

April 26, 1938.

F. P. ALLES ET AL

2,115,132

MANUFACTURE OF NONFIBROUS SHEETS AND FILMS

Filed May 31, 1934

2 Sheets-Sheet 1

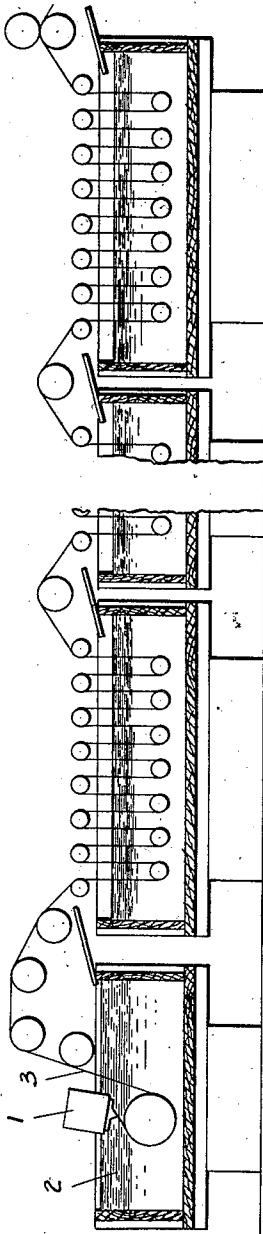


Fig. 1

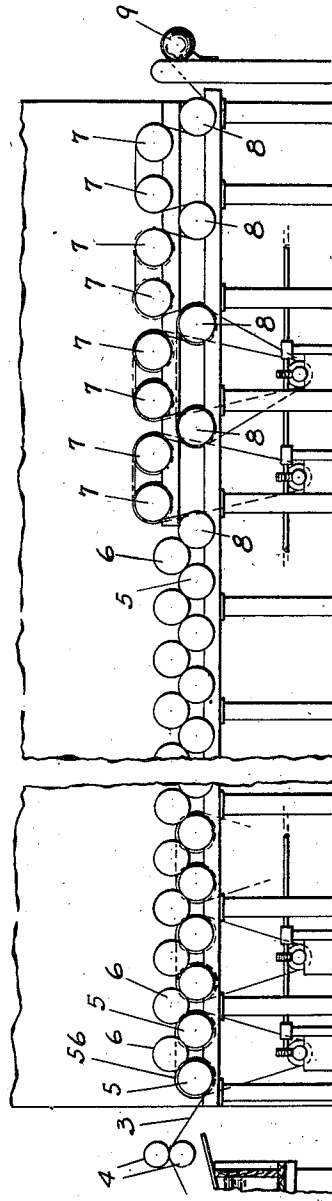


Fig. 2

INVENTORS.
Frank P. Alles
David H. Edwards
BY *Charles F. Daly*
ATTORNEY.

