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ACETYLATION OF CELLULOSE

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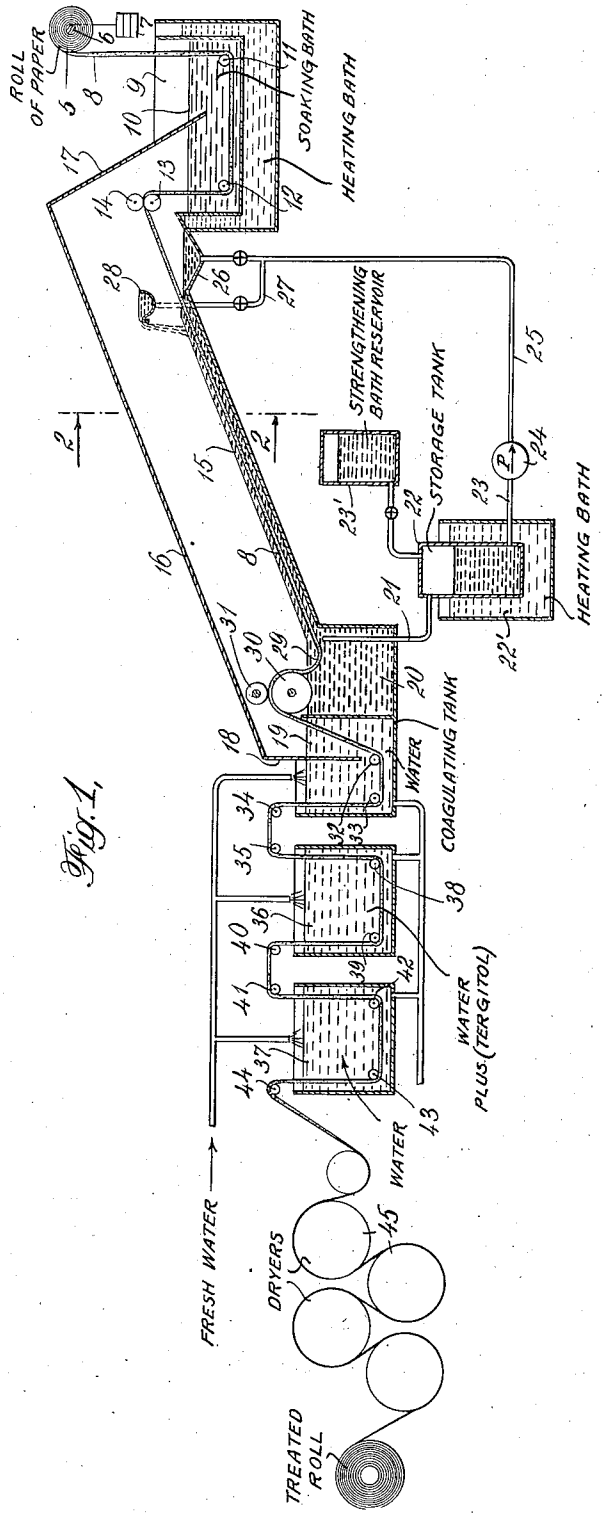


Fig. 1.

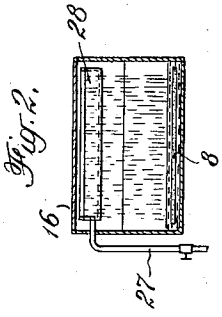


Fig. 2.

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ACETYLATION OF CELLULOSE

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This invention relates to the acetylation of cellulose and particularly to the continuous acetylation of a traveling web of cellulose material, such as paper or fabricated cellulose filaments to effect a modification of the characteristics of the material uniformly and progressively and thereby to produce a new material capable of uses for which the original is not adapted.

While the invention is particularly useful in the preparation of acetylated materials from paper stock, it has been found that desirable products may be produced also from fabrics produced from cellulose materials by weaving or otherwise when such fabrics are subjected to the method as hereinafter described.

