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METHOD FOR PRODUCING PELLICLES, FILMS AND SHEETS

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Fig. 1a

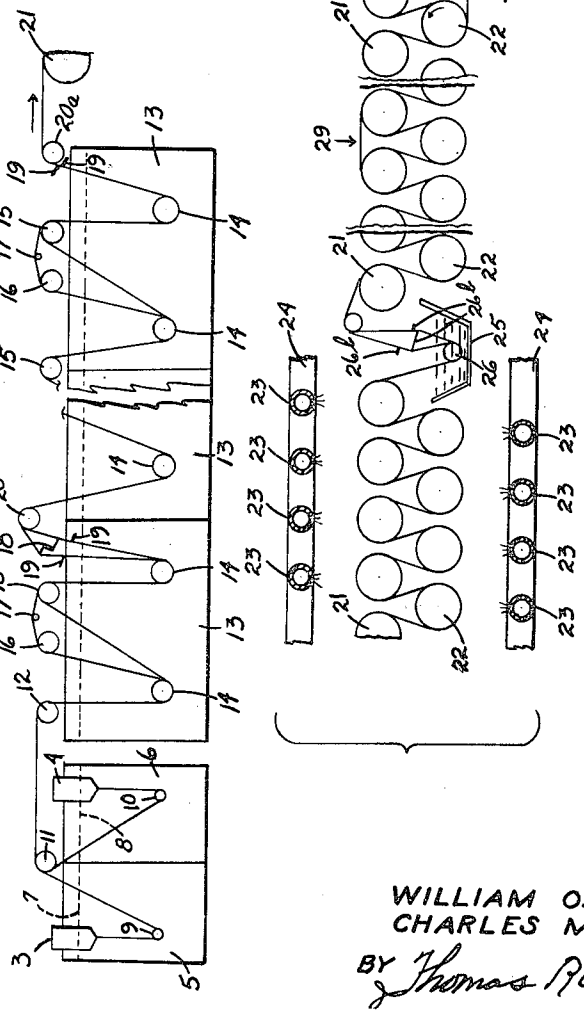


Fig. 1b



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METHOD FOR PRODUCING PELLICLES, FILMS, AND SHEETS

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4 Claims. (Cl. 18—57)

This invention relates to the production of pellicles, films and sheets in which two or more of such pellicles are produced simultaneously and processed on common equipment.

Heretofore, when two or more hydrophilic pellicles, such as regenerated cellulose, were produced and processed simultaneously, such as by extrusion through separate dies and then carrying the sheets together through common coagulating, regenerating, desulfurizing, bleaching, and other baths, the two films have been separated upon leaving the last bath of the series of liquid after-treating baths and passed through separate driers or about separate drying drums or guiding devices in a single drier common to both sheets. The use of separate driers was required to avoid the permanent lamination or cementation of hydrophilic pellicles that would result from drying them in contact as they pass over and about heated drying drums or rolls.

In accordance with the present invention, it has now been found that several welt gel hydrophilic pellicles, such as are simultaneously produced as stated above, can be satisfactorily dried without being laminated or cemented together permanently, on the same drying equipment as that normally used for drying a single wet gel pellicle, such as of cellophane, even at high speeds, such as 50 to 75 or more meters per minute.

In accordance with one embodiment of the invention, the several hydrophilic pellicles are maintained in contact during the early stages of drying until they have been dried down to a moisture content of 30% and no separation is made before this point unless it is accompanied by a thorough rewetting of the surfaces with a liquid, such as one comprising the liquid which is being dried out of the pellicle. The several pellicles are then separated while their moisture content is in the range of 12 to 30%, preferably about 15 to 20%. The separation need be only momentary; it may be permanent in which event the drying may be finished on separate guides or rolls in the same drying system or different drying systems; or it may be effected repeatedly in the remainder of the drying either before or after the 12% moisture content figure is reached.

It has been found that cockled pellicles, i. e., products in which the pellicle does not have a flat surface but contains portions which are bulged and some portions which are shrunk relative to the general plane of the pellicle, are frequently produced when separation of the two pellicles is effected before the moisture content has been sufficiently reduced. In producing cellophane from viscose, if the two pellicles are dried while in face to face contact after leaving the last liquid-treating bath, cockling is liable to occur if separation and reunions are attempted before the pellicles have been dried down to a moisture content of 30%. On the other hand, if the pellicles are not separated before the moisture content is reduced below 12%, the final products show optical distortions on their surfaces such as hazy spots or streaks and when initial separation is effected very late, such as at the end

of the drying system, tearing or breakage occurs because of the adhesion of the two contacting surfaces of the pellicles.

