

Jan. 17, 1939.

F. P. ALLES

2,144,356

METHOD FOR PRODUCING A CELLULOSIC STRUCTURE

Filed Dec. 6, 1935

2 Sheets-Sheet 1

FIG. 1.

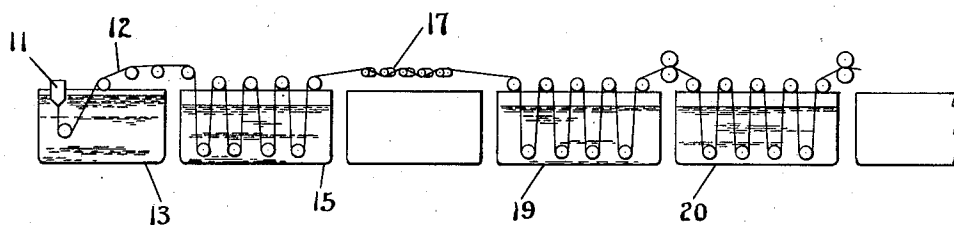
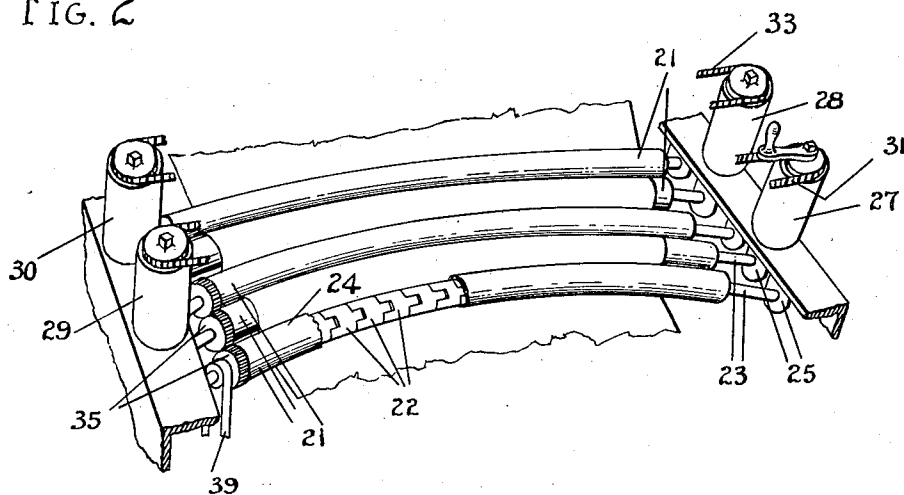


FIG. 2



INVENTOR.

Francis P. Alles

BY

Charles F. Daley
ATTORNEY.

Jan. 17, 1939.

F. P. ALLES

2,144,356

METHOD FOR PRODUCING A CELLULOSIC STRUCTURE

Filed Dec. 6, 1935

2 Sheets-Sheet 2

FIG. 3.

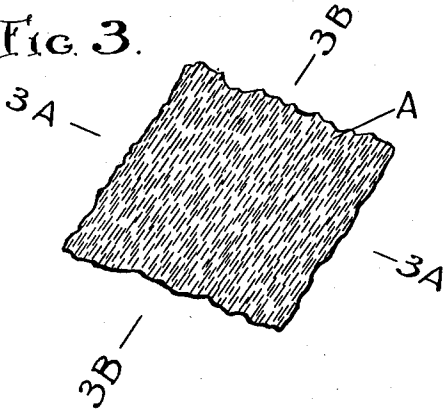


FIG. 4.

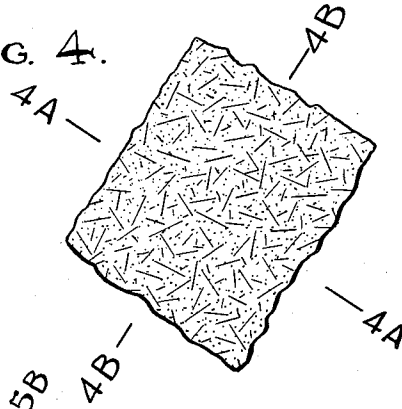


FIG. 5.