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2 Sheets-Sheet 2

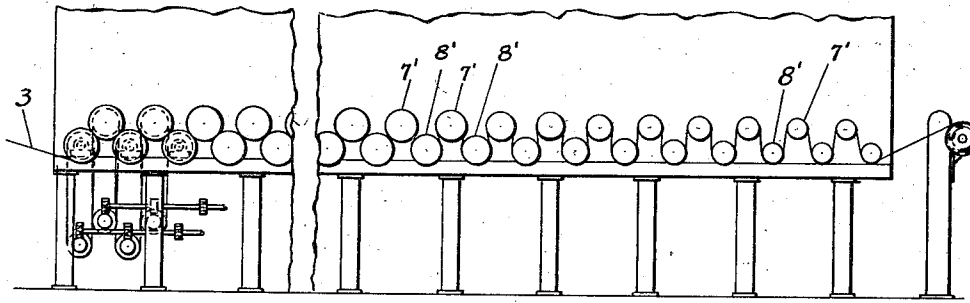


Fig. 3

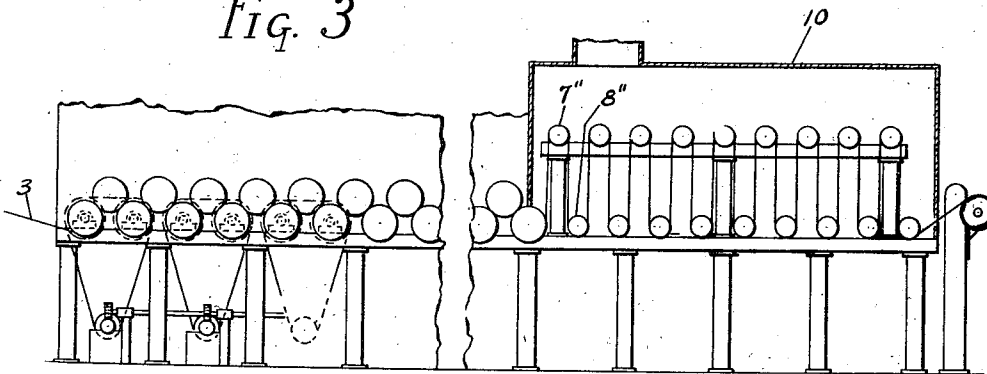


Fig. 4

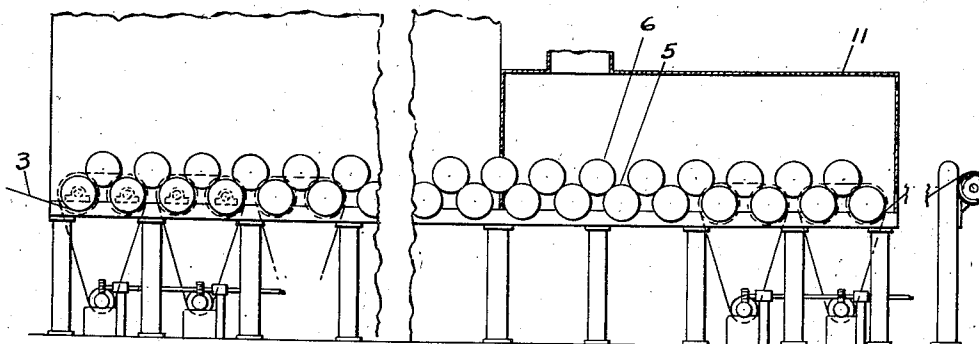


Fig. 5

INVENTORS.
Frank P. Alles
David H. Edwards
BY
Charles F. Daley
ATTORNEY.

UNITED STATES PATENT OFFICE

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MANUFACTURE OF NONFIBROUS SHEETS
AND FILMS

Frank P. Alles, Buffalo, and David H. Edwards,
Kenmore, N. Y., assignors, by mesne assign-
ments, to E. I. du Pont de Nemours & Company,
Wilmington, Del., a corporation of Delaware

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8 Claims. (Cl. 18—57)

This invention relates to the drying of non-fibrous sheets and films which are subject to shrinkage during drying, and in particular it pertains to the drying of regenerated cellulose sheeting cast from viscose and adapted to be used as wrapping tissue.

Heretofore, in the manufacture of such sheets and films of regenerated cellulose a film is cast from viscose into a coagulating and/or regenerating bath and subsequently passed through additional baths such as regenerating, desulfuring, washing, bleaching, and glycerinizing baths. Thence, it is passed through a drying apparatus, and wound up into rolls. In passing through the drying apparatus, the film loses approximately 30 to 40 parts of moisture per 10 parts of cellulose, so that at the windup the film contains about 0.6 to 0.8 part of moisture per 10 parts of cellulose. In losing this moisture, the film tends to shrink to a great extent, thus diminishing the area of the regenerated cellulose film and producing puckers and wrinkles. In order to produce a film which is comparatively large in area and without puckers or wrinkles, the drying apparatus customarily consists of a series of rotating heated rollers, over which the film passes and which keep it at all times under marked tension as it is dried.

