** and lower submerged rolls **9**, the latter being disposed adjacent the bottom of one or more suitable containers **10**. In one or more of the liquid-treating stages, there may be provided an edge-alignment device comprising tiltable rolls **11** and **12** and a cooperating guide roll **13** may be provided. The pellicles should make less than 180° contact, preferably about 90° to 130°, with the peripheral surfaces of rolls **11** and **12** which are tilted as described hereinafter.

Wiper rolls, rods, or bars **14**, **15** and **16** may also be provided adjacent the discharge end of each bath, the intermediate wiper **15** being arranged between a pair of the pellicles when two are being produced simultaneously. Of course, when three or more sheets are produced, additional wiper rods may be provided so that one may be spaced between each pair of the several pellicles in addition to the outside wipers for the outer surfaces of the outer pellicles.

From the last of the liquid-treating stages, the pellicle or pellicles proceed about a series of staggered drying drums comprising drums **17** in an upper row and drums **18** in a lower row. When a plurality of pellicles are produced, they preferably remain in superposed or face-to-face contact during most of the drying stage. From the drier, the pellicle or pellicles proceed to collecting or transverse cutting devices, such as wind-ups at **19** and **20** respectively.

During the liquid-treating stages, the edges of the pellicle or pellicles are trimmed. To effect this, a pair of slitting knives **21** are mounted to cooperate with one of the upper rolls **8**. The slitters **21** are disposed, as shown in Figure 2, adjacent the sides of the path of travel of the pellicle or pellicles through the system and are rotatably mounted in the side bearings **22** of the frame of the machine. Receptacles **23** are provided adjacent each side of the machine outside the container **10** near the point of slitting. As shown, each receptacle comprises a conduit **24** terminating with a flared opening **25** of funnel-like construction. A suction pump may be connected to the conduits **24** to suck the edge trimmings C through the conduit.

As shown in Figure 3, rolls **11** and **12** are mounted on shafts **11***a* and **12***a* so that they may tilt within the self-aligning bearings **26** at one side of the machine. The other ends of the shafts **11***a* and **12***a* project through slots **27** of their bearings **28** and springs **29** urge each shaft upwardly against a corresponding shoe **30** which is vertically adjustable by means of the screw-threaded stem **31** connected to the hand wheel **32**. If desired, the hand wheels **32** may be replaced by reversible motors which are controlled by a photocell system associated with the edge or edges of the pellicles just beyond the liquid treating system such as at point D (Figure 1) between the wet end and the drying system of the machine. Similarly, the slitters **21** may be automatically controlled by photoelectronic devices, such as by the mechanism shown in application Serial No. 268,612, filed January 28, 1952, so that the slitters may be shifted transversely of the pellicles either together to provide a sheet of constant width or independently to cut off the same amount from each edge as desired.

It is essential to the present invention that the slitting be effected during the wet-end or liquid-treating stages of the system. It may be effected immediately after the pellicle or pellicles leave the coagulating bath or baths, such as on roll **7**, or it may be effected at any point during the liquid treatment. In the preferred operation, the slitters act upon the pellicle or pellicles at a washing stage of the liquid treatment so that corrosion of the knives **21** may be minimized. Where it is necessary or desirable to locate the slitter knives at a stage wherein the pellicle or pellicles carry a corrosive liquid, it may be desirable to feed an inert or less-corrosive washing liquid directly against the knives in the cutting position, such as by means of nozzles, pipes or spray heads **33**. In all cases, it is desirable that the knives be made of suitable cutting material which is as corrosion-resistant as possible. An example of such a material is stainless steel.

It is essential, of course, that the removal of the marginal edges is not effected until the pellicle or pellicles have been substantially completely coagulated and rendered plastic so that liquid surface tension effects of the film-forming material making up the body of the pellicle or pellicles cannot re-exert themselves and reform a bead on the freshly cut edges. In general, the slitters should be mounted outside the body of the liquid-treating baths as shown.

Preferably, when a plurality of pellicles are simultaneously produced, the slitters are located immediately after an alignment system so that the edges of the pellicles are in alignment at the time the margins are slit away. If desired, an additional alignment system may be disposed immediately before the drying system to make any final adjustments before the pellicles proceed to the drier.

