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PROCESS OF MAKING CELLULOSE NITRATE SHEETING INCLUDING IMBIBITION

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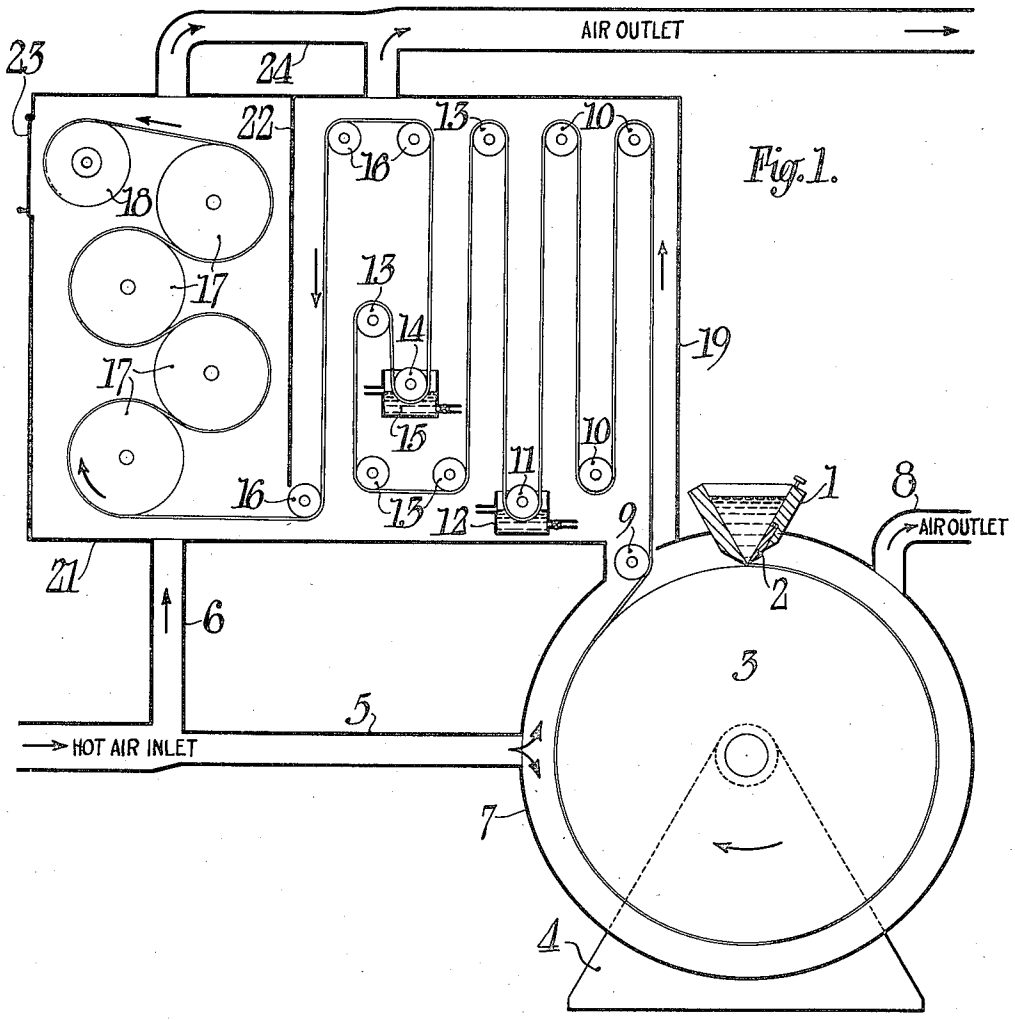

Fig. 1.

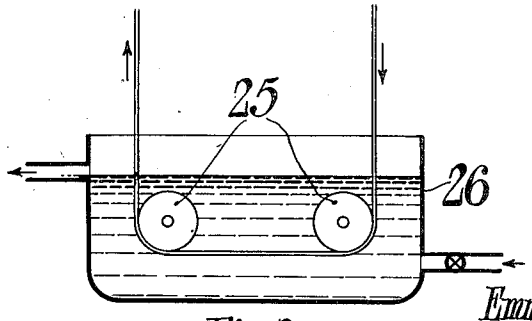

Fig. 2.