The prior art film so produced, however, attains its greater area at the sacrifice of other desirable properties. Particularly, the film is characterized by internal strains which, over a period of time, give rise to an irreversible shrinkage or loss in dimensions during use. Thus, for instance, when a box of candy is wrapped in a film containing the above described internal strains, it will be found that over a period of time, for instance one week to several months or more, the wrapper will gradually contract and tighten up around the box, thus impairing the otherwise neat appearance of the package and frequently breaking or shattering the wrap itself, and destroying its entire effectiveness. This irreversible contraction manifested as above is greatly accelerated if at some time during the life of the sheet it is exposed to high humidities of 80% or upwards. When exposed to such humidity conditions, the sheet absorbs moisture, seeming to effect a much more rapid release of the strains so that if the sheet next becomes exposed to lower humidities, it will thereupon contract to smaller dimensions than it initially possessed. This irreversible shrinkage we term throughout the specification and claims as "permanent shrinkage", and distinguish it from changes in

dimensions which result solely from gain or loss in moisture in the sheet.

In order to more clearly describe the scope of this invention, the term "deformation", in relation to regenerated cellulose, will be clearly defined and differentiated from "permanent shrinkage". By "deformation" we mean the reversible changes in dimensions which a sheet of regenerated cellulose undergoes with changes in its internal moisture content. Deformation manifests itself only upon changes in moisture content of the sheet while the process of relieving internal strains, which results in permanent shrinkage, takes effect more quickly on increasing the moisture content of the film, but also takes effect at other or constant moisture contents.

A sheet of regenerated cellulose which is free from permanent shrinkage and internal strains will expand or contract according to whether its moisture content becomes higher or lower. This moisture content of the sheet is primarily dependent upon the relative humidity of the circumambient atmosphere and to a lesser extent upon the temperature. For example, a freely suspended sheet free from permanent shrinkage, in equilibrium with a humidity of 35%, will expand when allowed to come to equilibrium with a humidity of 95%. Yet, when it is returned to and allowed to come to equilibrium with the original 35% relative humidity, it will return to substantially its initial dimensions. Likewise, if the same sheet is removed from an atmosphere of 35% relative humidity to an atmosphere of 5% relative humidity, it will contract. On returning to the original 35% relative humidity, it will again regain its original dimensions. This reversible change in dimensions of a sheet is here termed its deformation and is distinguished from permanent shrinkage in that it is reversible, whereas permanent shrinkage is irreversible.

Deformation is characteristic of sheets of regenerated cellulose even when softened with glycerine. It is furthermore characteristic of moistureproofed regenerated cellulose, but with such sheets the phenomenon is observed relatively infrequently since the moistureproof coating substantially prevents the transmission of moisture, and the moisture content of the film, therefore, remains approximately constant.

While we have described, for the purpose of clarity, an example of deformation in a film which is free from permanent shrinkage since the effect can be best observed in this way, it is to be understood that deformation in a film is independent of the presence or absence of per-

manent shrinkage. Ordinarily, when sheets of regenerated cellulose are dried in the usual manner with considerable tension, the resulting sheet will naturally possess both permanent shrinkage and deformation at the same time.

It has hitherto been thought necessary in order to overcome permanent shrinkage to dry regenerated cellulose with no tension at all, such as by drying in festoons. This permits free shrinkage and consequent release of or freedom from internal strains, but the resulting film is not smooth and free from wrinkles and is therefore not commercially useful. Furthermore, the film tends to be slightly opaque or milky, thus suffering by comparison with the appearance of the ordinary smooth, glossy surfaced transparent regenerated cellulose films. Finally, such a method is expensive in operation since it can only be performed discontinuously and requires relatively cumbersome apparatus.

It is an object of this invention to produce sheets or films of regenerated cellulose having substantially no permanent shrinkage and which at the same time are transparent, smooth, glossy, and free from wrinkles and other surface irregularities. It is a further object to produce laminated materials which do not appreciably permanently buckle, curl and/or wrinkle upon exposure to varying atmospheric conditions, in which at least one of the laminae is a sheet of regenerated cellulose. Other objects will appear hereinafter.

