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CELLULOSIC STRUCTURE AND METHOD OF
PREPARING SAME

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This invention relates to improvements in cel-
lulosic structures, and more particularly it re-
lates to improvements in cellulosic pellicles where-
by to materially reduce the cost of production and
increase their value to the consumer, and methods
for producing the same.

Transparent, non-fibrous pellicles of cellulosic
materials have been produced heretofore by ex-
truding a cellulosic dispersion for example,
viscose, through an elongated extrusion orifice
into a coagulating and/or regenerating bath,
from which the coagulated or regenerated film is
passed through suitable purification solutions, for
example, desulfuring, bleaching, and washing
solutions, then through a softener solution from
which it is led over a series of dryer rolls to be
finally collected in the form of a roll.

One very objectionable disadvantage in the
production of transparent, non-fibrous, cellulosic
films by the viscose or similar process, resides in
the very material shrinkage of such films during
their passage over the dryer rolls. It is customary
to maintain the surfaces of the various dryer rolls
as smooth as possible to prevent marring of the
pellicle during its passage thereover. Since non-
fibrous, transparent, cellulosic films are also very
smooth, they are substantially free to shrink in
width due to loss of moisture, even though they
may be stretched comparatively tautly between
rolls. This shrinkage commonly amounts to from
5 to 10% and may, under adverse conditions, be
as high as 15% or more based on the width of the
final dry film.

It has now been found that this objectionable
shrinkage of cellulosic sheets or films during dry-
ing thereof can be very materially reduced, if not
substantially eliminated, without noticeable loss
in quality of the resulting pellicle.

It is therefore an object of this invention to
provide a method for drying films, sheets or
pellicles of non-fibrous, cellulosic materials with
a reduced shrinkage thereof.

It is another object of this invention to provide
a method of drying films, sheets or pellicles of
non-fibrous, cellulosic materials with a reduced
shrinkage and without noticeable loss in quality
of the resulting product.

It is a further object of this invention to pro-
duce a non-fibrous, cellulosic film, sheet or
pellicle, having a greater covering area per weight
of material.

It is a still further object of this invention to
produce a non-fibrous, cellulosic film, sheet or
pellicle having a greater covering area per length
of extrusion orifice opening.

Other objects of the invention will appear here-
inafter.

The objects of this invention may be accom-
plished in general by applying a material in or on
the pellicle or film, after the formation thereof,
which will produce a certain amount of tackiness
or slight adhesion between the pellicle and the
dryer rolls during their contact with each other.

The process of this invention is applicable to
cellulosic pellicles which are smooth, dense, non-
fibrous and substantially non-porous, and par-
ticularly those water-sensitive cellulosic pellicles
which may be obtained by coagulation and/or
regeneration from aqueous cellulosic dispersions,
including regenerated cellulose; cellulose ethers
such as glycol cellulose, lowly substituted methyl
or ethyl cellulose, cellulose glycolic acid or cellu-
lose phthalic acid; lowly esterified cellulose esters
or ether esters, and the like.

In order to set forth more clearly the details
of the invention without prolixity, it will be de-
scribed with specific reference to pellicles of re-
generated cellulose; it is to be understood how-
ever that the invention may be likewise applied
to the production of other cellulosic pellicles of
the type mentioned above in any obvious manner.

In accordance with the process of this inven-
tion, the substance to be applied on the pellicles
to prevent shrinking thereof is preferably ap-
plied to pellicles in their gel state, that is, as they
are obtained in the course of manufacture in the
purified and washed but undried state. It is pos-
sible, however, to apply the same to pellicles
which have been dried or dried and later sub-
jected to a re-wetting step prior to the treatment
process of this invention. Obviously, it is much
more economical and practical to work with the
pellicle in the gel state. Although transparent
pellicles are to be preferred, it is within the scope
of the invention to use pigmented, colored, or
otherwise decorated pellicles. The process
furthermore does not interfere with subsequent
treatments, including lamination, coating, gluing,
or the like. Thus, the products of this invention
may be provided with coatings, such as, for ex-
ample, moistureproof surface coatings, without
harmful effect due to the treatment according to
this invention.