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PROCESS OF MAKING CELLULOSE NITRATE SHEETING INCLUDING IMBIBITION

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13 Claims. (Cl. 18—57)

This invention relates to cellulose nitrate sheeting and to a method of producing it. More particularly it relates to a method of preparing cellulose nitrate sheeting from a solution of nitrocellulose in solvent liquid in which acetone predominates by casting the sheet upon a suitable surface and then treating the sheet, after it has set but while still containing considerable acetone, with a liquid in which methyl alcohol predominates, and further drying the sheet.

In the manufacture of cellulose nitrate sheeting, such as in the production of cellulose nitrate film base ranging from .005 to .010 of an inch in thickness, and of any suitable width, the nitrocellulose is dissolved in a suitable solvent to make what is termed in the trade a "dope" of about the consistency of honey. This dope is permitted to flow upon a large wheel, such as a driven cast iron wheel having a smooth nickel or chromium plated surface, which wheel rotates in a casing through which air is circulated, permitting the solvent to evaporate from the dope and harden into a sheet of sufficient toughness to strip from the wheel before it has made a complete revolution, whereupon the sheet is led through curing chambers over idle rolls and curing drums maintained at a suitable temperature (and through which air is circulated) and then wound upon a shaft for storage or further use, such as coating with emulsion to form photographic film.

We have noted the rather striking fact that while sheeting may be produced more rapidly from a dope in which acetone predominates as a solvent than from a dope in which methyl alcohol predominates as the solvent liquid, nevertheless a film having better wearing properties, higher tensile strength and much higher flexibility results from sheeting produced from the methyl alcohol dope.

We have discovered a method of producing cellulose nitrate sheeting wherein the speed of coating from an acetone dope is utilized and yet the unusual micelle structure which gives the sheeting the higher wear and tear resistance, higher tensile strength and greater flexibility is obtained.

Accordingly, it is an object of our invention to provide a process for preparing nitrocellulose sheeting which will have the speed of coating obtained with acetone dopes and the physical structure of sheeting produced from methyl alcohol dopes. Other objects will be apparent from a further perusal of this specification.

In its broader aspects, our invention comprises preparing a suitable dope by dissolving cellulose nitrate in a solvent liquid in which acetone predominates (at least in its effect upon micelle structure), casting or coating this dope into the form of a sheet permitting sufficient acetone to evaporate from the sheet to permit stripping of the sheet from the casting or coating surface, then treating the sheet with a liquid in which methyl alcohol predominates and permitting further volatile liquid to evaporate from the sheet.

Our process is not to be confused with those involving the application to the sheeting (before it is stripped from the casting or coating surface and while it still contains a large proportion of solvent) of certain treating solutions, such as a solvent or solvent mixture, to prevent or modify curling tendencies of the sheeting, or of certain treating solutions, such as dyes, coatings and the like, to the sheeting while it is still on the casting surface for altering the color, moisture resistance, static properties, etc. of the sheeting. Nor is our process to be confused with that type of process wherein the sheeting, after it leaves the coating surface and passes through the curing chambers and as a substantially finished or cured sheet is treated with certain treating baths for removing a small percentage of residual solvent or other constituents of the dope used in forming the sheeting, this latter being done usually with an aqueous bath and in all events without scarcely softening the sheet and in no case being accompanied by a micelle rearrangement. The effective part of our process acts upon the film preferably at a point in between these two above mentioned types of treatments and, as will be apparent hereinafter, has an entirely different effect upon the sheeting, although, with less salient effect and economy and more difficult handling, our process is applicable to the treatment of substantially fully cured sheeting.

The type of cellulose nitrate which we employ is that ordinarily employed in the manufacture of cellulose nitrate sheeting, namely, nitrocellulose having a nitrogen content of from approximately 11.5% to about 12.2%. In converting this nitrocellulose into a so-called acetone dope, it is customary to employ a solvent liquid containing from 51 to 100% of acetone mixed with from 49% to 0% of methyl alcohol, both the acetone and methyl alcohol being the average commercial grade of substances obtainable upon the market. Highboilers, such as butyl alcohol, and plasticizers, such as camphor, may, of course, be added to the dope as already known. The speed with which it is possible to successfully coat the acetone dope depends, of course, upon the proportion of acetone contained in the dope—

the higher the acetone proportion, the higher the speed of coating which is possible. We have found a dope composed of approximately 85% acetone and about 15% methyl alcohol as being a very suitable solvent liquid, giving a high speed of coating and very good handling, such as good spreading, etc. It also has probably the highest evaporative rate, since it is a constant boiling mixture with a boiling point very slightly lower than pure acetone.