The various rolls **7**, **8**, **9**, **11**, **12**, **13**, **17** and **18** may all be positively driven or some of them may be driven and others allowed to idle. Certain of these rollers may be driven at higher speeds than others in order to stretch or allow shrinkage of the pellicle or pellicles at any desired stages of the liquid treatment and/or drying system. While the system shown is adapted to produce two pellicles simultaneously, additional extrusion hoppers **3** (and, if desired, additional coagulating baths **4**) may be provided to produce any larger number of pellicles. On the other hand, one of the hoppers **3** may be allowed to remain inactive so that a single pellicle may be produced on the system shown.

When a plurality of pellicles are produced simultaneously, they may be allowed to remain in contact through most of the liquid-treating stages except where necessary to separate them for separate passage over the tilting rolls **11** and **12** to assure subsequent alignment. Again, separation may be made as shown for the purpose of wiping excess liquid from the opposed surfaces of the superposed sheets as by the wiper **15**. On the other hand, numerous separations may be made while in the liquid-treatment baths for other purposes. The various rolls may be so mounted as to provide equal distances of travel of the several pellicles in each of the treating baths, but this is generally not essential, particularly when a system for edge-alignment is provided immediately before the pellicles proceed to the drying system.

When a plurality of pellicles are produced simultaneously, they may be momentarily separated at one or several points as they proceed over the drying rolls or they may be allowed to remain in contact throughout their passage through the drying system, but to facilitate their separation in the latter instance, it is preferable to

introduce a separation agent into the last liquid-treating bath immediately preceding the entry of the pellicles into the drying system.

The separation agent may be any finely particulate material which is insoluble in the liquid by which it is to be applied and capable of being dispersed therein such as in the form of colloidal particles. When an aqueous bath is used, colloidal silica is extremely satisfactory. Colloidal solutions of silica may be formed by reacting an acid, such as a mineral acid or any other acid capable of forming salts by reaction with silicates, with a water-soluble silicate such as sodium silicate in the manner customarily employed to form silica gel, washing the resulting gel with water to remove the electrolytes formed during the reaction, covering the gel with a weak aqueous solution of a substance capable of forming hydroxyl ions and, after removing the gel from the solution, heating the gel, while avoiding evaporation of water, until substantially all of the gel is converted to a sol.

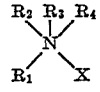
Other insoluble inorganic materials, such as calcium carbonate, magnesium carbonate, calcium silicate, may be used. Organic materials that may be used as the separation agent include many surface active dispersing agents, such as condensation products of a higher fatty acid, a higher fatty acid amide, or a higher fatty alcohol with an alkylene oxide such as ethylene oxide. For example, the condensation product of stearic acid with 12 to 15 mols of ethylene oxide per mol of stearic acid may be used. These condensation products are self-emulsifying and generally are included within the class of self-emulsifying agents. Other self-emulsifying dispersible agents include the ethers and esters of polyhydric alcohols containing one or more free hydroxyl groups, and condensates thereof with ethylene oxide containing, for example, from 1 to 20, 50, or even 100 or more ethylene oxide units per molecule. For example, the self-emulsifying material may be a partial ester of such alcohols as sorbitol, mannitol, glycol, glycerol, etc., with fatty acids such as stearic, oleic, myristic, lauric, etc.

Representative substances are:

Glycerol monopalmitate
Glycerol monostearate
Diethylene glycol monostearate
Ethylene glycol mono-oleate
Diethylene glycol mono-oleate
Sorbitol distearate
Sorbitol tristearate
Sorbitol tetrastearate

or other partial esters of the alcohols with the higher fatty acids, and preferably such acids containing at least 8 carbon atoms. Such compounds as sorbitol mono-, di-, tri-, or tetrastearate containing 6 ethylene oxide units, as well as substances of the type of polyethylene glycol monostearate containing 10 to 50 or more ethylene oxide units may be used. Esters from mixed fatty acids such as are obtainable from fish oils, vegetable oils, or animal fats, which may or may not be hydrogenated, may likewise be used. The esters may be in their pure state or in the form of their technical grades available on the market in which form they vary from liquid, oily, or pasty to firm masses which are generally readily meltable at temperatures slightly above room temperatures.

