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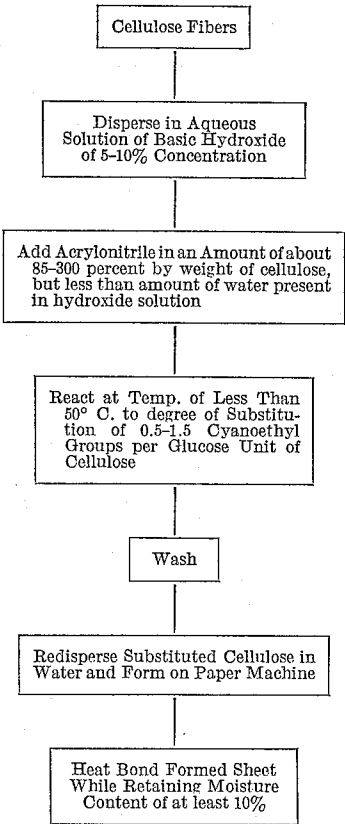
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MANUFACTURE OF CELLULOSIC PRODUCTS
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The present invention is concerned with the manufacture of cellulosic products. More particularly it relates to cyanoethylcellulose products and process for their manufacture.

Although the paper prepared from natural cellulose is one of the most versatile and inexpensive industrial products, it has been recognized that cellulose chemically modified could be made into paper of greatly improved characteristics. One modification which has been examined has been the cyanoethylation of cellulose, or the introduction of the cyanoethyl group, $-\text{CH}_2\text{CH}_2\text{CN}$, into the glucose unit of the cellulose molecule by treatment of the cellulose with acrylonitrile. It has been found that the cyanoethyl group can be substituted into the glucose unit of the cellulose molecule at one or more of the hydroxyl positions by the substitution of the cyanoethyl group for the hydrogen of the hydroxyl group in an ether type of bond. The partial cyanoethylation of cotton textile fibers has resulted in a new type of cotton textile with greatly improved resistance to micro-organism attack, to wet and dry heat degradation and to abrasion. The formation of paper from cyanoethylated cellulose fiber, however, has been found to be much more difficult principally because of the problem of bonding the cyanoethylated cellulose fibers into a paper sheet.

A simplified flow diagram of the process for cyanoethylating cellulose fibers and bonding the cyanoethylated cellulose fibers obtained thereby into a paper sheet in accordance with this invention is as follows:



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Press Moist Sheet or Laminated Sheets at Between 275° and 475° F.

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In the manufacture of paper from cellulosic raw materials the cellulosic fibers, after they have been freed from lignin or other material with which they are associated in nature, are usually beaten in an aqueous suspension to fray the fibers and expose a large surface area of fibrils or micro-fibrils. This is part of the process usually referred to in the paper industry as "hydration" of the pulp. A very dilute suspension of the beaten fiber is then prepared and flowed onto a fine wire screen or forming wire to form a thin layer of cellulose fibers. As water drains away from the layer of fibers on the wire the layer is converted into a weak fibrous web or sheet which is stripped from the wire onto a felt blanket when the fiber content of the web is 17 to 20 percent in a typical case. The web is then conveyed through a press section which presses water out of the sheet to a water content in a typical case of 67 percent. The paper may then be further dried in a dryer section (to a water content of 5 to 15 percent) by pressing and contact with heated rolls. The strength of the paper web is a function of the dryness and there is no difference in the strength of paper dried at an elevated temperature or room temperature.

The strength of a moist paper web on the forming wire depends somewhat upon the surface tension of the water content of the web. There is, however, a wide variation between the strengths of webs of various types of cellulose fibers. A web of a groundwood pulp having a moisture content of 80 percent may have a strength as measured by the breaking length in meters of 27, while a bleached sulfite pulp web of the same moisture content may have a breaking length of 106 meters. A web having a strength of 27 meters, however, has insufficient strength to be formed into paper by typical papermaking machinery and groundwood pulp is usually mixed with at least 25 percent of a strong pulp such as kraft or sulfite to give it additional strength. As the water content of the paper sheet in the press and dryer sections is reduced below about 60 percent water the reduction in strength from surface tension effects is replaced by an interfiber bonding between the cellulose fibers believed to be one of secondary valence or molecular cohesion between hydroxyl groups of adjacent fibrillae. The dry paper sheet will normally have a strength at least several times that of the wet web.