It has been suggested that a web of paper may be subjected to acetylation by leading it over suitable rolls through an elongated bath containing an acetylating agent and a non-solvent diluent. Nevertheless, acetylated paper in the form of webs or sheets has not heretofore been available as a commercial product, and industry has not had an opportunity to utilize such material for the purposes for which it is particularly useful. In theory, such material may be prepared without difficulty, but in practice there are many problems which heretofore have baffled those who sought to prepare acetylated paper as a commercial product. Consequently it has not been possible to manufacture acetylated paper on a commercial and economical basis.

Foremost among the problems is that of retaining the fibrous form of the paper or fabric in the acetylated product. Acetylation of cellulose is, if the acetylating agent is effective, a reaction which proceeds rapidly, and it is very difficult to control this reaction which, if uncontrolled, results in complete disintegration of the cellulose. In the case of fibrous material, acetylation results immediately and during the treatment with the acetylating agent in substantial loss of tensile strength. In the absence of suitable precautions the material loses its fibrous structure and cannot be maintained in the form of a sheet or web. A previously suggested method of acetylating a web of paper produces complete degeneration and not a web of acetylated paper as intended.

Assuming a suitable bath which is properly adjusted to effect acetylation without disintegration, it is necessary, since the tensile strength of the material is materially reduced, to avoid any stress which would tear the web, and thus prevent continuous travel thereof. Moreover, the acetylation of the material rapidly exhausts the acetic anhydride which is the acetylating agent, and as the material advances the acetylation formula becomes progressively less effective until it fails. Under this condition, the product is non-uniform and useless.

There are numerous other factors which must be considered. These will be referred to in more detail hereafter. The continuous maintenance of the essential conditions for the acetylation of webs of cellulose material has not been possible heretofore since some of the conditions were not recognized and no attempt had been made to employ suitable control in respect to other details.

It is the object of the present invention to provide a novel method of acetylating a web of cellulose material in a continuous operation which effects a uniform treatment of the material in a minimum of time, thus affording a practical commercial operation permitting the economical preparation of new products having advantageous properties and characteristics which make them useful for various purposes.

Another object of the invention is the provision of a method wherein a web of cellulose material is advanced continuously and subjected to uniform acetylation without the introduction of stresses which would break the web in its weakened condition.

Another object of the invention is the provision of a method wherein the web of cellulose material is subjected to an acetylating formula capable of rapidly and effectively modifying the material as it advances, the operation being controlled to avoid variations in the amount of acetylation effected in successive portions of the web.

Another object of the invention is the provision of a method in which the uniformly acetylated web is purified continuously and effectively to afford new and satisfactory products which will not deteriorate in use.

Another object of the invention is the provision of a method of effectively controlling the concentration of the acetylating agent so that successive increments of the web receive uniform treatment.

Another object of the invention is the provision of an effective acetylation formula and suitable pretreatment baths for use in the practice of the invention.

A further object of the invention is the provision of new and useful commercial products consisting of cellulose material acetylated by the method and having novel and desirable characteristics.

Other objects and advantages of the invention will be apparent as it is better understood by reference to the following specification and accompanying drawing, in which

Fig. 1 is a diagrammatic illustration in longitudinal section of an apparatus adapted for the practice of the invention; and

Fig. 2 is a section on the line 2—2 of Fig. 1.

The apparatus hereinafter described is not in all of its details essential to the invention. It is, therefore, merely illustrative of a preferred embodiment of practical means for accomplishing the desired results, which has been used successfully in a plant operation. Various modifications of such an apparatus may be used to accomplish the purpose of the invention, provided the essential conditions of operation are observed.

In carrying out the invention, the following variables govern the treatment and the characteristics of the finished product: type of material treated, conditions of pretreatment with acetic acid including temperature and time of immersion of the paper therein, strength of acetic anhydride in the acetylating bath, percentage of catalyst in the bath, maintenance of uniform composition of the bath, composition of addition agents employed to maintain uniformity in the bath, time of immersion and temperature of the acetylating bath, ratio of the total acetylating bath to the amount of paper being treated at any interval, purifying procedure and drying procedure. When all of these factors are properly correlated in accordance with their relative importance, it is possible to secure rapid and effective modification of the characteristics of the cellulose material without deterioration thereof and to maintain continuous operation.