In accordance with the present invention, it has also been found that the surfaces of the pellicles which are to be in contact during drying can be coated, impregnated or suffused with a substance herein called a "separation agent" and when so treated, the first separation during drying may be delayed beyond the point of 12% moisture content and in most cases separation can be omitted entirely without encountering difficulties with optical distortions and tearing mentioned above. This is advantageous for several reasons. It allows winding the pellicles together on a common core so that they can be transported as a single unit to the scene of the next operation therewtih, such as coating or package wrapping whether that be in the same plant or in a customer's plant, with assurance that the pellicles can be separated later without tearing. It allows the pellicles to remain in contact throughout the drying and to be separated without tearing immediately upon leaving the drier so that they can be wound separately. However, one of the most important advantages is the fact that the initial separation may be made while the pellicles have a moisture content below 12%. This is extremely valuable in the operation of the drying machine, especially when it is used in conjunction with the pellicle-casting and liquid after-treating devices. When first starting a pellicle-producing machine or when one of the pellicles is "lost" by breakage because of accident, defects in the pellicle, or other cause, such as machine breakdown or irregularity, it is frequently necessary to run the machine including the drying devices thereof at lower than normal speed so that pellicles passing through the point of first separation are dried below 12% even though, at normal speed of operation, the pellicles at this point would have a moisture content between 12 and 30%. The use of the separation agent allows this reduction of speed without producing optical distortions and breaks in the pellicles. It also prevents the development of wrinkles during winding in hot, humid weather, which would otherwise tend to occur in such weather, especially when the pellicle has a high plasticizing content.

The separation agent may be any organic substance whose molecule consists of, or comprises as a predominating part thereof, an essentially non-polar constituent or any extremely finely-subdivided water-insoluble particulate inorganic or organic substance or a mixture of such substances. The application of the material may be effected at any time prior to the drying stage, preferably in the last liquid-treating bath, or it may be applied during the early stages after initial drying by a rewetting step in which the partially dried pellicles are separated to allow treatment with a liquid containing the separation agent, with or without other materials such as resin precondensates, e. g. of melamine- or ureaformaldehyde, for producing anchoring coatings on the pellicles when moistureproof and/or heat-sealing coatings are to be applied later.

The drawing illustrates the process of the present invention. Fig. 1*a* is a diagrammatic vertical section of the wet end of a pellicle casting system and Fig. 1*b* is a similar view of the drying and winding systems to which the pellicles proceed from the wet end shown in Fig. 1.

As shown, two hoppers **3** and **4** are disposed in the upper portion of adjoining open-topped containers **5** and **6** respectively. These hoppers may be fed with the film-forming material, such as viscose, cuprammonium cellulose, or solutions of cellulose esters or ethers as mentioned hereinbelow and the solution is forced through hoppers **3** and **4** downwardly through a slot of a nozzle formed between suitable "lips" in conventional fashion,

The film-forming material discharged through the slots or nozzles is immediately coagulated in liquid baths 7 and 8 respectively. The coagulated films or pellicles proceed down about guide rollers 9 and 10 respectively and then together about the upper guide roller 11. The two films then proceed around a guide roller 12 down into one or more liquid-treating baths contained in the vessels 13.

In proceeding through each of the baths, the films may be guided about separate systems of rolls but preferably, at least some of the rolls associated with each of the containers 13 serve to guide both sheets or pellicles, i. e. they are common to the guiding system for both pellicles. For example, in the first container 13, the bottom rolls 14 and the upper roll 15 are common to the guiding system for both pellicles. If desired, the pellicles may be separated for part of their travel through each bath in the several containers 13 and this may be effected by a roll 16 about which the upper of the two pellicles may be separately guided. Between the rolls 15 and 16, a guide roll 17, which is mounted to be adjustably tilted about an axis extending longitudinally of the general direction of travel of the pellicles through the system, may be provided to shift the upper pellicle laterally relative to the lower to re-align the two pellicles as they proceed to the next upper roll 15 or to provide any desired lateral displacement in which the two pellicles are only partially overlapped. As the pellicles proceed between adjacent containers, they may pass separately over an internal double-edged wiper 18, between the external wipers 19, and over the roll 20. Excess liquid is removed by means of the wiper blades 18 and 19 which extend transversely of the pellicles, at least the entire width thereof.

In accordance with the present invention, the two pellicles proceed from the last liquid-treating bath 13 about a common guide roll 20*a* to the drier system comprising the driven staggered drying rollers, the upper ones of which are designated 21 and the lower ones 22. Conduits 23 may extend from headers 24 transversely of the pellicle above or below each of the drying drums or rolls 21 and 22 respectively. The conduits 23, when used, have openings facing the passing pellicle to direct heated air of controlled humidity thereagainst.