However, it will be understood that the micelle arrangement which occurs when a pure acetone dope of nitrocellulose is cast into the form of a sheet and evaporated, prevails with all nitrocellulose of the sheeting type (11.5 to 12.2% nitrogen) down to an acetone content of as low as 30% for the solvent liquid, even though the remainder be methyl alcohol. With nitrocellulose in the lower range of nitrogen content, for instance of from 11.5% to about 12% nitrogen, this "acetone effect" or micelle arrangement prevails when a solvent liquid of even a little less than 30% acetone is used. In this specification, therefore, when we refer in its broader sense to a dope in which acetone predominates, we refer to a dope in which the acetone effect upon micelle structure predominates. The effect of acetone upon micelle structure in the sheet may be recognized not only by the lower tensile strength, wear and tear, and flexibility of the sheet but by its character of tear. Where acetone asserts its predominance one will obtain a rather straight tear, whereas a sheet in which methyl alcohol asserts its predominance will give a bevelled tear.

The nitrocellulose may be added to the acetone-methyl alcohol solvent liquid in the proportion of one part of nitrocellulose to about five parts of solvent liquid, although frequently anywhere from four to six parts of solvent liquids are employed.

In the drawing we have illustrated several of the preferred embodiments of our invention in which:

Figure 1 is a diagrammatic sectional elevation of one form of apparatus for carrying out our imbibition process, and illustrating a convenient method of forming a cellulose nitrate sheet, causing it to imbibe a treating solution and subsequently drying the treated sheet.

Figure 2 is a sectional elevation of a modified form of the device for applying the imbibition solution to the sheet.

Referring now to the drawing accompanying this specification and forming a part hereof and in which like reference numerals refer to like parts, Fig. 1 is a diagrammatic side elevation of a suitable apparatus for carrying out our invention. In this apparatus the dope is fed to the hopper 1 which is provided with an adjustable blade or knife 2 for regulating the thickness of the coating. This coating is thus deposited upon the surface of a large driven wheel 3 of suitable diameter and width, which is mounted upon standards 4. As this wheel 3 rotates slowly in the direction indicated by the arrow, heated air is admitted through the line 5 into the casing 7, as well as through the line 6, into another portion of the apparatus. The air admitted through line 5 passes in the direction of the arrows around the wheel 3 within the casing 7, the line and casing both being suitably insulated as desired. That part of the air which passes around the major periphery of the wheel is withdrawn—laden with solvent, at the air outlet 8 while the remainder travels up through the casing 19. The wheel 3 is rotated at a speed which, with the amount of air being circulated and the amount of dope being used, will permit sufficient hardening of the dope to allow the sheet to be stripped from the wheel at the point where the roll 9 is placed. A rotational speed of from 5 to 8 revolutions per hour for a wheel having a diameter of 18 to 20 feet, namely a peripheral speed of about 300–400 feet per hour, with a plentiful circulation of air at an inlet temperature of approximately 175–200° F., has been found satisfactory.

While this sheeting might be conducted through the curing apparatus and sheeting satisfactory for some purposes be thus obtained, it is desirable for use as photographic film base, particularly motion picture film base, that the sheeting have a higher wear and tear resistance and greater flexibility. While theoretical considerations are of no particular importance, the evidence points to the fact that sheeting produced from a methyl alcohol dope have a different micelle structure, namely, a different manner by which the nitrocellulose molecules are fitted together than has sheeting produced from an acetone dope. We have made the very valuable discovery that sheeting produced from an acetone dope, even though hardened sufficiently to permit handling thereof, or even completely cured, can be converted to sheeting having the methyl alcohol micelle structure by imbibition of the sheeting in a liquid in which methyl alcohol predominates.

This is accomplished by conducting the nitrocellulose sheet over a set of rolls 10 and over submersion roll 11, which latter roll submerges the nitrocellulose sheet into an imbibition solution contained in submersion hopper 12. From this hopper, the nitrocellulose sheet passes over the rolls 13 and under submersion roll 14, so that the sheeting is submerged in the imbibition solution contained in the immersion hopper 15. From roll 14, the sheet passes over rolls 16 and thence to steam or water heated curing drums 17, which are preferably driven, and thence to wind-up 18. For convenience, we have illustrated a casing 19 in which the rolls 10, 13 and 16 are contained and a casing 21 in which the curing drums 17 are contained. These two casings are separated by a baffle 22 which leaves an opening adjacent the lower roll 16, through which the film enters into casing 21 and which permits any desired communication between the casings 19 and 21.