The procedure is conducted preferably in an apparatus in which the cellulose material is first subjected to a preliminary treatment or soaking in acetic acid of suitable concentration and thereafter subjected to the action of acetic anhydride of suitable concentration and at a proper temperature in the presence of a catalyst and under conditions in which both sides of the web are subjected progressively to an acetylation formula of uniform concentration. The web advances continuously, without being subjected to any substantial stress which would tend to tear it in its weakened condition, until it is delivered to a bath of water which promptly quenches the reaction and restores partially the tensile strength of the paper. This water bath should be constantly renewed and may contain suitable agents to facilitate purification. The web is then led through a succession of water baths which are similarly freshened and thence to the dryers.

To maintain uniformity of acetylation it is necessary to circulate constantly the acetylation formula, with suitable additions to fortify and maintain it at its maximum concentration so that each increment of the web as it comes from the soaking bath is uniformly affected by the acetylating formula at its maximum strength, that is to say, each increment of the web as it advances receives precisely the same treatment.

In order that the operation may be more clearly understood, reference is made to the accompanying drawing, in which 5 indicates a roll of cellulose material to be treated, which is mounted on a spindle 6. Unrolling of the web is retarded by a suitable brake indicated diagrammatically by the weight 7. The web 8 is delivered to a receptable 9 which may be made of any suitable material which is not affected by the soaking bath 10 consisting of acetic acid. Provision is made for the addition of acetic acid as required and likewise to maintain the bath at a predetermined temperature. The web 8 passes under rollers 11 and 12 and is drawn through the soaking bath by driven rollers 13 and 14 which squeeze the excess of acetic acid from the paper as it advances. The web is fed by the rollers 13 and 14 to the acetylation chamber comprising an inclined plane surface 15 enclosed by a suitable hood 16 having an extension 17 covering the soaking bath 10 and an extension 18 which dips into the first water bath 19 so that fumes from the acetic acid and acetic anhydride are prevented from escaping to the surrounding atmosphere.

The angle of the inclined plane 15 is such that the web will travel downwardly thereover under the influence of the acetylating agent which flows continuously with the web. The web advances continuously without being subjected to any stress which is likely to tear it, a condition which cannot be maintained if an attempt is made to draw the web through a bath by the application of tension. The angle of the inclined plane 15 may be varied considerably depending upon the nature of the material, but an angle of approximately 22° from the horizontal has been found to be satisfactory with most types of webs.

The acetylating agent flows with the web into a receptacle 20 from which it is withdrawn continuously through a pipe 21 and delivered to a storage tank 22, provided preferably with a heating bath 22'. Water may be used for heating to a constant temperature. Suitable provision is made for the addition of materials to the storage tank from a tank 23' to maintain a precise composition of the acetylating agent at a uniform temperature. From the tank 22 the acetylating agent is withdrawn continuously through a pipe 23 by a pump 24 and delivered by a pipe 25 to a trough 26 and by a branch 27 to a trough 28. The troughs 26 and 28 overflow continuously, supplying the acetylating agent beneath and above the web 8 as it advances to and down the inclined plane 15. This arrangement ensures that each increment of the web is subjected under precisely uniform conditions to an acetylating agent of exact formula. Also, the amount of acetylating agent overflowing from the troughs 26 and 28, beneath and above the web, and the force with which the liquid from those troughs flows down the inclined surface 15 is such as to maintain the web suspended in the acetylating agent, as shown in Fig. 1, so that both sides of the web are subjected to treatment with the acetylating agent as it passes over the inclined surface and acetylation of the web proceeds uniformly and cannot vary substantially in respect to the predetermined conditions.

In the receptacle 20 the web 8 forms a loop 29, thus avoiding any possibility of substantial ten-

sion in the descending web, and adheres to a roll **30** which dips into the acetylating agent in the receptacle **20**. A co-operating driven roll **31** causes the web to advance and at the same time removes the excess of the acetylating agent. At this point there is, of course, a certain loss of the acetylating agent due to "drag out," which loss must be taken into account in maintaining the precise strength of the acetylating formula by suitable additions thereto. The web passes into the water in the receptacle **19** which promptly quenches the acetylating reaction. Passing under rollers **32** and **33**, the web is drawn out of the bath **19** over rollers **34** and **35** and thence into successive water baths **36** and **37** under rollers **38** and **39**, over rollers **40** and **41**, under rollers **42** and **43**, over roller **44** and thence to a series of drying cans **45** where the web is subjected to drying under regulated conditions. As hereinbefore indicated, the water in the receptacles **19**, **36** and **37** is constantly renewed in order to effect rapid and complete purification, it being essential that all of the acetylating agent be removed from the paper together with any other impurities which may be present.