The strength characteristics of a layer of cyanoethylated cellulose fibers having a degree of substitution of 0.5 or greater, developed during drying are quite different than those of a cellulose web. The wet web has very little strength and even in a typical cyanoethylated sheet which has been dried by drainage and pressed to a water content of 44 percent the strength may only have developed to a breaking length in meters of 4.2. This strength is too low to permit the removal of this web from the wire and further handling by conventional papermaking apparatus. Furthermore, upon complete air drying of the sheet to normal air dry moisture content, the sheet will lose substantially all strength. Since the strength of the formed paper sheets depends upon the hydroxyl group it is apparent that cyanoethylated cellulose fibers in which any substantial amounts of the hydroxyl group have been substituted by cyanoethyl groups will have little tendency to bond with other such fibers by the typical paper forming bonds to form a paper sheet.

In addition to the problems of making paper of cyanoethylated cellulose, it has also been found that the method of cyanoethylation of the cellulose and the extent to which it is carried out may greatly affect the resulting product.

For example, under certain reaction conditions the terminal cyano portion of the substituted cyanoethyl group may be hydrolyzed so as to become converted into the carboxyethyl group which will have a considerable effect upon the properties of the cyanoethylated cellulose. Furthermore, if cellulose fibers are cyanoethylated so that the degree of substitution (D.S.) of the hydroxyl groups of a glucose unit by cyanoethyl groups is increased to the 2-3 range the resultant product is soluble in organic solvents and tends to lose its fibrous character if contacted with organic solvents. Thus the cyanoethylated cellulose may dissolve in the acrylonitrile used to cyanoethylate the cellulose. The suitability of cyanoethylated cellulose for particular uses is therefore strongly dependent upon the manner in which the cellulose is cyanoethylated.

It is an object of the present invention to provide a method of manufacturing a fibrous cyanoethyl cellulose pulp having a degree of substitution between about 0.5 and 1.5 and suitable for the manufacture of paperlike sheets.

Additional objects of the invention will be apparent from the following description.

In accordance with the process of the present invention it has been found that cyanoethylated cellulose fibers having between about 0.5 and 1.5 cyanoethyl groups per glucose unit, in a form particularly suitable for the preparation of durable paper sheets, can be formed by treating cellulosic fibers in an aqueous solution of about 5 to 10 percent sodium hydroxide, then adding acrylonitrile to the mixture in an amount of about 85-300 percent of the weight of the cellulose fibers, reacting the mixture until a desired degree of substitution is attained while maintaining the mixture at a temperature of less than about 50° C., then separating the fibers from the solution.

The cellulosic raw material which is converted into cyanoethylated fibrous cellulose by the process of the present invention can be any type of fibrous cellulose suitable for the manufacture of paper, such as wood pulp, cotton fibers, esparto fibers, bagasse fibers and other typical cellulosic fibers. The wood pulp may be prepared by conventional methods such as the kraft and sulfite processes and may be bleached or unbleached. The cellulose fibers are first treated in an aqueous alkaline bath of a strongly basic hydroxide having a hydroxide concentration of between about 5 and 10 percent. Sodium hydroxide is the preferred alkaline material although other water soluble strongly basic hydroxides such as the other alkali metal hydroxides and strongly basic quaternary ammonium hydroxides may be used. The alkaline treatment of the cellulose fibers apparently swells the fibers so that a large surface area is available for the cyanoethylation reaction. The fibers should be thoroughly contacted with the alkaline solution and ten minutes agitation of the cellulose fibers in the alkaline solution is usually sufficient. The ratio of pulp to the aqueous hydroxide is subject to considerable variation based upon the other conditions employed in the hydroxide treatment, such as the time and temperature of the treatment. Drastic conditions are avoided in order to minimize degradation of the cellulosic material. The ratio of cellulose to alkaline solution is not critical and it has been found that a treatment of one part of pulp per nine parts of alkaline solution for a period of about 10 or more minutes at a temperature of the order of room temperature, is generally suitable.