The objects of this invention are accomplished by drying the sheet or film of regenerated cellulose at such low tension that it is allowed to shrink freely, but with sufficient tension to prevent the formation of unsightly wrinkles and other blemishes. This may be to a certain extent accomplished by rewetting the dried film to the desired moisture content and redrying according to the method of this invention, but preferably the method is practiced on the gel film in the conventional drying apparatus, modified as hereinafter described. More particularly, it has been found that it is possible to dry the film in the conventional manner down to a certain critical moisture content, which we have observed to be at a point when the film contains about 6 parts moisture per 10 parts of regenerated cellulose plus glycerin or other softener, and thereafter according to the method of this invention. By reducing the moisture content of the film from the usual 30 to 40 parts of moisture per 10 parts of cellulose as it enters the drying apparatus down to about 6 parts of moisture per 10 parts of cellulose in the conventional manner, and thereafter at reduced tension according to this invention, a final film is produced of low permanent shrinkage, complete transparency and good smoothness. Furthermore, this procedure necessitates minimum changes in the conventional drying apparatus, and results in a film comparatively large in area. Accordingly, the invention will be specifically described in terms of this procedure, but it will be understood that this is illustrative and not limitative.

In the accompanying drawings, Figs. 1 and 2 are side views, partly in section, illustrating one form of apparatus adapted to the practice of the invention, these figures, when placed end to end, representing a complete film-casting machine. Figs. 3, 4, and 5 are side views, partly in section, showing other forms of apparatus which may be used in the application of the invention.

Referring now to the drawings, Fig. 1 shows the front end of a conventional film-casting machine in section, and Fig. 2 shows the end of the casting machine where the drying of the films takes place. Viscose is extruded through a narrow slit in the bottom of a hopper 1 into a suitable coagulating bath 2 to form a continuous sheet or film 3 of regenerated cellulose which may then be passed through various treating tanks (only partly shown in Fig. 1) and is subjected to various processing steps such as washing, desulfuring, washing, bleaching, washing and glycerinizing, the film then being passed through the dryer shown in Fig. 2.

Referring to Fig. 2, the film is drawn through squeeze rollers 4 and alternately under positively driven rolls 5 and over rolls 6, which are driven by friction from rolls 5 as by means of tires 56 which also serve to space rolls 6 from rolls 5. Dryer rolls 5 and 6 are of the same diameter, rolls 5 being internally heated by means of fluid such as hot water or steam. When the sheet reaches the last rolls 6 in the first part of the dryer, it has lost the most of its moisture. For example, the film, when it first enters the dryer, contains about 30 to 40 parts of moisture per 10 parts of cellulose and, under preferred conditions, when it leaves the last rolls 6 contains about 6 parts of moisture per 10 parts of cellulose. In general, the moisture content of the film as it leaves the last rolls 6 should not be in excess of 10 parts or less than 4 parts per 10 parts of cellulose.

The film, after leaving the last rolls 6 in the first part of the dryer, is then drawn under positively driven roll 8 from which the last roll 6 is frictionally driven, over rollers 7, down again over a similar roll 8, up over roll 7, and so on, until it is wound up on the take-up roller 9. Rollers 7 and 8 are of substantially the same size. Rollers 7 and 8 may all be internally heated, or alternatively rollers 8 alone may be heated.

Dryer rolls 5 and 6 are driven at the same peripheral and angular speed. Rollers 7 and 8, on the other hand, are driven at a gradually decreasing speed, going from the wet end to the dry end of the dryer, corresponding to the period in which the film decreases in moisture content to that of the finished product wound up on the wind-up roll, the film thus being allowed to shrink substantially freely in the longitudinal direction, while producing a smooth, unwrinkled surface due to the fact that tension is maintained on the film during the whole drying operation.

Dryer rolls 7 and 8 can be given a progressively decreasing peripheral speed in any known manner, such as providing individual drives for each dryer roller 7 and 8, or for each group of dryer rollers.

Alternatively, all or some of the dryer rollers 7 and 8 may be driven by contact with the film only. In such case, for example, the lower rolls 8 may be positively driven at diminishing speed toward the dry end of the machine while upper rollers 7 are driven only by contact with the film; or, the first roller 8 and the last roller 8 may be positively driven, the first roller being driven at a speed greater than that of the last roller while the other rollers 7 and 8 are driven only by friction from the film.