These shrinkage-preventing agents are pref-
erably applied to gel regenerated cellulose sheets
during impregnation of the sheets with the usual
softening agent, such as, glycerol, ethylene glycol,
diethylene glycol, triethylene glycol, invert cane
sugar, glucose, sorbitol, calcium chloride, tri-
ethanolamine, carbamide, or a suitable combina-

tion thereof, or immediately after such impregnation with the softening agent. The shrinkage-preventing agents may be applied to the pellicles as aqueous dispersions or solutions in the treating bath containing the aqueous softener solution, and just prior to drying thereof. Before the pellicle enters the dryer, the excess liquid may be removed by suitable means, such as squeeze rolls, scraper rods, doctor knives, or the like. The amount of shrinkage-preventing agent applied may be controlled by adjusting the concentration of the agent in the treating bath or by varying the amount of excess removed. If it is desired to apply the shrinkage-preventing agent separately, the pellicle may be treated with the softener bath, the excess removed, and then the liquid or molten shrinkage-preventing agent or the solution or dispersion or emulsion of shrinkage-preventing agent applied by dip rolls, sprays, or the like. When a water-soluble softener is used, it is preferred not to immerse the softener-treated pellicle in a separate aqueous treating bath containing only a solution of shrinkage-preventing agent since a part of the softener would thereby be removed from the pellicle.

It has been found that a large variety of materials may be used as shrinkage-preventing agents in the practice of this invention. Generally speaking, those substances which remain slightly tacky or sticky or which exhibit rather high frictional coefficients will be found useful. More particularly substances having rather large molecules which do not penetrate the pellicular structure but are deposited more as a surface layer on the pellicle will be of value. The substances having these characteristics will generally fall into one of two classes, namely, those which are water-soluble and those which though water-insoluble can be readily dispersed, colloidized or emulsified in water. The last mentioned class, namely, the water-insoluble class comprising resinous materials is generally preferable. Among the substances of outstanding utility, irrespective of the above-mentioned classification, may be mentioned dewaxed shellac, cumar (cumarone) resins, rosin, salts of rosin or the rosin acids such as sodium rosinate or sodium abietate. Other readily dispersible resinous substances include the so-called water-soluble alkyd resins (i. e. those which are derived by the interaction of polyhydric alcohols and polybasic acids, with or without modifying ingredients, and which are dispersible in an aqueous ammonia solution), other alkyd resins which are dispersible by means of suitable emulsifying agents, phenol-aldehyde resins, halogenated diphenyl resins, polymerized terpene resins or even drying oils which have been treated so that they have reached the stage of nearly complete dryness, such as blown tung oil. Among the other useful substances, the bori-borate resins obtained by the condensation of boric acid with polyhydric alcohols such as glycerol, glycol, diethylene glycol, etc., and commonly sold under the trade-name "Aquaresin", water-soluble cellulose derivatives such as certain types of methylated cellulose, sugar-formaldehyde resins, gum arabic, dextrin, pectin, or the like, may be mentioned.

In those cases where a dispersing or emulsifying agent is required for the emulsification or dispersion of shrinkage-preventing agents, any of the well-known materials capable of functioning in this manner may be used, the choice being dependent on the substance to be emulsified.

Thus an aqueous ammonia solution may suffice, or a small amount of a soap such as sodium oleate, triethanolamine stearate, or emulsifiers such as the sulfonated oils and their salts, e. g. sodium petroleum sulfonate, or the alkali metal salts of sulfuric acid half-esters of the higher fatty alcohols such as stearyl, oleyl, lauryl, cetyl or myristyl alcohols, e. g. sodium oleyl sulfate, may be used.

Optionally, stabilizing agents may be added to the emulsion. Alternatively, in some cases, small amounts of organic solvents may be used to facilitate the preparation of suitable aqueous dispersions. Furthermore any suitable procedure may be employed for introducing the various substances into the dispersions or treating baths and/or for maintaining the treating baths at proper concentration by compensating for the loss of material from the treating bath as it is removed by the pellicle in the course of its passage therethrough. The treating bath may contain solutions, dispersions, suspensions, emulsions and/or colloidal solutions depending on the choice of shrinkage-preventing substance and/or the product desired.

Preferably only very minute quantities of shrinkage-preventing agent are applied to the transparent, regenerated cellulose pellicles, which substances, after drying of the pellicle, will usually and preferably amount to less than 2% of the product and may even amount to as little as a few hundredths of one per cent.