After completion of the treatment of the cellulose fibers with the alkaline solution the acrylonitrile can be added directly to the mixture of cellulose fibers and alkaline solution. It has been found that the addition of acrylonitrile in an amount of between about 85 and 300 percent by weight of the cellulose fibers furnishes a reaction solution which can be most conveniently employed to obtain cyanoethylated cellulose having the desired de-

gree of substitution of 0.5 to 1.5. The reaction between cellulose and the acrylonitrile is exothermic. It has been found that if the temperature of the reaction mixture is permitted to rise above about 50° C., excessive hydrolysis may occur resulting in a cyanoethylated cellulose containing an excessive proportion of carboxyl groups. It may therefore be necessary to cool the reaction mixture to maintain it within the desired temperature range. The cyanoethylated cellulose pulp is removed from the reaction mixture when the pulp has a degree of substitution of cyanoethyl groups for hydroxyl groups per glucose unit of the cellulose between about 0.5 and 1.5. This is equivalent to a nitrogen content of the cyanoethylated cellulose of about 3.72-8.75 percent. The pulp is then washed with water to free it of all excess alkaline material and acrylonitrile. Thorough washing is particularly important if the cyanoethylated pulp is to be made into electrical grade paper. It has been found that cyanoethylated pulp prepared in this manner has a low carboxyl content and is particularly suitable for use in the preparation of dielectric materials.

Now that the process of cyanoethylation of cellulosic fibers of the present invention has been generally described the process may be further illustrated by the following examples. Unless otherwise specified, all parts are by weight.

EXAMPLE 1

One hundred parts by weight (on an oven dry basis) of a bleached kraft made from northern softwood, predominately spruce, was introduced into 880 parts of an aqueous 9.4 percent sodium hydroxide solution. The pulp was slurried in the solution for 10 minutes at room temperature. Two hundred and seventy-five parts of acrylonitrile were then added to the solution and the resultant reaction mixture stirred for 70 minutes. The temperature of the reaction mixture was controlled so that the temperature did not rise above 48° C. The pulp was then separated from the reaction mixture and thoroughly washed with water until all caustic and acrylonitrile were removed. The resultant pulp was analyzed for nitrogen and found to contain 7.52 percent nitrogen, equivalent to a D.S. of 1.19.

EXAMPLE 2

Two hundred and five parts of unbleached kraft pulp was introduced into 1751 parts of an aqueous 8.6 percent sodium hydroxide solution. The pulp was slurried in the solution for 10 minutes at room temperature. Five hundred and fifty parts of acrylonitrile was then added to the slurry to form the reaction mixture. This reaction mixture was agitated for 90 minutes while the temperature was not permitted to rise above 49° C. The resultant cyanoethylated pulp was removed from the solution and washed. Analysis of the pulp disclosed that the pulp had a nitrogen content of 8.24 percent, equivalent to a D.S. of 1.37.

EXAMPLE 3

Twenty-four parts of commercial bleached kraft wood pulp was slurried with 156 parts of 10.0 percent sodium hydroxide for 10 minutes at room temperature. Fifteen parts of acrylonitrile was then added to the slurry and the resultant reaction mixture agitated for 90 minutes at a temperature of not greater than 27.5° C. The cyanoethylated pulp was removed from the reaction mixture and thoroughly washed. The resultant cyanoethylated pulp on analysis was found to contain 3.38 percent nitrogen, equivalent to a D.S. of 0.45. This pulp was a doughy gelatinous pulp which tended to be resinous or pasty rather than fibrous in character and was unsuitable for conversion into paper.

EXAMPLE 4

Twenty-four parts of commercial bleached kraft wood pulp was slurried with 156 parts of 10 percent sodium

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hydroxide for 10 minutes at room temperature. Twenty-one parts of acrylonitrile was then added to the slurry and the resultant reaction mixture agitated for 90 minutes at a temperature not greater than 27.5° C. The cyanoethylated pulp was removed from the reaction mixture and thoroughly washed. The resultant cyanoethylated pulp on analysis was found to contain 5.49 percent nitrogen equivalent to a D.S. of 0.80. This product had the typical fibrous appearance and was suitable for papermaking according to the process of the present invention.

EXAMPLE 5

Seventy-three parts of commercial bleached kraft wood pulp was slurried with 552 parts of 8.0 percent sodium hydroxide for 10 minutes at room temperature. Ninety-nine parts of acrylonitrile was then added to the slurry and the resultant reaction mixture agitated for 90 minutes at a maximum temperature of 28° C. The pulp was then separated from the mixture and thoroughly washed. Upon analysis the pulp was found to contain 6.37 percent nitrogen, equivalent to a D.S. of 0.96 and a carboxyl content of 0.14 percent.