In order to accomplish transverse shrinkage of the film, it has been found that due to the relatively loose condition of the film when longitudinal shrinkage is permitted, in some cases no further modification of the dryer construction

tion is necessary. However, in order to accomplish better results, the surfaces of the rollers 7 and 8 may be altered so as to permit the film to slip freely thereover. Alternatively, certain of the rollers in the conventional dryer may be skipped or they may be eliminated entirely as has been shown in Fig. 2, thereby maintaining the film out of contact with a supporting surface for a substantial portion of the drying operation. The spacing of rolls 7, as shown in Fig. 2, contributes to this result since the film between succeeding rollers 7 is supported freely and out of contact with the rollers.

In Fig. 3 is shown a modification according to the method of Fig. 1, wherein the positively driven dryer rollers 7' and/or 8' are of gradually reducing size, going from the wet end to the dry end. All the rollers may then be driven at a constant angular speed but at a decreasing peripheral speed. It is easily seen how the same result as in the first example can be obtained. Here also, rollers 8' may alone be internally heated, or both rolls 7' and 8' may be heated.

In Fig. 4 is shown a modification of the methods according to Fig. 2 or 3. This modification is adapted to drying by suitably directed air currents instead of or in addition to internally heating the rollers 7' and/or 8', this result being attained by enclosing rollers 7' and 8' in an enclosed chamber 10 adapted to dry the sheet by means of heated air or other suitable gas. When this drying means is adopted, it is preferred to space rollers 7' considerably apart from rollers 8', thereby causing the film to be freely suspended during a large portion of the drying period. In this modification also the rollers 7' and 8' are driven at progressively diminishing peripheral speeds.

It will be understood that the methods and apparatus described in the preceding paragraphs with respect to Figs. 3 and 4 may be combined with the various means for decreasing the speed of the film which have been described in connection with the form of the invention shown in Fig. 2.

In Fig. 5 is shown a modification wherein the film passing over rollers 5 and 6 is partially dried and then passed through a chamber 11 or other similar apparatus where it is brought to a constant moisture content of 6 parts per 10 parts of cellulose or to whatever other moisture content within the range 4-10 parts per 10 parts of cellulose that is desired, and thereafter dried in one of the modifications shown in Figs. 2, 3, and 4, or other suitable method. If the film entering the chamber 11 contains too much moisture, it will be dried in chamber 11, in which case chamber 11 is simply a drying chamber. If, on the other hand, the film going into chamber 11 is too dry, its moisture content will be raised to the desired amount within the range specified, in which event, chamber 11 is a humidifying chamber.

According to any of the above examples, the speeds at which the mechanically driven rollers are to be driven to produce the required tensions can be easily determined by one skilled in the art and will depend largely on other factors in the manufacturing process, such as kind of cellulose or pulp used, temperature of drying, amount and character of softener used, etc.

The tension necessary to produce the results contemplated by this invention, during that part of the drying operation where the permanent shrinkage is avoided, is quite low, being in the

neighborhood of 0.1 pound per linear inch across the width of a film which, when dry, is approximately 0.0009 inch thick. Thicker films will require correspondingly greater tensions. It is to be understood, of course, that variations are possible, such as from 0.5 lb. to 0.02 lb. per linear inch, but normally the best results have been secured by using a tension of 0.1 lb. The best results are secured, of course, when the tension is low enough to reduce permanent shrinkage to a reasonable minimum, but high enough to prevent the formation of wrinkles and other unsightly distortion of the film.

The most satisfactory moisture content at which to release the tension to the desired value is about 6 parts of moisture per 10 parts of cellulose, but it is to be understood that this, too, may vary within limits. For example, if the tension is released at a moisture content of about 10 parts per 10 parts of cellulose, the finished film will not show undue loss in dimensions. On the other hand, if the tension is not released until after the film reaches a moisture content of 4 parts per 10 parts of cellulose, the resulting permanent shrinkage in the finished film is still comparatively low. Operating outside of these limits, however, tends to produce unsatisfactory results and for these reasons we prefer to release the tension at a moisture content of approximately 6 parts per 10 parts of cellulose. The preferred ranges which we disclose, of course, depend in large part on other factors in the manufacturing process, such as kind of cellulose or pulp used, speed of drying, temperature of drying, amount and character of softener used, etc.