For the practice of the invention, it is usually most convenient to prepare concentrated solutions, dispersions, or the like, of suitable shrinkage-preventing compositions and then appropriate amounts of these concentrates may be added to the proper treating bath in order to produce the results desired.

Because of the usual tacky nature of the shrinkage-preventing materials, the treated pellicle, after drying, is preferably provided with a surface coating to avoid objectional adhesion of contiguous pellicular surfaces although in many instances the treated but uncoated pellicle may be useful or, indeed, preferable for certain purposes. When a surface coating is applied it may be of any type desired so long as it provides a smooth, non-tacky surface. Preferably it will be transparent and if desired it may be moistureproof. Various varnishes, lacquers or the like will be found useful depending on the ultimate characteristics desired of the product.

The following examples, which are merely to be taken as illustrative in nature, disclose sizing compositions and methods for applying the same to cellulosic pellicles which may be used to enable production of relatively wide pellicles within the spirit of the invention.

Example I

Parts by weight	
Dewaxed shellac (44% solution in alcohol)-----	45.4
Ammonium hydroxide-----	5.0
Water-----	49.6

Mixture of the above mentioned ingredients results in a substantially clear, colloidal dispersion of the dewaxed shellac. This concentrated solution may be added to the treating bath in an amount sufficient to provide a dewaxed shellac concentration of about 0.05-1.0%. If the sizing is added to the softener bath so as to effect simultaneous softening and sizing, the softener content may be adjusted to about 4-7%, depending on

the gage of the pellicle and the amount of softener desired. After the pellicle has been passed through the treating bath, the excess bath is removed, as by squeeze rolls, and the pellicle is led over a series of heated dryer rolls. The dewaxed shellac clinging to the pellicle surface provides a tackiness between the pellicle and the dryer rolls which prevents transverse slipping of the pellicle to such an extent that when the final dried pellicle is secured, the width is 5%, 10%, or even more, greater than the width of a pellicle prepared in the usual way without the use of the sizing composition. The dried film is tack-free and is suitable for all uses to which the ordinary commercial product may be put including subsequent coating, as for example with a moistureproof lacquer. The sizing composition hereby illustrated does not improve the sticking resistance, but, on the other hand, the product is not appreciably poorer in this respect than the present commercial, untreated product. The economically important gain in width of product is, however, substantial.

Example II

	Parts by weight
Cumar resin (110° C. melting point) -----	50
Benzene -----	25
Sodium oleate -----	20
Water -----	100

The cumar resin is dissolved in the benzene while the sodium oleate is separately dissolved in the water. The resin solution is then added, gradually with violent agitation, to the sodium oleate solution. A stable emulsion is obtained which contains approximately 25% of resin. This emulsion may be added to the softener bath in amounts sufficient to yield a final resin concentration of about 0.1-0.5%. The amount of softener may be adjusted to approximately 4.0-7.0%, depending on the pellicle being treated.

Alternatively, the benzene may be removed from the emulsion by evaporation and the resulting aqueous dispersion may be used as the concentrate in preparing the treating bath. This is particularly advantageous where rubber squeeze rolls are used to remove the excess bath. The treated pellicle is dried as previously described and resembles the product of Example I in its various characteristics. The treated pellicle of this example is then coated with a moisture-proofing coating composition such as disclosed in the U. S. patent to Charch and Prindle No. 1,737,187.

It is within the scope of this invention, therefore, to provide means for controlling the ultimate width of cellulosic pellicles as they are manufactured, as well as to impart improved surface characteristics. This is of great economic importance in view of the following considerations. Cellulosic pellicles of the type described are frequently destined for use as wrapping tissues. Although they are usually sold by weight, it is important that a given weight of pellicle shall offer as large an area as possible so that a maximum of "covering area" will be obtained. As the pellicles are cast, a certain weight of cellulosic material is made available and this weight remains the same whether the pellicle is finally obtained as very wide or relatively narrow. It is therefore economically advantageous to obtain as wide a pellicle as possible with a given weight of cellulosic material and therein lies a very important contribution of the present invention.

It is possible, therefore, in accordance with the present invention, to use considerably narrower

apparatus for the forming and purification of the pellicles than is necessary in cases wherein there is considerable shrinkage of the film. More practically, however, it is possible to produce wider pellicles on the existing apparatus thus taking advantage of the facilities for width in such apparatus. Furthermore it has been found that considerably thinner pellicles can be produced than has been possible heretofore because the shrinkage usually suffered in width exerts its effect in the thickness of the pellicle.