A door 23 is provided for removing the sheeting as it is wound up at 18. Heated air for curing the sheeting is supplied to the casing 21 through the line 6 as previously adverted to. Solvent-laden air is removed from the casings 19 and 21 by means of the air outlet 24 which conducts the solvent-laden air (along with air from the outlet 8) to the solvent recovery apparatus, which removes the solvent from the air and returns it to the apparatus through the lines 5 and 6.

Fig. 2 illustrates a diagrammatic sectional elevation of a different type of immersion hopper which may be employed. With this type of hopper, the nitrocellulose sheeting passes under rolls 25 and is thereby suspended in the imbibition solution contained in the hopper 26.

While we have illustrated the nitrocellulose sheeting as being subjected to imbibition upon both sides of the sheeting and the most complete conversion of the micelle structure of the sheeting from the acetone dope type to the methyl alcohol dope type is thereby obtained, we may subject the sheeting to only a single immersion, such as in either of the hoppers 12 or 15, if a less complete

change of the micelle structure is desired. Possibly the most complete change of micelle structure is effected by employing the type of immersion hopper shown in Fig. 2 although it will be understood that this type of hopper gives to the sheeting a rather drastic treatment and the tension of the sheeting must be more carefully regulated, in order not to pull the sheet in two.

The imbibition solution employed in the hoppers 12, 15 and 26 is one composed of a preponderance of methyl alcohol. Considerable latitude is permitted in compounding the imbibition solution, the factors which limit the constituents of the imbibition solution being (1) methyl alcohol must predominate (2) non-solvents must not be employed in such proportion as to substantially negative the action of the methyl alcohol upon the nitrocellulose sheeting (3) solvents must not be present in such proportion as to so drastically attack the nitrocellulose sheeting that it will become so soft as to be pulled apart by the tension required to pull the film over the idler rolls 10, 13 and 16 and the curing drums 17, (4) the time that the sheeting is immersed in the imbibition solution must be so regulated as to give the desired length of treatment to the sheeting but not to unduly soften the sheeting and (6) acetone must not be present in sufficient amount to control the micelle structure formed instead of having it controlled by the methyl alcohol, as pointed out in the early part of this specification.

Provided the nitrocellulose employed in producing the sheeting is not too readily soluble in methyl alcohol, we may employ 100% methyl alcohol as the imbibition solution. More preferable, however, is methyl alcohol containing from 1 to 5% of water. Inasmuch as ethyl alcohol has only slight solvent action upon nitro cellulose of this type, we have found it satisfactory to employ as high as 30% ethyl alcohol with as low as about 70% methyl alcohol to form a suitable imbibition solution. Either of these solutions will tolerate a small percentage of solvent, such as acetone, and as a matter of fact, it will be apparent that some acetone will be taken up by the imbibition solution as the sheeting—still containing a fairly high percentage of acetone—passes through the imbibition solution. We prevent the acetone from accumulating to an extent which would unduly soften the sheeting or prevent the micelle rearrangement desired, by regulating the flow of imbibition solution through the immersion hopper at such a speed that the acetone does not accumulate to a detrimental proportion. With for instance three seconds immersion of the sheeting in the imbibition solution, we have found that the acetone content of any of the above imbibition solutions, when used for treating a skin made from a nitrocellulose whose nitrogen content is about 12%, should not be permitted to increase beyond approximately 1.0%. With nitrocellulose of lower nitrogen content, the acetone to be tolerated would be slightly less than 1%.

The time of immersion of the sheeting in the imbibition solution is regulated by the speed of the sheeting as it passes through the apparatus and by the depth of immersion of the sheeting in the imbibition solution. We have found that from 1 to 3 seconds immersion time in each, or either, of the hoppers 12 and 15 is satisfactory, or that 1 to 2 seconds immersion in the imbibition solution contained in the hopper 26 may be employed.