Cationic dispersing agents may be used as the separation agent. Examples are the quaternary ammonium compounds having the general formula:



in which

R_1 denotes an alkyl group of at least 12 carbon atoms, R_2 and R_3 denote alkyl groups of 1 to 20 carbon atoms, R_4 denotes an alkyl group of 1 to 3 carbon atoms, and X denotes an organic or inorganic anion such as Cl^-, HSO_4^-, $CH_3SO_4^-$, etc.

These compounds are prepared by the exhaustive methylation of primary, secondary, or tertiary fatty amines, such as amines from hydrogenated tallow, octadecyl amine, heptadecyl amine, nonadecyl amine, methyl octadecyl amine, dimethyl octadecyl amine, etc., with an excess of methyl chloride or dimethyl sulfate, and the like, in a closed container at temperatures of 30 to 130° C. The primary, secondary, and tertiary fatty amines are easily prepared from the corresponding acids by well-known procedures.

Among the cationic compounds particularly suited to the practice of the present invention may be listed octadecyltrimethylammonium chloride and dimethyldialkylammonium chloride where the alkyl groups are produced by the hydrogenation of tallow. These compounds are also self-dispersible in water.

Mixtures of a finely divided inorganic particulate material, such as colloidal silica, with any of the organic agents mentioned above may be used when the ingredients are compatible, and the organic compounds serve to disperse the inorganic colloidal material or as a protective colloid to stabilize the dispersion.

The silica in the dispersions containing cationic compounds may be derived from any hydrolyzable water-soluble or water-dispersible silicic acid ester, for example, ethylene glycol silicate, propylene glycol silicate, etc. However, the silica is preferably derived from ethyl silicates, such as tetraethyl orthosilicate, and the like. The two materials, i. e., the ethyl silicate and the cationic compound may be mixed together, or melted together if the cationic compound is a solid, before being added to water, or the water may be heated and the cationic compound dispersed therein before the ethyl silicate is added, or the emulsion of the cationic compound may be cooled to a moderate temperature before the silicate is added.

In some cases, especially where it is desired to use hard water to make up the medium for applying the separation agent, a sequestering agent may be added, particularly with the anionic type of surface-active agent. As an example, the tetrasodium salt of ethylene diamine tetra-acetic acid, is particularly useful for this purpose.

The following exemplary embodiments are given to illustrate the preparation of a separation agent applying medium when such is desired to be used. Ten parts of dimethyl dialkyl (the mixture of 30% of hexadecyl and 70% of octadecyl radicals obtained by the hydrogenation of tallow) ammonium chloride were emulsified in 100 parts of water at 65° C. The emulsion was cooled with stirring to 45–50° C. and then 5 parts of tetraethyl orthosilicate were added with vigorous stirring. The emulsion was then allowed to stand 24 hours to complete the hydrolysis of the silicate to silica at the end of which time it was ready for use. The emulsion was then added to the plasticizer bath, which contained 5% glycerol, to give a solids content in the bath of 0.5%. In another preferred embodiment, the final bath through which the two sheets of regenerated cellulose pass contained about 5% by weight of glycerol, 0.1% of colloidal silica and 0.1% of glycerol monostearate. In a third preferred embodiment, the final bath through which the regenerated cellulose gel films passed before proceeding to the drying stage contained 5% of glycerol, 0.2% of colloidal silica and 0.2% of the condensation product of stearic acid with an average of 15 mols of ethylene oxide.

In general, the amount of separation agent dispersed in the liquid medium through which the pellicles pass may vary from 0.05 to 2% but preferably from 0.1 to 0.5%. The amount of separation agent left on the pellicle may be as low as 0.02 to 0.05% by weight as determined after drying of the pellicle to normal moisture content. However, it may be applied in larger amounts up to 0.1 to 0.2% or more as determined on the same basis.