It is to be understood that all variations or modifications which conform to the spirit of the invention are intended to be included within the scope of the claims.

I claim:

1. In the production of non-fibrous, cellulosic pellicles, the method of restraining the shrinkage of said pellicles due to the removal of moisture therefrom which comprises treating said pellicles with a liquid containing a shrinkage preventing agent, and drying the said pellicles by contact with the heated surface of a drying element, said agent causing an adhesion between said heated surface and said pellicles during the drying of the latter.

2. In the production of non-fibrous, cellulosic pellicles, the method of restraining the shrinkage of said pellicles due to the removal of moisture therefrom which comprises treating said pellicles while in their undried, gel state with a liquid containing a shrinkage preventing agent, and drying said pellicles by contact with the heated surface of a drying element, said agent causing an adhesion between said heated surface and said pellicles during the drying of the latter.

3. In the production of non-fibrous, cellulosic pellicles, the method of restraining the shrinkage of said pellicles due to the removal of moisture therefrom which comprises treating said pellicles while in their undried, gel state with a liquid containing a shrinkage preventing agent taken from the group consisting of dewaxed shellac, cumar resins, rosin, salt of rosin acids, alkyd resins, phenol-aldehyde resins and polymerized terpene resins, and drying said pellicles by contact with the heated surface of a drying element, said agent causing an adhesion between said heated surface and said pellicles during the drying of the latter.

4. In the production of non-fibrous, cellulosic pellicles, the method of restraining the shrinkage of said pellicles due to the removal of moisture therefrom which comprises treating said pellicles while in their undried, gel state with a liquid containing an aqueous dispersion of a resin, and drying said pellicles by contact with the heated surface of a drying element, said resin causing an adhesion between said heated surface and said pellicles during the drying of the latter.

5. In the production of non-fibrous, cellulosic pellicles, the method of restraining the shrinkage of said pellicles due to the removal of moisture therefrom which comprises treating said pellicles while in their undried, gel state with a liquid containing an aqueous dispersion of a substantially water-insoluble resin, and drying said pellicles by contact with the heated surface of a drying element, said resin causing an adhesion between said heated surface and said pellicles during the drying of the latter.

6. In the production of regenerated cellulose pellicles, the method of restraining the shrinkage of said pellicles due to the removal of moisture therefrom which comprises treating said pellicles with a liquid containing a shrinkage preventing

agent, and drying the said pellicles by contact with the heated surface of a drying element, said agent causing an adhesion between said heated surface and said pellicles during the drying of the latter.

5 7. In the production of regenerated cellulose pellicles, the method of restraining the shrinkage of said pellicles due to the removal of moisture therefrom which comprises treating said pellicles
10 while in their undried, gel state with a liquid containing a shrinkage preventing agent, and drying said pellicles by contact with the heated surface of a drying element, said agent causing an adhesion
15 between said heated surface and said pellicles during the drying of the latter.

8. In the production of regenerated cellulose pellicles, the method of restraining the shrinkage of said pellicles due to the removal of moisture therefrom which comprises treating said pellicles
20 while in their undried, gel state with a liquid containing a shrinkage preventing agent taken from the group consisting of dewaxed shellac, cumar resins, rosin, salt of rosin acids, alkyd resins, phenol-aldehyde resins and polymerized
25 terpene resins, and drying said pellicles by contact with the heated surface of a drying element, said

agent causing an adhesion between said heated surface and said pellicles during the drying of the latter.

9. In the production of regenerated cellulose pellicles, the method of restraining the shrinkage
5 of said pellicles due to the removal of moisture therefrom which comprises treating said pellicles while in their undried, gel state with a liquid containing an aqueous dispersion of a resin, and drying
10 said pellicles by contact with the heated surface of a drying element, said resin causing an adhesion between said heated surface and said pellicles during the drying of the latter.

10. In the production of regenerated cellulose pellicles, the method of restraining the shrinkage
15 of said pellicles due to the removal of moisture therefrom which comprises treating said pellicles while in their undried, gel state with a liquid containing an aqueous dispersion of a substantially water-insoluble resin, and drying said pellicles by
20 contact with the heated surface of a drying element, said resin causing an adhesion between said heated surface and said pellicles during the drying of the latter.

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