The conditions other than those already mentioned, under which the operation is conducted, involve particularly the character and strength of the treating solutions as well as the temperature and time of treatment. For the soaking of the web preliminary to acetylation, we prefer to use commercial glacial acetic acid of a purity approximating 99.5%. It is believed that the presence of a minute amount of water equivalent to approximately 0.5% is necessary. Up to 2% of water in the acetic acid is permissible. The temperature of the pre-soaking bath is preferably between 80° and 110° F., or from 5° to 10° F. lower than the temperature maintained for the acetylating agent. The time of pre-soak will vary with the degree of acetylation desired, which is controlled by the speed of travel of the web. It will be usually one-third to one-half the time required for acetylation. As hereinbefore indicated, provision is made for the maintenance of the temperature and concentration of the pre-soaking bath so that it will remain uniform during the entire operation, thus effecting uniformity in the treatment of the web as it advances progressively.

The acetylation formula consists preferably of a liquid having the following composition by weight:

	Per cent
Acetic anhydride (97% technical grade)	50.75
Acetic acid (99.5% glacial)	49
Catalyst—perchloric acid (dry basis)	0.25

This formula may be varied slightly especially with respect to the catalyst. While we prefer to employ approximately 0.25% of the catalyst, the proportion may be increased to about 1.0%.

The acetylating agent is maintained continuously at a temperature of preferably between 80° F. and 120° F. at the point where it is delivered to the web. It is necessary, as previously indicated, to add continuously a strengthening formula to fortify and maintain the acetylating agent at uniform concentration. This will necessarily vary depending upon conditions, but a suitable strengthening formula consists of acetic anhydride 64.5%, acetic acid 35.25%, and perchloric acid 0.25%. The percentages mentioned are by weight, and the materials are those described in connection with the formulation of the acetylating agent. Obviously the acetylating agent must be subjected continuously to control by suitable analyses, and changes will be made in the strengthening formula depending upon the conditions observed. The time of treatment will vary, depending upon the degree of acetylation desired, from 2 minutes to approximately 12 minutes. Economy in operation, that is to say the output of the apparatus, depends upon the speed of treatment and corresponds to the speed of travel of the web, and it is therefore desirable to limit the time of treatment to the minimum.

Purification is effected in three or more consecutive tanks, all supplied with circulating and refreshed water at approximately 100° F. The first purifying tank containing water stops the reaction and coagulates or hardens the material, thus restoring its tensile strength. The second tank will include approximately 0.1% of a suitable wetting agent such as "Tergitol," a sodium secondary-alcohol sulphate (The Journal of Industrial and Engineering Chemistry, volume XXIX, 1937, page 1234). The function of the wetting agent is to facilitate the removal of impurities, and any other suitable wetting agent may be used. The third tank contains pure water to complete purification of the material. The web is purified to a pH of approximately 6.5, it being important to remove all free acid and ionizable salts which, if retained, would interfere with the electrical properties of the material under humid conditions. Any number of purifying tanks, required to effect the desired purification of the web, may be used.

The web is dried continuously by passing over copper drying cans surfaced with a phenolic resin. It is dried at about 220° F. until optimum electrical values are reached. It is important to dry the material properly, since the fibres seem to set with proper drying, producing high electrical values. The speed of drying and the drying temperature are limited by the size of the equipment and the temperature available. The drying temperature is subject to wide variation and temperatures stated herein are merely illustrative of the preferred procedure. Higher temperatures could be used and the drying operation correspondingly limited with respect to time.