If desired, a rewetting or dip bath may be provided in a container 25 disposed in the early part of the drying system. The rod 26 submerges the pellicles as they pass through the bath 25 and an internal wiper 26*a* separates them. External wipers 26*b* are also provided to render the coating on the outermost surface uniform. When the separation agent is applied in bath 25, the two pellicles should be separated as they proceed therethrough. However, a very useful procedure for certain purposes, such as for producing pellicles which are later coated on one side only with a moistureproofing and/or heat-sealing lacquer, is to apply a separation agent in the last bath 13, which may also contain a plasticizer, such as glycerine for cellophane, and then pass the pellicles after partial drying through bath 25 without separation. The bath 25 may contain any material that is desired to be placed on one side only of the pellicles, such as moistureproofing, heat-sealing, or coloring materials, or an anchor coating or "subbing" material which serves to facilitate the adherence of a subsequently applied coating, as of a moistureproofing, heat-sealing or other material. The coating applied is preferably compatible with any previously applied material that remains on the pellicle at this stage, such as a plasticizer. When an anchor coating is applied in 25 without separation, the two pellicles may, after completion of the drying without separation, be passed through the final coating bath still without separation, or they may first be wound up together and then passed without separation through the final coating. After final drying, the pellicles can be separated whenever desired. Separation at this stage may be facilitated by humidification. The pellicles, when a separation agent has been applied to the opposed surfaces thereof either in bath 13 or 25, may proceed about the single system of staggered drying rolls 21 and 22 throughout the drying stage to the normal dryness of 4 to 6% without separation and then proceed to be taken up by winding together upon a common core, such as 27, or by winding upon separate take-up cores as at 27 and 28.

The pellicles may be separated as at 29, from one another during the drying stage at any time that the moisture content of the pellicles is within the range of 12 to 30%. As shown, the upper pellicle passes alone along the horizontal line between two adjacent upper rolls 21 at point 29 while the lower pellicle proceeds alone around the intervening lower roll 22. Whether or not a separation agent is used, when this system is used, the two films may be wound together on a common core 27 or separately on the cores 27 and 28 as shown. After separation is made at 29, the pellicles may thereafter proceed separately about separate drying devices to complete the drying, but preferably they are returned to the same system as shown. The pellicles may also go through an additional separation point such as that indicated at 30 where the lower pellicle passes alone horizontally between two adjacent lower rolls 22 while the upper pellicle passes around the intervening upper roll 21. As stated before, the later separations may occur at any point regardless of moisture content. Also by having an additional separation nearer the end of the drying system, relacing (after breaking or loss of one pellicle at the winding stage, such as at the completion of a winding roll) is facilitated because the operator need not go so far back along the drying system to seize the pellicles separately. This also results in a reduction of the amount of pellicle lost or damaged during relacing.

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-vinyl-pyridine, 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-treating 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 13. The pellicles may be stretched or allowed to shrink, such as during their passage from the coagulating bath in the vessels 5 and 6 to the regenerating bath in the first of the vessels 13 or at any subsequent stage. Other liquid treatments may include desulfurization, washing, bleaching, neutralization, washing, and plasticizing.

The separation agent may be introduced between the films or sheets as they pass through the last bath, such as in the softening bath which may also contain plasti-

cizers such as glycerin, glycols, sorbitol, urea, sodium lactate, condensation products of urea or a sorbitol with ethylene oxide, or mixtures thereof. The separation agent may be colloidally dispersed in a separate liquid bath following the plasticizer bath, such as that in 25. It is essential that, whether or not the films are separated during any other part of their passage through the liquid-treating baths, they be separated at least during a part of their travel through the liquid bath containing the separation agent dispersed therein. This is necessary to assure that the surfaces of the pellicles which are subsequently to face each other during the drying are coated, impregnated, or suffused with the separation agent.

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 the plasticizer when the latter is used.

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 which 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.

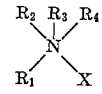
Representative substances are:

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 tetra-stearate 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 tetra sodium 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.

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.

We claim:

1. A process for drying pellicles which comprises the steps of positioning a plurality of wet gel pellicles in face-to-face contact, passing said contacting pellicles into a drying stage, separating said pellicles during the drying stage only after the moisture content thereof is less than 30% by weight, restoring said pellicles into face-to-face contact after the separation thereof, and completing the drying thereof.

2. A process for drying pellicles which comprises the steps of positioning a plurality of wet gel pellicles in face-to-face contact, passing said contacting pellicles into a drying stage, separating said pellicles during the drying stage when the moisture content thereof is in the range of 12 to 30% by weight, restoring said pellicles into face-to-face contact after the separation thereof, and completing the drying thereof.

3. A process for drying pellicles which comprises the steps of positioning a plurality of wet gel pellicles in face-to-face contact, maintaining the pellicles in face-to-face contact while drying the pellicles until the moisture content thereof is less than 30% by weight, separating said pellicles, and completing the drying of the pellicles.

4. A process for drying pellicles which comprises the steps of positioning a plurality of wet gel pellicles in face-to-face contact, maintaining the pellicles in face-to-face contact while drying the pellicles until the moisture content thereof is in the range of 12 to 30% by weight, separating said pellicles, and completing the drying of the pellicles to reduce the moisture content below 12% by weight.

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