EXAMPLE 6

Seventy-three parts of commercial bleached kraft pulp was slurried in 600 parts of a 6.0 percent sodium hydroxide solution for 10 minutes. Ninety-nine parts of acrylonitrile was then added to the slurry and the resultant mixture agitated for 90 minutes at a maximum temperature of 28° C. The pulp was then removed from a mixture and thoroughly washed. An analysis of the pulp showed that the nitrogen content was 4.36 percent, equivalent to a D.S. of 0.60 and the carboxyl content was 0.20 percent.

EXAMPLE 7

Two hundred and five parts of unbleached kraft pulp was slurried with 1759 parts of an 8.6 percent sodium hydroxide solution at room temperature for 30 minutes. Two hundred and seventy parts of acrylonitrile was then added to the mixture and reacted with agitation for one hour at a maximum temperature of 32.5° C. The resultant pulp was removed from the mixture and thoroughly washed. The pulp was then analyzed and found to contain 6.76 percent nitrogen, equivalent to a D.S. of 1.05 and to have a carboxyl content of 0.33 percent.

It has been found in accordance with the process of the present invention that cyanoethylated cellulose fibers can be formed into a sheet and bonded together to produce a cyanoethylated paper which has a wet strength equivalent to that of conventional cellulose papers and which is sufficient to permit the cyanoethylated cellulose sheet to be handled in the same manner as conventional cellulosic webs. Broadly, the process comprises forming a layer of the cyanoethylated cellulose fibers and then heating the layer under moist conditions until bonding takes place. The strength of a moist web of cyanoethylated cellulose fibers may be increased in a typical web from a breaking length in meters of 4 meters to a breaking length in meters of 50 meters. It is thus apparent that a web of moist cyanoethylated cellulose fibers too weak to be removed from the forming wire by conventional papermaking techniques can be bonded by this process into a web having a strength equivalent to conventional cellulose moist webs and capable of being removed from the forming wire and further treated by the conventional methods of papermaking.

While the process is particularly applicable to the formation of a paper sheet from cyanoethylated cellulose fibers having a degree of substitution between about 0.5 and 1.5 it may be applied to the formation of a bonded sheet of cyanoethylated cellulose fibers having a greater or lesser degree of substitution as long as the cellulose has retained its original fibrous character.

The cyanoethylated cellulose fibers can be prepared for forming into sheets and formed into the unbonded web

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on a paper forming wire in much the same manner as cellulose fibers are treated in the forming of conventional papers. The fiber lengths of the fibers should be substantially the same as the corresponding lengths of cellulose fibers used in the manufacture of paper. If there are any fiber clumps, these should be broken up or dispersed by a defibering action. The cyanoethylated pulp need not be beaten however in the usual manner of beating cellulose pulps to increase the fibrils exposed and cause hydration of the pulp if the pulp has a D.S. greater than 0.5. It has been found that beating has substantially no effect upon the bond forming tendencies of the cyanoethylated cellulose fibers.

The defibered cyanoethylated cellulose pulp is dispersed in an aqueous phase to form a pulp stock having a consistency of approximately 0.05–1.5 percent in substantially the same manner as conventional cellulose pulp is formed into a stock. The term "consistency" is used to mean the percentage by weight of oven dry pulp in a combination of pulp and water. The stock is then flowed onto a mechanical support or paper forming wire to form a uniform layer of cyanoethylated cellulose fibers. This can be accomplished in the same manner as the layer of cellulose fibers is formed in a conventional papermaking operation, for example, on a Fourdrinier machine or a cylinder machine.

The heating of the cyanoethylated cellulose pulp layer in the presence of moisture, very rapidly develops the necessary strength to form the layer into a self-sustaining web. Various methods of applying heat to a moist layer of fibers may be utilized. A preferred method employs steam as the heating agent. Low pressure, low temperature steam, will bond a moist layer of the cyanoethylated cellulose fibers into a sheet within a very short time, for example 4 to 12 seconds. The steam may be applied to the layer of cyanoethylated fiber on the forming wire by conventional methods of steaming fiber webs. Other conventional methods of applying heat such as heated rollers, infra red heaters, etc., may also be employed to apply the heat to the cyanoethylated cellulose fiber layer. The heat source should be capable of raising the temperature of the moisture in the web to about the boiling point. Lower temperatures for example 180° F., may be used but corresponding longer time to complete the bonding will then be required.