The air temperature in the cabinet 19 will, of course, be somewhat less than that at which it enters the casing 7. It is preferable to regulate the temperature of the curing drums 17 at a temperature ranging from 175 to 225° F., depending, of course, upon the number of drums that are employed. While for purpose of illustration we have shown only four curing drums, it will be quite apparent that any number of curing drums may be employed, it being desirable at times to employ as many as ten to fifteen or more curing drums, depending upon the degree to which it is desired to remove the solvent liquids from the film. Also the temperature of the curing drums 17 may be increased in the direction of the travel of the film, such for instance as a temperature of 175° F. for the first drum and 225° F. for the tenth drum, with the temperature thereafter being tapered off to 175° F. at the fifteenth drum. Also the drums may be in a vertical stack as shown, or they may be horizontal or in the shape of an upright or inverted U, for instance.

While we have illustrated the point of imbibition of the sheeting at approximately the central position of the air-drying section 19 in which the film passes over a series of rolls, it will be understood that it is intended only that the imbibition take place, in the preferred embodiment of our invention, at a point relatively adjacent to the point at which the sheeting is stripped from the surface upon which it is formed. Because of considerable solvent being in the sheet at this point it permits more ready permeation of the sheet by the imbibition solution and, consequently, more efficient conversion of the micelle structure to the methyl alcohol type than if the sheet were first permitted to cure more thoroughly, although it will be understood that our process is applicable to sheeting at any stage of curing after it has been stripped from the casting surface.

As explained above, the entire imbibition may take place at the hopper 12 or at the hopper 15 by immersion in either of these hoppers of a single side of the sheeting, or the hopper 12 may be replaced by a hopper 26 of the type shown in Fig. 2, and the hopper 15 dispensed with, or the hopper 15 may be so replaced and the hopper 12 dispensed with. Furthermore, as pointed out above, there may be any number of the rolls 10, 13 and 16 as may be found necessary for the particular result desired. In other words, the sheeting may be given more or less air-curing prior to its imbibition, between the two imbibitions, or following the single or last imbibition, depending, of course, upon how well cured the sheeting may be when stripped from the wheel or what temperatures are employed in the air-curing cabinet 19.

Suffice it to say that, preferably we imbibe the sheet with our imbibition solution while the sheet contains a relatively high percentage of acetone and is thus readily susceptible to an exchange in the nitrocellulose sheet of methyl alcohol for acetone. Comparatively speaking, we have found it preferable to imbibe the sheet with methyl alcohol while the sheet is in as green or uncured a state as is consistent with proper handling of the sheet without tearing it in two, or unduly extending it. While there is no limiting point at which the sheet may be subjected to imbibition we would state that it is less desirable to substantially completely cure the sheet before subjecting it to imbibition as the micelle structure of the nitrocellulose has then become rather firmly fixed. Such long immersion may also be accompanied by undue softening of the surface of the sheet before penetration of the imbibition solution into the center of the sheet can take place and thus cause difficulties in the handling of a

long strip of sheeting. However, it is to be understood that our process may be employed with substantially fully cured nitrocellulose sheeting even after it has been in storage. Particularly is this true of small sheets which can be handled by suspending them in the imbibition solution from clips or where a machine especially designed for handling soft sheets is available.

In this same connection, while we have shown an apparatus for continuously producing sheeting in accordance with our invention, it will be quite apparent that it may be carried out in batch form, such as by coating the acetone dope upon plates, permitting the solvent to evaporate from the sheet, stripping it therefrom substantially as soon as it is susceptible of stripping and handling, or even after it has more thoroughly cured, and then imbibing the sheet merely by dropping it into an imbibition solution. This hand operation will, of course, not be very practical commercially (because expensive) but illustrates the principles of our invention.

As a guide to those skilled in the art, we would state that from our experience with the process we find that a nitrocellulose sheet may be stripped from its coating surface at a time when it still has remaining therein roughly 10–15% of acetone (or solvent liquid) and that it should preferably be imbibed with our methyl alcohol solution any time from that point up to a point in the subsequent curing of the sheet at which it still contains roughly 2% acetone, although as above pointed out, a more thoroughly cured sheet may successfully be subjected to imbibition. These percentages of acetone are given not as a limiting factor to our invention, but merely as a guide to those skilled in the art so as to teach them the principles of our invention.

Motion picture film having a base of nitrocellulose sheeting produced according to our process will be found to endure the wear and tear of the ordinary cine projection machine for as much as ten to 100 percent longer than sheeting produced from an acetone dope without being imbibed in accordance with our invention, the degree of improvement depending on the degree of imbibition obtained. The sheeting of our invention, furthermore, has been found to possess considerably more flexibility than the flexibility which the acetone dope type of sheeting possesses, for instance, as much as 20 to 25% more flexibility. The imbibed sheeting also possesses a higher tensile strength.