While we prefer to use perchloric acid as the catalyst, we may employ any of the known acetylation catalysts such as sulphuric, hydrochloric, hydrobromic and trichloracetic acids, salts such as copper chloride, copper sulphate, copper perchlorate, zinc chloride, zinc acetate, zinc sulphate and meta potassium periodate, and neutral esters such as dimethyl and diethyl sulphate. Certain of the catalysts mentioned, such as the sulphuric acid, perchloric acid and meta potassium periodate, are more active and rapid than others. Sulphuric acid is so active and rapid that unless it is used in very small quantities and the conditions of the reaction are very carefully controlled as to time and temperature, the final product may not have good mechanical and electrical properties. Zinc chloride is a fairly slow-acting catalyst and is particularly suitable in the case of cellulosic materials such as cotton rag papers and high alpha pulp papers. When meta potassium periodate is used, it should be mixed with an equivalent amount of a mineral acid to liberate meta periodic acid, which appears to be the active catalyst.

The procedure as described is adaptable for use

with various types of papers, but is particularly useful in the treatment of kraft papers and produces therefrom products of excellent quality. The most striking characteristic of the product produced by the method described for the treatment of various kinds of papers is the relatively high volumetric resistivity of the paper under humid conditions which may vary from 5000 megohm inches up to or beyond 10,000,000 megohm inches. This remarkable increase in volumetric resistivity adapts the product to numerous applications in the electrical field, as for example in the production of condensers and other similar electrical devices.

To amplify the foregoing description, we have included the following examples. These examples afford detailed description of procedures which we have followed successfully to produce satisfactory products in a continuous and readily maintainable operation. The examples are illustrative and are not to be considered as limiting the disclosure of the invention.

Example 1

A. Paper
A cotton paper made from uncooked raw rags. (M-957)
Thickness—.0055''
Basis weight—60# (24 x 36—500)
Viscosity—66–100 centipoises. (The test for viscosity is the standard method developed by Tappi.)
pH—6
Percentage of alkalinity in paper—low

B. Bath used for treatment
Acetic anhydride (97% technical grade)—50.75%
Acetic acid (99.5% glacial)—49%
Catalyst—perchloric acid—0.25% (dry basis). (This is percentage by weight)

C. Strengthening formula added
Acetic anhydride—64.5%
Acetic acid—35.25%
Perchloric acid—0.25%. (Composition by weight)

D. Treatment conditions
Presoak—100% acetic acid at 80 to 85° F.
Treating time—2½ minutes' immersion in bath at 97° F.

E. Purifying

Purify continuously in three consecutive tanks, all with circulating and refreshed water, at 100° F. The second tank contains water with 0.1% wetting agent such as Tergitol. The paper is pured to a pH of 6.5 approximately. It is important to remove all free acid and ionizable salts at this point since they interfere with the electrical properties under humid conditions.

F. Drying conditions

The treated paper is dried continuously over copper drying cans surfaced with phenolic resin. Paper is dried at about 220° F. until optimum electrical values are reached.

G. Description of the acetylated paper produced by the above method

The paper was treated to a basis weight (24 x 36—500) on a dry basis of 66–67 pounds, and had a percentage combined acetic acid of 19–20 per cent. When tested in humid air at 90% R. H. and 25° C. the paper had a volumetric resistivity of 6,000 to 7,500 megohm-inches.

Example 2

A. Paper
Same as in Example 1

B. Bath used for treatment
Same as in Example 1

C. Strengthening formula added
Approximately as in Example 1

D. Treatment conditions
Presoak—100% acetic acid at 80–85° F.
Treating time—3¾ minutes' immersion in bath at 93 to 94° F.

E. Purifying
Same as in Example 1

F. Drying conditions
Same as in Example 1

G. Description of the acetylated paper produced by the above method

The paper was treated to 70–71 pounds basis weight (24 x 36—500) on a dry basis and a percentage combined acetic acid of 23½ to 24½ per cent. The acetylated paper when exposed to humid air at 90% R. H. at 25° C. has a volumetric resistivity of 60,000 megohm-inches.