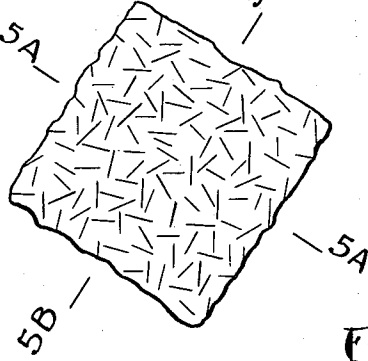


FIG. 3A.



FIG. 3B.



FIG. 4A.



FIG. 4B.



FIG. 5A.



FIG. 5B.



INVENTOR.
Francis P. Alles
BY Charles F. Daley
ATTORNEYS.

UNITED STATES PATENT OFFICE

2,144,356

METHOD FOR PRODUCING A CELLULOSIC STRUCTURE

Francis P. Alles, Buffalo, N. Y., assignor, by mesne assignments, to E. I. du Pont de Nemours & Company, Wilmington, Del., a corporation of Delaware

Application December 6, 1935, Serial No. 53,265

4 Claims. (Cl. 18—57)

This invention relates to the production of sheets and films of regenerated cellulose, and more particularly it relates to the production of regenerated cellulose sheets and films having improved uniformity of strength in all directions. The invention further relates to improvements in the method of producing regenerated cellulose sheets and films whereby to obtain films having a greater width with equipment of a given size than was possible heretofore.

Sheets and films of regenerated cellulose have commonly been produced, heretofore, in accordance with one of two conventionally known processes. One of these processes, usually referred to as the extrusion hopper casting process, comprises the extrusion of a cellulosic solution, such as viscose, into a coagulating and/or regenerating bath through the slit-like orifice of a hopper through which the cellulosic solution is passed. The other method, usually referred to as the wheel casting process, comprises forming a thin layer of viscose or the like on the surface of a rotating casting wheel by gravity flow from a trough containing the viscose, the rotating wheel carrying the layer of viscose into a coagulating and/or regenerating bath. In both of these conventional methods the films or sheets are passed from the coagulating and/or regenerating bath through various treating baths such as washing, desulfuring, bleaching and softening baths. After emerging from the final treating bath, it is further led over a series of heated rollers in order to dry the film, and is finally wound up at the other end of the machine.

A viscose solution is composed of about 7% cellulose, 6% caustic and the remainder water. Therefore the regeneration, purification and drying of films produced from viscose must be accompanied by the loss of about 87% water. This loss of water indicates a tremendous collapse of the colloidal cellulosic structure, and is manifested by great shrinkage of the pellicle at various points in the process. In the production of sheets and films by previously known processes, the sheets or film are restrained from shrinking in their longitudinal direction since the peripheral speed of the rollers, which continuously pull the film through the machine, is substantially constant and the slippage of the film in the machine direction is substantially negligible. On the other hand, since the sheets or films are wet and slippery, and are unsupported in a direction transverse to the machine direction, they are substantially free to shrink in their transverse direction or in width. The sheets and films produced by the extrusion of viscose from an orifice of 71" in length, for example, have been found to shrink about 20" in width during regeneration, about 4" in width during desulfuring, and about 10" in width during drying.

As a result of this shrinkage in the transverse direction and prevention of shrinkage in the longitudinal direction, the elongated cellulose micelles of the resulting sheets or films of the prior art are found to be pulled around and oriented somewhat in a direction longitudinally of said sheets and films. Such sheets or films are therefore much stronger in their longitudinal direction than in their transverse direction. This is probably due to the micelles being positioned somewhat in the manner of the fibers in wood, which is said to have "grain" in the direction of orientation of the cellulose fibers. Since the final film when used for wrapping tissue or other well known uses, is subject to approximately equal strains in all directions in the plane of the film, it will have a tendency to rupture along a line taken in the longitudinal direction of the film.

It will be obvious from the above discussion that a sheet or film will also be free to shrink in thickness. Since the micelles of sheets and films, produced in accordance with the above described processes, are pulled around and oriented somewhat in a direction longitudinally of said sheets and films, the latter will also be somewhat weaker or will be more subject to tearing or splitting along planes taken parallel to the plane of the film than they would be with complete random orientation of the micelles. This, however, is substantially immaterial since sheets or films are not subject to material strains in this direction. Sheets or films will ordinarily fail only by rupture along a line in the plane of the said sheets or films, and it is necessary, therefore, to be concerned only with the orientation of the micelles in the plane of the sheets or films.