The process of the present invention may be used for the production of films, pellicles, sheets, or the like from any film-forming material which requires treatment in liquid baths and subsequent drying and it is particularly advantageous for the drying of hydrophilic pellicles. For example, it may be used for the production of regenerated cellulose or cellophane pellicles from viscose, cuprammonium cellulose, or alkaline solutions of water-insoluble alkali-soluble cellulose ethers, such as methyl cellulose, ethyl cellulose, hydroxyethyl cellulose, mixed ethers thereof and other hydrophilic materials; it may also be used for the production of films from cellulose acetate or other cellulose esters by wet spinning procedures; it may also be used for the production of pellicles from vinyl resins, synthetic linear polymers, such as nylon, polyethylene, polyvinylidene chloride, polyvinyl chloride, polyacrylonitrile, copolymers of polyacrylonitrile with vinyl chloride, vinyl acetate, methacrylonitrile, 2-vinylpyridine, 5-methyl-2-vinyl-pyridine, or with a mixture of

any two of the last-mentioned monomeric compounds, copolymers of vinyl chloride with acrylonitrile and with vinyl acetate, casein, prolamines, and other proteins.

The particular liquid-reacting baths used for the production of the pellicles depends of course upon the particular film-forming material and properties desired in the final product. For example, in producing regenerated cellulose pellicles from viscose, the viscose may be extruded directly into a regenerating medium or first into a liquid which coagulates but does not regenerate the viscose. The coagulation is effected either simultaneously with regeneration or is followed by regeneration in one of the containers **10**. The pellicles may be stretched or allowed to shrink, such as during their passage from the coagulating bath in the vessels **4** to the regenerating bath in the first of the vessels **10** or at any subsequent stage. Other liquid treatments may include desulfurization, washing, bleaching, neutralization, washing, and plasticizing.

When the film-forming material comprises an alkaline solution of a cellulose ether, the coagulating bath may be simply an acid bath and no regeneration bath is required as in the case of viscose. This may be followed by a washing bath, optionally a bleaching bath, and a plasticizing bath. The latter may include the plasticizers mentioned above with reference to viscose. When protein spinning solutions are used, a curing agent, such as a chromate salt or formaldehyde may be used in one of the baths to harden the material.

When moistureproof coatings are to be applied to the materials and it is desired to apply preliminary anchor coatings thereto, the anchor agents may be included in the same bath by which the separation agent is applied provided the various constituents are sufficiently compatible. For example, a precondensate of melamine and formaldehyde or urea and formaldehyde may be dissolved in the same bath along with a plasticizer when the latter is used.

It is to be understood that changes and variations may be made without departing from the spirit and scope of the invention as defined in the appended claims.

I claim:

1. A process for producing a non-fibrous pellicle from a film-forming solution comprising extruding such a solution through a slot into a coagulating bath to form a coagulated pellicle, removing the edges of the pellicle after coagulation is complete and while the pellicle is still in the wet gel state, and then drying the pellicle.

2. A process as defined in claim 1 in which the slitting is effected while the pellicle carries thereon a wash liquid.

3. A process of producing a plurality of pellicles simultaneously from a film-forming solution comprising passing a plurality of streams of such solution through slot orifices into a coagulant therefor to form a plurality of coagulated pellicles, passing the plurality of pellicles together through a plurality of liquid-treating stages, slitting off marginal edges of said pellicles while they are still in the wet gel state, then passing the wet gel pellicles through a drying zone, and maintaining the films in contact with each other during most of the drying stage.

4. Apparatus for producing a pellicle comprising means for extruding a thin, wide stream of a film-forming solution, a container for supporting a coagulating bath in proximity to the extrusion means, means for drawing the pellicle through the coagulating bath, means for drying the pellicle, means for drawing the pellicle through the drying means, and means in advance of the drying means for slitting off the marginal edges of the pellicle while it is still in the wet gel state.

5. Apparatus for producing a plurality of pellicles comprising means for forming a plurality of thin, wide streams of a film-forming solution, means for supporting a liquid coagulant adjacent the stream-forming means, means for drawing the pellicles through the coagulant, means for slitting off the edges of the pellicles while in the wet gel state, and means beyond the slitting means for drying the pellicles simultaneously.

6. Apparatus for producing a plurality of pellicles comprising receptacle means for containing a plurality of liquid-treating stages, drying means beyond the liquid-treating stages, means for extruding a plurality of thin, wide streams of film-forming material into a coagulating liquid in said receptacle means for forming a plurality of pellicles therein, means for drawing the coagulated pellicles through the receptacle means and the drying means, and edge-slitting means positioned along the path of travel of the coagulated pellicles through the liquid-treating stages.

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