Example 3

A. Paper
A saturating paper made from 100% kraft fibres (S-118)
Thickness—.0058''
Basis weight—48 to 50 pounds (24 x 36—500)
Viscosity—38 to 40 centipoises
pH—6.5
Percentage alkalinity—low

B. Bath used for treatment
Same as in Example 1

C. Strengthening formula added
Acetic anhydride—79%
Acetic acid—20.75%
Perchloric acid—0.25%. (All composition by weight)

D. Treatment conditions
Presoak—100% acetic acid at 80° F.
Treating time—10 minutes' immersion in bath at 87 to 88° F.

E. Purifying
Same as in Example 1 to a pH of 6.5

F. Drying conditions
Same as in Example 1

G. Description of the acetylated paper produced by the above method

Paper was acetylated to 75 pounds basis weight (25 x 36—500) and a percentage combined acetic acid of 45 to 46 per cent. The acetylated paper when exposed to humid air at 90% R. H. at 25° C. had a volumetric resistivity of 1,250,000 and 1,500,000 megohm-inches.

Example 4

A. Paper
Same as in Example 3

B. Bath used for treatment
Same as in Example 1

C. Strengthening formula added
Acetic anhydride—60.5%
Acetic acid—39.25%
Perchloric acid—0.25%. (All composition by weight)

D. Treatment conditions
Presoak—100% acetic acid at 80° F.
Treating time—8 minutes' immersion in bath at 86 to 87° F.

E. Purifying
Same as in Example 1

F. Drying conditions
Same as in Example 1

G. Description of the acetylated paper produced by the above method

The paper was acetylated to a basis weight of 60 pounds (24 x 36—500) and a percentage combined acetic acid of 38 to 39 per cent. The acetylated paper when exposed to humid air at 90% R. H. at 25° C. had a volumetric resistivity of 20,000 megohm-inches.

Example 5

A. Paper
A light weight paper made from 100% kraft fibres (S–124)
Thickness—.003''
Basis weight—30 to 31 pounds (24 x 36—500)
Viscosity—44 centipoises
pH—6
Percentage alkalinity—low

B. Bath used for treatment
Same as in Example 1

C. Strengthening formula added
Acetic anhydride—69.5%
Acetic acid—30.25%
Perchloric acid—0.25%. (All composition by weight)

D. Treatment conditions
Presoak—100% acetic acid at 85 to 88° F.
Treating time—10 minutes' immersion in bath at 96 to 97° F.

E. Purifying
Same as in Example 1

F. Drying conditions
Same as in Example 1

G. Description of the acetylated paper produced by the above method

The paper was acetylated to a basis weight of 46 to 47 pounds (24 x 36—500) and a degree of combined acetic acid of 45 to 46 per cent. The acetylated paper when exposed to humid air at 90% R. H. at 25° C. had a volumetric resistivity of 500,000 megohm-inches.

Example 6

A. Paper
Same as in Example 5

B. Bath used for treatment
Same as in Example 1

C. Strengthening formula added
Acetic anhydride—60.5%
Acetic acid—39.25%
Perchloric acid—0.25%. (All composition by weight)

D. Treatment conditions
Presoak—100% acetic acid at 78 to 80° F.
Treating time—8 minutes' immersion in bath at 86° F.

E. Purifying
Same as in Example 1

F. Drying conditions
Same as in Example 1

G. Description of the acetylated paper produced by the above method

The paper was acetylated to a basis weight of 38 to 39 pounds (24 x 36—500) and to a per cent combined acetic acid of approximately 35%. When exposed to humid air at 90% R. H. at 25° C. the acetylated paper had a volumetric resistivity of 10,000 megohm inches.

The treatment of cotton cloth in accordance with the invention produces equally desirable products. Following are examples of such treatment.

The runs were made making use of our standard metering device and standard amount of bath (160 lbs.). After treatment, the material was purified with water by using a system of three tanks (with circulation) and 0.1% Tergitol solution. Purification was continued until a pH of six or better was reached. The acetylated cloth was dried in continuous rolls over can dryers, the drying being completed at temperature of 230° F. to afford optimum electrical properties. After drying, the cloth was tested for electrical properties at 90% relative humidity, 25° C., for 24 hours, and for mechanical properties.

Example 7

A. Cloth
Purified cotton fabric (0–40)
Thickness .0082''–.0084''
Weight 3.16 ozs./sq. yd.
Count 80 x 80
Viscosity 95 to 179 cps.