In order to overcome these disadvantages it has been proposed to stretch a pellicle in the lateral or transverse direction thereof during the step of coagulating and/or regenerating the same. When viscose is cast into a coagulating, non-regenerating bath, such as, ammonium sulfate to produce a water-soluble ammonium cellulose xanthate film, it is too fragile and too elastic to be stretched to a useful extent without rupturing or returning to its original dimension when the force is removed. On the other hand, to attempt to stretch a film when it is cast into a regenerating bath can produce only unsatisfactory results. As soon as the film strikes the acid bath it starts to regenerate, and this regeneration progressively increases, so that the film constantly changes and offers constantly increasing resistance to stretching force. The result is that the stretching force tends both to rupture the film and to stretch it nonuniformly.

Furthermore, the production of regenerated cellulose film, prior to the present invention, always resulted in a final product which was little more than one-half as wide as the orig-

inally cast film. The size of the equipment therefore placed practical limits on the width of the film possible of production.

It is therefore an object of this invention to produce, by a continuous process, regenerated cellulose film, the strength and other characteristics of which are substantially the same in all directions in the plane of the film.

It is another object of this invention to produce a film having a substantially complete orientation of the micelles along lines in the plane of the film, as against orientation through the thickness of the film, and at the same time having a random orientation of the micelles in the plane of the film.

It is a further object of this invention to produce regenerated cellulose film which is substantially wider than those known heretofore, without increasing the size of the equipment.

It is a still further object of this invention to produce finished regenerated cellulose films which are substantially as wide as, or wider than the film as cast at the hopper or casting wheel.

Other objects of the invention will appear hereinafter.

These objects are, in general, accomplished by coagulating viscose in the form of a thin, wide sheet in a bath containing a solution of zinc, aluminum, lead or certain other metal salts to produce zinc, aluminum, lead or other water-insoluble metal cellulose xanthate in sheet form, then transversely stretching the so-formed sheets by suitable means, and finally passing the stretched and coagulated sheets through an acid regenerating bath, such as, for example, a sulfuric acid-sodium sulfate bath.

In accordance with the present invention it has been found that certain metal cellulose xanthate pellicles produced by coagulation of viscose in zinc, aluminum, lead or other metal salts have a unique combination of properties. They are relatively stable, water-insensitive, very tough, and possess substantially no elastic properties. For example, they can be stretched more than 50% without exhibiting any tendency to contract upon release of the stretching force. The metallic cellulose xanthate pellicles may be passed through a suitable stretching device without change in the chemical composition thereof. The pellicles may be stretched, for example, in the lateral direction, to orient the micelles in a direction laterally of the pellicles, and thereby impart a considerably greater tenacity to the pellicles in this direction. For example, when the pellicle is stretched about 33% the tenacity in the stretched direction is increased about 75%. After stretching, the pellicle can be regenerated and further treated in the stretched condition, and of course it is then subject to the usual shrinkage forces so that the final film is not as wide as the stretched film, but still may be substantially as wide or wider than the film as cast.

The formation of the metal cellulose xanthate may be carried out in any desired fashion. For example, viscose may be first coagulated in a bath comprising an aqueous solution of ammonium sulfate. This serves to coagulate the viscose but not to regenerate it. In this form the coagulated film can pass into the next bath, which contains a zinc or other metal salt, without carrying with it large quantities of the sodium hydroxide contained in the alkaline viscose. The ammonium sulfate is preferably present in such concentration that it will have a sufficiently acid reaction so that all the alkali

is neutralized before the coagulated sheet passes into the second bath. In this way, the second bath can contain a metal salt without an additional quantity of acid to prevent the formation of metal hydroxide.

It is also possible to pass the viscose directly into a bath containing a zinc, lead, aluminum or other metal salt. In this case, however, it is necessary to add a small quantity of a weak acid, such as acetic acid, to prevent the formation of the corresponding hydroxides. Alternatively a salt having an acid reaction such as ammonium sulfate may be included, together with the metal salt in the first bath. This procedure of course dispenses with the necessity of an additional bath.