The layer of fibers may be formed by air forming or other conventional methods of forming fiber layers as well as by water forming but in this case the layer should be moistened prior to the application of the heat. The moisture content of the web when heat is applied must be at least about 10 percent in order for bonding to take place and is preferably greater than 15 percent. When the web is water formed on the wire, the moisture content will normally be much greater. Bonding, however, is equally effective in webs having high moisture contents, although it may take a longer heating period to raise the fibers to the bonding temperature because of the amount of moisture present.

Because of the extreme weakness of the unbonded cyanoethylated cellulose web, the web is normally heated on the forming wire to effect bonding. However, the web may be bonded at any stage of the papermaking operation if the conditions of heat and moisture content are complied with and the nature of the support is not critical.

In a normal papermaking operation the paper web is removed from a forming wire at a consistency of about 17 percent. The cyanoethylated cellulose web of the present invention retains water with less tenacity than normal paper web and the drying action of the applied heat further tends to decrease the water content of the web on the wire so that the cyanoethylated bonded paper sheet will normally leave the forming wire at a lower consistency than a corresponding paper web. Therefore, the drying operation which normally follows the forming operation with conventional paper can be greatly de-

creased with the cyanoethylated cellulose web or even omitted entirely.

The bonding process of the present invention may be applied to the bonding of cyanoethylated cellulose fibers mixed with other fibers, into webs of sufficient strength to be handled and made into paper. It is particularly applicable to forming webs of cyanoethylated cellulose mixed with the non-hydrating synthetic fibers such as glass, polyacrylonitriles, copolymers of polyvinylidene chloride and polyvinylchloride, polyethylene terephthalates, nylons, polyurethanes and the non-hydrating rayons. These hydrophobic fibers are not bonded by drying of the web, so that ordinarily they are made into bonded webs by the application of adhesives. The bonds developed in the cyanoethylcellulose fibers by the method of the present invention are sufficiently strong that webs of a mixture of a synthetic fiber and cyanoethylated cellulose containing as little as 5 percent cyanoethylcellulose can be bonded into a self-sustaining web. Non-fibrous additives may also be incorporated into the cyanoethylcellulose webs.

For example, a highly decorative paper may be made by mixing as much as 50 percent glass flakes with cyanoethylcellulose fibers, forming a layer of the mixture and bonding the layer into a web in accordance with the process of the present invention.

The formation of cyanoethylated cellulose sheets may be further illustrated by the following examples.

EXAMPLE 8

Fifteen hundred parts of commercial wood pulp was slurried with 13,500 parts of 8.6 percent sodium hydroxide solution for 15 minutes. Acrylonitrile in an amount of 3,859 parts was then added to the slurry over a 15 minute interval. The resultant mixture was agitated for an additional 105 minutes while the mixture was maintained below a temperature of 31° C. The pulp was then separated from the mixture and thoroughly washed. The pulp had a nitrogen content of 8.4 percent, equivalent to a D.S. of 1.35. The pulp was slurried with water and refined until all fiber clumps were broken up. The pulp was then further diluted with water to a consistency of 0.05 percent and a uniform layer of pulp stock formed into a sheet on a conventional paper forming wire. The sheet was removed from the wire and a sample of the sheet tested on a Brecht Initial Wet Strength Tester. The sample as tested was a 42 pound basis weight sheet (25 x 38—500 basis) and had a moisture content of 44 percent. The breaking length in meters was 4.2 meters. Sheets of 100 percent cellulosic conventional papers having the same basis weight but a moisture content of 80 percent were also tested and it was found that the breaking length in meters of a groundwood sheet was 27 meters, a bleached spruce kraft sheet 84 meters, and a bleached sulfite sheet was 106 meters. Samples of the cyanoethylated cellulose web having a moisture content of 44 percent were then subjected to steaming for 5 seconds and for 10 seconds. Samples of the resulting webs were again tested with the Brecht Initial Wet Strength Tester and it was found that the 5 second steaming operation had increased the breaking length of the web to 49.6 meters. The moisture content of the steamed web was 36 percent. The 10 second steaming operation had increased the breaking length of the web to 71.2 meters and dried the web to a water content of 32 percent. Samples of the steamed webs were completely dried and tested for tensile strength in accordance with TAPPI Standard No. T-220. Both webs were found to have a tensile strength equivalent to 2.0 pounds per 15 millimeter strip (42 pounds basis weight—25 x 38—500 sheet ream).