B. Treating bath

	Per cent by weight
(97.5% tech. grade) acetic anhydride	50.0
(99.5% pure) glacial acetic acid	49.0
(Solid basis) perchloric acid	1.0
	100.0

C. Treating conditions
Ran in 7 sections, designated A to G.
Presoak and temperature of presoak
1. A, B, C—100% acetic acid at 100° F.
2. D, E, F—100% acetic acid at 110° F.
3. G—98% acetic acid and 2% water at 100° F.

Immersion time in bath and temperature of bath

Section A—2 minutes at 100° F.
Section B—3 minutes at 100° F.
Section C—3½ minutes at 100° F.
Section D—4½ minutes at 110° F.
Section E—8 minutes at 110° F.
Section F—11½ minutes at 110° F.
Section G—2 minutes at 100° F.

D. Cloth was purified and dried.

Example 8

A. Cloth
Same as in Example 7

B. Treating bath

	Per cent by weight
(97.5% tech. grade) acetic anhydride	49.25
(99.5% pure) glacial acetic acid	50.50
(Solid basis) perchloric acid	0.25
	100.00

C. Treating conditions
Ran 6 sections, designated A to F.
Presoak and temperatures of presoak
1. A, B, C—100% acetic acid at 110° F.
2. D, E, F—98% acetic acid and 2% water at 110° F.

Immersion time in bath and temperature of bath

Section A—5 minutes at 110° F.
Section B—8 minutes at 110° F.
Section C—11½ minutes at 110° F.
Section D—5 minutes at 110° F.
Section E—8 minutes at 110° F.
Section F—11½ minutes at 110° F.

D. Cloth was purified and dried.

The material resulting from the procedure as outlined in Examples 7 and 8, when subjected to standard electrical tests, demonstrated its su-

perior properties. The untreated cloth had volumetric resistivity in megohm-inches of 42, and after treatment a maximum of 3,500,000. The insulation resistance of the untreated cloth in megohms was 189, and after treatment reached a maximum of 3,000,000.

There was no substantial loss of mullen or tensile strength in any of the samples, and in most cases a gain in these factors. The acetylation in terms of per cent of combined acetic acid varied from 14.5 to 40, best results being indicated with acetylation in excess of 35%.

Various changes may be made in the apparatus and in the procedure as described without departing from the invention or sacrificing the advantages thereof.

We claim:

1. The method of acetylating cellulose material which comprises continuously advancing a web of the material, subjecting it successively to treatment with acetic acid, thereafter to an acetylating agent and finally to washing with water, maintaining the composition of the acetylating agent by adding fresh reagents thereto, and ensuring uniform treatment of the material by circulating the refreshed acetylating agent and directing it into contact with the non-aceylated increment of the advancing web.

2. The method of acetylating cellulose material which comprises continuously advancing a web of the material, subjecting each increment of the web to an acetylating agent of predetermined uniform composition, and maintaining uniformity of the acetylation of the web by continuously withdrawing and fortifying a portion of the acetylating agent and returning said fortified portion to contact wtih successive increments of the non-acetylated portion of the web.

3. The method of acetylating cellulose material which comprises continuously advancing a web of the material, subjecting each increment of the web to initial contact with an acetylating agent of predetermined uniform composition flowing in the direction of travel of the web, withdrawing and fortifying a portion of the acetylating agent, and returning the fortified portion of the acetylating agent for contact with successive increments of the non-acetylated portion of the web.

4. The method of acetylating cellulose material which comprises continuously advancing a web of the material, subjecting it to treatment with acetic acid, thereafter applying an acetylating agent to each increment of the advancing web, floating the web with the flowing acetylating agent downwardly over an inclined surface thereby avoiding longitudinal stress in the web while it is subjected to the acetylating agent, maintaining the composition of the acetylating agent by adding fresh reagents thereto, ensuring uniform treatment of the material by circulating the refreshed acetylating agent and directing it into contact with the non-acetylated increment of the advancing web, and finally washing the web.