Care must be taken that the bath containing the zinc or other metal salts, or the preceding bath do not contain any substantial quantity of a strong acid. The presence of any substantial quantity of strong acid will regenerate the film and prevent the formation of zinc or other metal cellulose xanthate.

As metal salts suitable for use in forming the water-insoluble metal cellulose xanthates, water-soluble salts of the heavy metals generally will be operative. Very useful results have been obtained by the use of lead chloride, zinc chloride, zinc sulfate, zinc acetate, aluminum acetate, aluminum chloride and aluminum sulfate, and particularly desirable results have been obtained by the use of the above-named zinc salts.

The concentration of zinc or other metal salt in the bath may vary within wide limits. It needs, however, to be only sufficient to react with all the viscose or ammonium sulfate-coagulated viscose present. It is preferred, however, to keep the quantities as low as possible in order to prevent the accumulation of undesirable quantities of zinc or other metal salts in the film. There should, however, be a sufficient excess of salt to prevent disintegration of the coagulated film. When using a very low concentration of metal salt in the bath there should be added a small quantity of another salt, such as ammonium chloride, sodium chloride, sodium sulfate or the like which will coagulate but not regenerate the viscose.

After passing through the bath containing the zinc or other metal salts, the film is subjected to a stretching operation. The stretching of the film may be carried out in successive steps or stages, or it may be carried out in one step. Furthermore, the film may be subjected to a stretching operation in one direction, followed by a stretching in another, preferably opposite, direction. The stretching of the film may be carried out in one operation in which the film is stretched simultaneously in both the longitudinal and transverse directions. Preferably the film is stretched substantially entirely in the transverse direction to orient the micelles in positions transversely of the film, which orientation is later equalized by the longitudinal pull on the film through the machine. Any suitable stretching device may be employed for this purpose, for example, a tentering frame may be employed in which the sides gripping the film diverge in the direction of the travel of the film. Particularly desirable results may be obtained by passing the sheets or films through a series of rolls mounted on bowed expander bars and covered with a gripping surface such as rubber. The stretching of sheets and films in accordance with the present invention will be more

clearly apparent by reference to the following detailed description taken in connection with the accompanying drawings illustrating a specific embodiment of the apparatus suitable for carrying out the invention.

In the drawings:

Figure 1 is a diagrammatic elevational view of a stretching means connected in series with other film producing apparatus.

Figure 2 is a perspective view showing a bowed expander bar stretching apparatus.

Figures 3, 4 and 5 are highly enlarged plan views of regenerated cellulose pellicles illustrating generally the orientation of micelles.

Figures 3A, 3B, 4A, 4B, 5A, and 5B are sections taken along the lines 3A—3A, 3B—3B, 4A—4A, 4B—4B, 5A—5A, and 5B—5B respectively of Figures 3, 4, and 5.

Referring to Figure 1 of the drawings, numeral 11 designates a hopper from which film 12 is extruded into a coagulating, non-regenerating bath, such as, for example, ammonium sulfate in tank 13. From tank 13 the film 12 is passed successively through tank 15, stretching device 17, tank 19, tank 20 and thence through conventional film producing apparatus such as is well known in the art. Tank 15 will contain a bath containing a metal salt solution, such as zinc chloride which is capable of reacting with the coagulated cellulose xanthate to form a colorless, tough, non-elastic water-insoluble metal cellulose xanthate. If desired, the tank 15 may be omitted by adding the metal salt solution to the bath in tank 13 whereby to coagulate and form a metal cellulose xanthate film in a single stage. After passing through tank 15 the film is stretched in a transverse direction or pulled in a transverse and longitudinal direction, by means of the stretching apparatus 17, after which the film is regenerated by passage through the acid regenerating bath in tank 19. From the tank 19 the film is passed through the washing bath in tank 20. After being washed the film may be subjected to desulfuring, bleaching, softening and drying in a conventional manner.

The bowed expander bar stretching apparatus illustrated in Figure 2 of the drawings is particularly suitable for obtaining uniformly stretched film. The details of this type of stretching apparatus are disclosed in U. S. Letters Patent Nos. 687,847; 1,233,059; and 1,697,830; which apparatus comprises expander bars 21 which include non-rotatable parallel shafts 23 having a predetermined bow or bend. A plurality of interlocking rollers 22 are rotatably mounted on the shaft 23.