While we do not desire to be limited by theories, it appears that the results obtainable by this invention are due to the fact that film containing 6 parts of moisture per 10 parts of cellulose is sufficiently plastic to allow free adjustment of the cellulose micelles, thereby eliminating strains. If, therefore, in the course of manufacture, substantially no strains are introduced in the film on drying from this point down to the finished film, then the finished film will be substantially in its final form. On the other hand, if the film is dried in the ordinary manner, that is, with marked tension, and the film subsequently never allowed to reach the degree of plasticity of a film containing 6 parts of moisture per 10 parts of cellulose, the process of relieving strains will be extremely slow although it will eventually manifest itself as a decrease in dimensions. If a similar piece of freshly prepared film, however, is subjected to an atmosphere of 95% relative humidity, which is a very high relative humidity in practice, and allowed to come to equilibrium therewith, it is observed to contain approximately 6 parts of moisture per 10 parts of cellulose, based on the weight of the dried film plus softener. Such a film, as pointed out above, thus becomes sufficiently plastic to quickly allow a free release of strains and, on returning to the normal atmosphere again, will have exhibited a loss in dimensions, based on the dimensions in the normal atmosphere before subjection to this high humidity. A finished film produced in accordance with our invention, however, can be subjected to an atmosphere of 95% relative humidity substantially without the release of strains since there are substantially no strains present, and when it returns to a normal condition again, the film will be substantially in the same condition as it was initially. Furthermore, our improved film, over

a period of time, will substantially not exhibit the above mentioned gradual decrease in dimensions of the prior art film when not allowed to reach this high humidity.

5 Based on the above observations, and for the purpose of measuring permanent shrinkage and defining the term "substantially no permanent shrinkage", a method has been evolved for reducing the strains in a finished piece of film and
10 measuring the resulting changes in dimensions. The method, which is carried out at a constant temperature of about 30.5° C., is as follows: A sample of the finished film to be tested is allowed to come to equilibrium with respect to moisture
15 content in an atmosphere of 35% relative humidity, and the dimensions then measured. The film is next placed in an atmosphere of 95% relative humidity for a period of two hours, during which time substantially all the permanent shrinkage is
20 eliminated since strains are more quickly relieved at high moisture contents of the film. Finally, the film is brought back to the atmosphere of 35% relative humidity, allowed to come to equilibrium with respect to moisture content, and
25 again measured. The percentage decrease in dimensions between initial and final measurement is the amount of permanent shrinkage in the film. In the ordinary films of the prior art it amounted to about 3.5% to 4% in each direc-
30 tion on a rectangular piece of film, or a total of about 8%. For the purposes of this invention the term "substantially no permanent shrinkage" will mean a total permanent shrinkage, including both directions, of less than 2%, and preferably less than 1%.

Film produced in accordance with this invention has many advantages over the prior art materials. It has greatly increased durability at average relative humidity and at low relative
40 humidities and at low temperatures. It has superior gloss, thereby enhancing the appearance of the material. It is possible to store film manufactured according to my process for much longer lengths of time, due to the fact that it will not
45 pucker or exhibit "washboard" effects. The film has much less tendency to stick together or cake under pressure and elevated humidities than ordinary film. For example, a stack of ordinary sheets and a stack of sheets manufactured ac-
50 cording to our process were each subjected to relative humidities of 80% and a pressure of 1 pound per square inch. The stack of ordinary sheets stuck together at the end of four days while the stack of improved sheets did not stick to-
55 gether until the end of seventeen days. Packages wrapped with material manufactured by our improved method will have much less tendency to distort, buckle or collapse, especially when sub-
60 jected to high humidity conditions and subsequently returned to normal again. Laminated materials in which at least one of the plies comprises a sheet or film of regenerated cellulose, manufactured according to our process, e. g., a
65 laminated material comprising a sheet of heavy paper surfaced on one or both sides with an adhering sheet of regenerated cellulose, do not exhibit any appreciable permanent buckling, curling and/or wrinkling upon exposure to the atmosphere.