5. The method of acetylating cellulose material which comprises continuously advancing a web of the material, subjecting it to treatment with acetic acid, thereafter causing it to pass downwardly over an inclined surface, supplying an acetylating agent both beneath and above the web as it passes downwardly over the inclined surface, the acetylating agent being supplied beneath and above the web in such amounts and with such force as to maintain the web suspended in the acetylating agent as it passes downwardly over the inclined surface, and finally washing the web with water.

6. The method of acetylating cellulose material which comprises continuously advancing a web of the material, subjecting it to treatment with acetic acid, thereafter causing it to pass downwardly over an inclined surface, supplying an acetylating agent containing at least 49% by weight of acetic anhydride both beneath and above the web as it passes downwardly over the inclined surface, the acetylating agent being supplied beneath and above the web in such amounts and with such force as to maintain the web suspended in the acetylating agent as it passes downwardly over the inclined surface, and finally washing the web with water.

7. The method of acetylating cellulose material which comprises continuously advancing a web of the material, subjecting it to treatment with acetic acid, thereafter causing it to pass downwardly over an inclined surface, supplying an acetylating agent both beneath and above the web as it passes downwardly over the inclined surface, the acetylating agent being supplied beneath and above the web in such amounts and with such force as to maintain the web suspended in the acetylating agent as it passes downwardly over the inclined surface, and finally washing the web with water, and maintaining the composition of the acetylating agent by adding fresh reagents thereto.

8. The method of acetylating cellulose material which comprises continuously advancing a web of the material, subjecting it to treatment with acetic acid, thereafter causing it to pass downwardly over an inclined surface, maintaining the web in contact with an acetylating agent as it passes downwardly over the inclined surface, and finally washing the acetylated web with water, maintaining the composition of the acetylating agent by adding fresh reagents thereto, and insuring uniform treatment of the material by circulating the refreshed acetylating agent and directing it into contact with the non-acetylated increment of the advancing web.

9. The method of acetylating cellulose material which comprises continuously advancing a web of the material, subjecting it to treatment with acetic acid, thereafter causing it to pass downwardly over an inclined surface, supplying an acetylating agent both beneath and above the web as it passes downwardly over the inclined surface, the acetylating agent being supplied beneath and above the web in such amounts and with such force as to maintain the web suspended in the acetylating agent as it passes downwardly over the inclined surface, and finally washing the web with water, maintaining the composition of the acetylating agent by adding fresh reagents thereto and insuring uniform treatment of the material by circulating the refreshed acetylating agent and directing it into contact with the non-acetylated increment of the advancing web.

10. The method of acetylating cellulose material which comprises continuously advancing a web of the material, subjecting it to treatment with acetic acid, thereafter causing it to pass downwardly over an inclined surface, supplying an acetylating agent both beneath and above the web as it passes downwardly over the inclined surface, the acetylating agent being supplied beneath and above the web in such amounts and with such force as to maintain the web suspended

in the acetylating agent as it passes downwardly over the inclined surface, the incline of the web during its passage over the inclined surface being such that it advances without longitudinal stress, and finally washing the web with water.

11. The method of acetylating cellulose material which comprises continuously advancing a web of the material, subjecting it to treatment with acetic acid, thereafter causing it to pass downwardly over an inclined surface, supplying an acetylating agent both beneath and above the web as it passes downwardly over the inclined surface, the acetylating agent being supplied beneath and above the web in such amounts and with such force as to maintain the web suspended in the acetylating agent as it passes downwardly over the inclined surface, the incline of the web during its passage over the inclined surface being such that it advances without longitudinal stress, and finally washing the web with water, maintaining the composition of the acetylating agent by adding fresh reagents thereto and insuring uniform treatment of the material by circulating the refreshed acetylating agent and directing it into contact with the non-acetylated increment of the advancing web.

12. The method of acetylating cellulose material which comprises advancing a web of the material, subjecting it to treatment with acetic acid, thereafter causing the web to pass through an acetylating zone in a direction such that the force of gravity normally would cause a sagging of the web, supplying an acetylating agent both beneath and above the web as it passes through said acetylating zone, the acetylating agent being supplied beneath and above the web in such amounts and with such force as to maintain the web suspended in the acetylating agent as it passes through the acetylating zone.

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