The rollers 22 are preferably covered with a smooth, yieldable material 24, such as rubber, to prevent marring or otherwise deleteriously affecting the pellicle to be stretched. The shafts 23 are fixed in members 25 which may be adjusted relatively to each other to increase or decrease the spacing between the expander bars. For example, each alternate member 25 may be raised or lowered by means of the adjusting devices 27, 28, 29 and 30. Each pair of adjusting devices 27, 29 or 28, 30 are operated together by means of a sprocket chain 31 or 33 whereby to maintain an equal adjustment on opposite sides of the machine. Preferably the interlocking rollers are driven in any desired manner, such as, by means of intermeshing gears 35 and belt 39, however, by proper modification of the equipment it may be desirable to pull the pellicle through the series of expander bars to rotate the

rollers on the shaft and thereby longitudinally and transversely stretch said pellicle.

As the stretching proceeds the micelles in the cellulose compound are oriented in the direction of stretching. This orientation is more or less complete according to the amount of stretching taking place. If the primary requisite is width, this stretching can take place up to the maximum width of the machine. If, on the other hand, it is desired to produce a finished film having uniform characteristics in all directions, the amount of this stretching will be so regulated that the stretching of the metal cellulose xanthate film in the transverse direction will be substantially counteracted by the orientation produced by subsequent shrinkage in the transverse direction and simultaneous substantial inhibition of shrinkage in the longitudinal direction, occurring especially during the regenerating, desulfuring and drying operations.

After being led through the transverse stretching device, the film is led into a regenerating bath which transforms the metal cellulose xanthate into regenerated cellulose. This bath will preferably consist of a solution of sulfuric acid and sodium sulfate such as is well known for use in the coagulation of viscose. The film is led through successive treating baths in the well known fashion, such as washing, desulfuring, bleaching, glycerinating, until it reaches the drying apparatus. The latter customarily consists of a series of heated rollers over which the film is led to the wind-up apparatus.

During many of the subsequent steps, and particularly the regenerating, desulfuring and drying operations, the film has a great tendency to shrink and its opportunity to so shrink is much greater in the transverse than in the longitudinal direction. The inhibition of shrinkage in the longitudinal direction will cause the cellulose micelles to be oriented in this direction, thus offsetting the orientation of the micelles induced in the film by the transverse stretching of the metal cellulose xanthate. It will be seen that the stretching of the metal cellulose xanthate can be so controlled that the said orientation in the transverse direction during coagulation will be exactly offset by the orientation in the longitudinal direction during subsequent operation, so that the net result is a complete random orientation of the micelles in the plane of the film, and the production of a film which has uniform properties in longitudinal and transverse directions. Due to the stretching in both directions in the plane of the film, there is very little, if any, orientation of micelles perpendicular to the plane of the film.

In order to more clearly picture the orientation of micelles in the new film produced in accordance with the present invention, reference is made to Figures 3, 3A, 3B, 4, 4A, 4B, 5, 5A, and 5B in which the positions of the micelles are indicated by fine lines and points.

The enlarged views of film shown in Figures 4, 4A and 4B illustrate the orientation of micelles as they will be found in a film produced by placing a layer of viscose on a plate and regenerating, purifying and drying the same without tension. It will be noted that in such a film the micelles will be found in perfect random orientation in all directions, both in the plane of the film and through the thickness (a cross-section) of the film.

Figures 3, 3A, and 3B illustrate the orientation of micelles in a film produced by the conven-

tional continuous film casting method known prior to the present invention. Due to tension on the film only in the longitudinal direction, the micelles are pulled around so as to be oriented in positions longitudinally of the film. Such film will be stronger and will resist tearing by longitudinal pull much more than the film shown in Figure 4, but will be weaker and will resist tearing by transverse pull much less than the film shown in Figure 3. This film when used as a wrapping tissue, or the like, will fall along a line in the longitudinal direction thereof as shown at A.

The film illustrated in Figures 5, 5A, and 5B show the approximate orientation of micelles when the film has been produced in accordance with the present invention. This film will resist tearing substantially equally in all directions across the plane thereof and will resist such tearing in any of said directions much more than the film of Figure 4. This film will be somewhat less resistant to splitting in a plane taken parallel to the plane of the film as shown at B and C than the film of Figure 4, but it is clearly apparent that there is very little, if any, strain on film in this direction as compared to the strain on film across the plane thereof.