EXAMPLE 9

Cyanoethylated cellulose pulp having a nitrogen content of about 6.8 percent, equivalent to a D.S. of 1.05

which had been prepared in accordance with the method described in Example 7 of the present specification was slurried with water and all pulp knots broken up by a brief refining treatment. The pulp was diluted to a consistency of 0.05 percent. A layer of pulp was formed on a conventional paper forming screen. This layer was then steamed for 10 seconds. The resultant sheet of cyanoethylated paper was self-sustaining. Tensile tests of the cyanoethylated paper in accordance with TAPPI Standard No. T-220 showed that the sheet had a tensile strength equivalent to 1.25 pounds per 15 millimeter strip (for a basis weight of 42 pounds—25 x 38—500). An unbeaten commercial bleached kraft paper tested by the same method had a tensile strength of 1.65 pounds per 15 millimeter strip (for a basis weight of 42 pounds—25 x 38—500).

A 57 pound basis weight sheet of cyanoethylated paper prepared as in the present example to be used as filter material was tested for porosity. It was found that a sheet which had a tensile strength of 2.2 pounds per 15 millimeter test strip had a Frazier porosity of 173 cubic feet per minute per square foot under a standard pressure drop of ½ inch of water.

The cyanoethylated paper formed in this manner has the typical characteristics of cyanoethylated cellulose in that it is very resistant to aging, and to attack by microorganisms. It is particularly useful as a filter material because webs of this type can be made with considerable porosity and with high thermal stability. It also may be further treated as described in the present invention to form a dielectric paper sheet of outstanding characteristics.

Paper because of its flexibility, low cost and outstanding dielectric properties has found wide application as a dielectric material. It is very commonly used as dielectric or insulating material in transformers, condensers, motors, cables, generators and related electrical components. Paper has certain disadvantages when used as a dielectric material, particularly its loss of mechanical strength and resiliency upon aging. The exact nature of the aging of paper has not been fully determined but it is believed that it is probably a combination of hydrolysis and oxidation of the cellulose molecule resulting in the splitting of molecular chains and in the opening of glucose rings.

Paper has been made from slightly cyanoethylated cellulose fibers, i.e. having a nitrogen content of less than about 2.8 percent. It was found that this paper was a better dielectric than conventional paper, and that the dielectric constants of the paper increased as the degree of substitution by cyanoethyl groups increased. Cyanoethylated pulp having a nitrogen content greater than about 2.8 percent however could not be beaten and made into paper.

I have discovered that paper made from cyanoethylated cellulose fibers can be processed to form sheet material having exceptional dielectric performance and good resistance to aging. Broadly, the process of making the dielectric material comprises passing a moist cyanoethylated paper sheet between a resilient non-metallic roll and a non-resilient metallic roll at a temperature of at least about 250° F., under a pressure of at least about 10 pounds per linear inch and preferably above about 50 pounds per linear inch. A single cyanoethylated paper sheet may be formed into a dielectric sheet in this manner or several sheets may be passed through rolls simultaneously in a stack to form a laminated dielectric sheet.

The usual cellulosic substance employed in conventional papermaking may be cyanoethylated to form the desired pulp. Although several methods may be employed to cyanoethylate the raw cellulosic material, it is important that the carboxyl content of the resultant cyanoethylated pulp be minimized and therefore pulp cyanoethylated in accordance with the manner previously described in the present specification is preferred. The

process may be applied to cyanoethylcellulose sheets of various degrees of substitution. It has been found that as the number of cyanoethyl groups substituted in pulp is increased, the dielectric constants of papers made from the resulting paper is increased. Dielectrics made from paper having a D.S. of 0.5–1.5 in accordance with the present process are particularly desirable. The dielectric material may be made from webs consisting of cyanoethylated cellulose fibers or may be made from webs of cyanoethylated cellulose fibers mixed with other materials such as natural cellulose fibers, or synthetic materials such as nylon fibers, glass fibers, glass flakes and polyethylene terephthalate fibers (Dacron). The cyanoethylated pulp can be formed into a paper sheet or web as previously described.