70 While the invention has been described in connection with the manufacture of clear, transparent film, it may also be applied with advantage to the manufacture of film containing an opaquing agent, e. g., a pigment such as titanium
75 oxide.

While this invention has been described in terms of regenerated cellulose obtained from viscose, it is to be understood that it is equally applicable to the drying of film obtained from cuprammonium cellulose solution, and may also
5 be applied to the treatment of other cellulosic films subject to shrinkage and strains during drying, and formed from an aqueous dispersion, e. g., films made from glycol cellulose and other cellulose ethers, casein, gelatin and others.

Any modification or variation which conforms to the spirit of the invention is intended to be included within the scope of the claims.

What is claimed is:

1. In the method of making pellicles from 15 aqueous solutions or dispersions of cellulosic material, the steps which comprise casting and processing said pellicles, removing most of the moisture from said pellicles and simultaneously restraining the shrinkage thereof, and then con-
20 tinuing the drying of the pellicles under a tension which will prevent wrinkling or distortion of said pellicles while permitting substantially free shrinkage thereof.

2. In the method of making pellicles from 25 aqueous solutions or dispersions of cellulosic material, the steps which comprise casting and processing said pellicles, removing moisture from said pellicles and simultaneously restraining the shrinkage thereof until they contain not more
30 than 10 parts of moisture per 10 parts of cellulose, and then continuing the drying of the pellicles under a tension which will prevent wrinkling or distortion of said pellicles but which will permit substantially free shrinkage thereof.

3. In the method of making pellicles from aqueous solutions or dispersions of cellulosic material, the steps which comprise casting and processing said pellicles, removing moisture from
40 said pellicles and simultaneously restraining the shrinkage thereof until they contain not more than 10 parts and not less than 4 parts of moisture per 10 parts of cellulose, and then continuing the drying of the pellicles while progressively decreasing the linear speed thereof whereby to sub-
45 ject the pellicles to a tension which will prevent wrinkling or distortion of said pellicles but which will permit substantially free shrinkage thereof.

4. In the method of making pellicles from aqueous solutions or dispersions of cellulosic material, the steps which comprise casting and processing said pellicles, removing moisture from
50 said pellicles and simultaneously restraining the shrinkage thereof until they contain not more than 6 parts and not less than 4 parts of moisture per 10 parts of cellulose, and then continuing the drying of the pellicles while progressively decreasing the linear speed thereof whereby to
55 subject the pellicles to a tension which will prevent wrinkling or distortion of said pellicles but which will permit substantially free shrinkage thereof.

5. In the method of making pellicles from aqueous solutions or dispersions of cellulosic material, the steps which comprise casting and
65 processing said pellicles, removing moisture from said pellicles and simultaneously restraining the shrinkage thereof until they contain not more than 10 parts and not less than 4 parts of moisture per 10 parts of cellulose, and then continuing the drying of the pellicles under a tension
70 which will prevent wrinkling or distortion of said pellicles but which will permit substantially free shrinkage thereof.

6. The method described in claim 5 character- 75

ized in that tension is applied during the drying operation in an amount sufficient to prevent wrinkling or distortion of the pellicle during drying, the tension being equivalent to from 0.5
5 pound to 0.02 pound per linear inch on the basis of a pellicle approximately 0.0009" thick.

7. The method described in claim 5 characterized in that tension is applied during the drying operation in an amount sufficient to prevent
10 wrinkling or distortion of the pellicle during drying, the tension being equivalent to about 0.1 pound per linear inch on the basis of a pellicle approximately 0.0009" thick.

8. In the method of making pellicles from
15 aqueous solutions or dispersions of cellulosic

materials, the steps which comprise casting and processing said pellicles, removing moisture from said pellicles and simultaneously restraining the shrinkage thereof in a drying atmosphere until the pellicles contain not more than 10 parts and
5 not less than 4 parts of moisture per 10 parts of cellulose and the moisture in said pellicles approaches equilibrium with said atmosphere, and then continuing the drying of the pellicles under a tension which will prevent wrinkling or dis-
10 tortion of said pellicles but which will permit substantially free shrinkage thereof.

FRANK P. ALLES.
DAVID H. EDWARDS. 15