Accordingly, it will be observed that we have provided a process which permits the high speed of coating accompanying the use of an acetone dope but having the desirably high wear and tear resistance, increased tensile strength, and increased flexibility of the methyl alcohol dopes which, though desirable to produce, are of such slow coating speeds as to increase the expense of production to a point substantially prohibiting their competition with other types of sheeting.

What we claim as our invention and desire to be secured by Letters Patent of the United States is:

1. The process of preparing nitrocellulose sheeting which comprises casting a dope of nitrocellulose dissolved in a liquid in which acetone predominates in its effect upon the micelle structure of the sheeting, evaporating sufficient solvent therefrom to permit stripping of the sheet, stripping the sheet and treating at least one surface of the sheet with a solution in which methyl alcohol predominates.

2. The process of preparing nitrocellulose sheeting which comprises casting a dope of nitrocellulose dissolved in a liquid in which acetone predominates in its effect upon the micelle structure of the sheeting, evaporating sufficient solvent therefrom to permit stripping of the sheet, stripping the sheet and submerging at least one surface of the sheet in a solution in which methyl alcohol predominates.

3. The process of preparing nitrocellulose sheeting which comprises casting a dope of nitrocellulose dissolved in a liquid in which acetone predominates in its effect upon the micelle structure of the sheeting, evaporating sufficient solvent therefrom to permit stripping of the sheet, stripping the sheet and submerging the sheet for a time in a solution in which methyl alcohol predominates.

4. The process of preparing nitrocellulose sheeting which comprises casting a dope of nitrocellulose dissolved in a liquid in which acetone predominates in its effect upon the micelle structure of the sheeting, evaporating sufficient solvent therefrom to permit stripping of the sheet, stripping the sheet and submerging the sheet in substantially pure methyl alcohol.

5. The process of preparing nitrocellulose sheeting which comprises casting a dope of nitrocellulose dissolved in a liquid in which acetone predominates in its effect upon the micelle structure of the sheeting, evaporating sufficient solvent therefrom to permit stripping of the sheet, stripping the sheet and submerging at least one surface of the sheet with an imbibition solution containing more than 95% methyl alcohol and the remainder substantially water.

6. The process of preparing nitrocellulose sheeting which comprises casting a dope of nitrocellulose dissolved in a liquid in which acetone predominates in its effect upon the micelle structure of the sheeting, evaporating sufficient solvent therefrom to permit stripping of the sheet, stripping the sheet and submerging at least one surface of the sheet with an imbibition solution containing more than 95% methyl alcohol, less than 1% acetone and the remainder substantially water.

7. The process of preparing nitrocellulose sheeting which comprises casting a dope of nitrocellulose dissolved in a liquid in which acetone predominates in its effect upon the micelle structure of the sheeting, evaporating sufficient solvent therefrom to permit stripping of the sheet, stripping the sheet and submerging at least one surface of the sheet with an imbibition solution consisting of approximately 70% methyl alcohol and about 30% ethyl alcohol.

8. The process which comprises subjecting nitrocellulose sheeting which has been prepared from a dope in which acetone predominates in its influence upon the micelle structure, to imbibition by a liquid in which methyl alcohol predominates and drying the sheet.

9. The process which comprises submerging nitrocellulose sheeting which has been prepared from a dope in which acetone predominates in its influence upon the micelle structure in a liquid in which methyl alchol predominates and drying the sheet.

10. The process which comprises submerging nitrocellulose sheeting which has been prepared from a dope in which acetone predominates in its influence upon the micelle structure in a liquid consisting of substantially pure methyl alcohol.

11. The process which comprises submerging

nitrocellulose sheeting which has been prepared from a dope in which acetone predominates in its influence upon the micelle structure in a liquid consisting of more than 95% methyl alcohol and the remainder substantially water.

12. The process which comprises submerging nitrocellulose sheeting which has been prepared from a dope in which acetone predominates in its influence upon the micelle structure in a liquid consisting of more than 95% methyl alcohol, less than 1% acetone and the remainder substantially water.

13. The process which comprises submerging nitrocellulose sheeting which has been prepared from a dope in which acetone predominates in its influence upon the micelle structure in a liquid consisting of approximately 70% methyl alcohol and about 30% ethyl alcohol.

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