Naturally the micelles will not all be oriented in the exact positions illustrated in Figures 3 and 5, but the micelles will be pulled around to be oriented substantially along the lines illustrated and will have the resultant effect upon the strength of the film as above described.

In order to more fully describe the invention, the following non-limitative, specific examples are given of coagulating baths suitable for use in the practice of this invention.

Example I

A normal viscose containing 7.5% of cellulose and 6.3% of alkali is forced under pressure into a bath containing 18% of ammonium sulfate. The coagulated film is then led into a second bath containing 10% zinc chloride, and thence over expander rolls into a regenerating bath. The film is further treated and dried in accordance with the known art.

Example II

The same procedure is followed as in Example I except that 10% of aluminum chloride replaces the 10% of zinc chloride in bath 2.

Example III

A viscose containing 7.5% of cellulose and 6.3% of alkali is led under pressure into a bath containing 5% of zinc acetate and 1% of acetic acid. Thence the coagulated film is led over expander rolls into a regenerating bath and purified and dried in the known manner.

Example IV

The same procedure is followed as in Example III except that the bath contains 5% of zinc sulfate and 5% of ammonium sulfate.

All of the films produced in accordance with the above described examples are found to be wider than films produced in the same apparatus heretofore, the film is uniformly strong in all directions, and will resist wear and tear when subjected to commercial usage much more readily and consistently than film of similar thickness produced prior to this invention.

As hereinabove pointed out, the metal salts specifically set forth above can be replaced by other metallic salts which are capable of producing a metallic cellulose xanthate which is substantially colorless, tough, inelastic and insoluble in water.

It is evident that the practice of this invention will produce films of uniform physical characteristics in both longitudinal and transverse directions. Furthermore, the improved strength characteristics are secured mostly at the expense of the strength characteristics through the thickness of the sheet where they are not needed and where they are therefore reduced to a minimum.

Film produced in accordance with the present invention is much wider than film produced heretofore in apparatus of a given size, and therefore results in a greatly increased production without additional cost for raw materials. This will obviously effect great economies in production and at the same time will improve the quality of the film.

Obviously many changes and modifications can be made in the above detailed disclosure without departing from the nature and spirit of the invention, and it will therefore be understood that the invention is not to be limited except as set forth in the appended claims.

I claim:

1. In the method of making a continuous regenerated cellulose pellicle the steps comprising passing a liquid sheet of viscose into a coagulating, non-regenerating bath, passing said coagulated sheet of viscose into a second bath containing a colorless, water-soluble metal salt taken from the group consisting of zinc, aluminum and lead salts whereby to form a metal cellulose xanthate pellicle, stretching said pellicle transversely and longitudinally thereof, and regenerating the same.

2. In the method of making a continuous regenerated cellulose pellicle the steps comprising passing a liquid sheet of viscose into a coagulating, non-regenerating bath comprising ammonium sulfate, passing said coagulated sheet of viscose into a second bath containing a colorless, water-soluble metal salt taken from the group consisting of zinc, aluminum, and lead salts whereby to form a metal cellulose xanthate pellicle, stretching said pellicle transversely and longitudinally thereof, and regenerating the same.

3. In the method of making a continuous regenerated cellulose pellicle the steps comprising passing a liquid sheet of viscose into a coagulating, non-regenerating bath, passing said coagulated sheet of viscose into a second bath containing a colorless, water-soluble metal salt taken from the group consisting of zinc, aluminum and lead salts whereby to form a metal cellulose xanthate pellicle, stretching said pellicle transversely thereof and regenerating the same.

4. In the method of making a continuous regenerated cellulose pellicle the steps comprising passing a liquid sheet of viscose into a coagulating, non-regenerating bath, passing said coagulated sheet of viscose into a second bath containing a colorless, water-soluble metal salt taken from the group consisting of zinc, aluminum and lead salts whereby to form a metal cellulose xanthate pellicle, stretching said pellicle longitudinally thereof and regenerating the same.

FRANCIS P. ALLES.