The cyanoethylated paper sheet or stack of sheets entering the rolls should have an initial moisture content of at least 15 percent and preferably about 20 percent. Passage between the rolls of the moistened sheet causes densification of the sheet and imparts a shiny surface to the face of the sheet adjacent to the metallic roll. The sheet or stack is not ordinarily completely densified in a single pass through the rolls but a series of passes through the rolls is made. Although the sheet or stack is moistened prior to the first pass of a series to the initial moisture content of at least about 15 percent subsequent passes of the series are usually made without remoistening until the desired densification is attained, or substantially all water is removed from the sheet or stack. If desired, the sheet may then be remoistened to a 15 percent or more water content and a series of passes made through the rolls with the face of the sheet reversed so that the previously polished side is now adjacent to the non-metallic roll. The sheet may, however, be passed through the rolls a number of times with one face of the sheet alternately adjacent to the resilient roll and then to the non-resilient roll. When a blend of cyanoethylated cellulose and synthetic fibers are used, fewer passes are normally required than when a pure cyanoethylated cellulose web is used.

The metallic roll is normally maintained at a temperature of at least about 275° F. If the temperature is increased much beyond 450° F., there is a tendency for the cyanoethylated cellulose to char. The temperature may however be limited to a lesser figure by the material of the non-metallic roll. The metallic roll may be made of steel, bronze or other suitable metal. The resilient non-metallic roll is preferably of a synthetic material such as nylon but cotton filled rolls, paper rolls and other such resilient rolls may be used. Laminates may be prepared of the sheets by stacking a plurality of the sheets together and passing the stack between the rolls. Laminates of considerable thickness can be formed in this manner.

Now that the process has been generally described it will be further illustrated by the following examples.

EXAMPLE 10

A cyanoethylated cellulose wood pulp was prepared as described above. Two hundred and five parts of unbleached kraft pulp of northern softwood, predominately spruce, was slurried with 1751 parts of an 8.6 percent solution of sodium hydroxide for 10 minutes at room temperature. Five hundred and fifty parts of acrylonitrile was then added to the solution and mixing was continued for 90 minutes. The temperature of the reaction mixture was controlled so that the maximum temperature was 49° C. The pulp was then separated from the mixture and thoroughly washed until all free sodium hydroxide and acrylonitrile were removed. The resultant cyanoethylated pulp had a nitrogen content of 8.24 percent. The pulp was then slurried with water and given a 10 minute refining treatment to break up fiber clumps. The pulp was then slurried with water to a consistency of 0.05 percent to form a pulp stock. The stock was flowed onto a paper

forming screen to form a uniform layer of cyanoethylated cellulose fibers. This layer was drained to a moisture content of 44 percent, and then steamed for 10 seconds. The steaming converted to stock layer into a self-sustaining sheet or web. Five of these webs were stacked together and this stack which had a moisture content of 32 percent was passed through the nip of a pair of rolls. One of the rolls was a 9.5 inch diameter polished steel roll and the other roll was an 8 inch diameter nylon roll. The surface temperature of the steel roll was maintained between 300 and 320° F., during the rolling operation. The laminate was passed through the rolls 30 times with the sheet being turned after each rolling operation so that a face was alternately presented to the steel roll and then to the nylon roll. The pressure of the rolls on the laminate was approximately 250 pounds per linear inch of the line of contact of the rolls. The product obtained by this densifying treatment was a semi-transparent dense fibrous paperlike material having a basis weight of 225 pounds (25 x 38—500 sheets). The product had a flexibility which was equivalent to that of an 100 percent cotton content electrical grade paper laminate.

EXAMPLE II

A cyanoethylated cellulose pulp having a nitrogen content of 6.37 percent was prepared from a bleached kraft pulp from northern softwoods, predominately spruce, in a manner similar to that described above. This cyanoethylated pulp was then converted into self-sustaining paper sheets as described in Example 10. The sheets were dried. Four of the sheets 4 inches wide by 10 inches long were stacked and the stack wetted to a water content of 24 percent. The laminate was prepared by passing the stack of 4 of these sheets through the nip of a steel-nylon pair of rolls. The surface temperature of the steel was maintained at 280–290° F., and a pressure of 150 pounds per linear inch was maintained on the nip. The laminate was passed through the nip with the same side of the laminate presented to the steel roll on the first series of 6 passes. The laminate was then remoistened and reversed for the second series of 5 passes. Several additional passes were then made.

The resistance to voltage breakdown of cyanoethylated fibrous paperlike materials prepared in this manner is substantially greater than that of conventional paper dielectrics. Furthermore, this high resistance to breakdown is substantially retained in the dielectric material even after long periods of aging at high temperatures. In order to illustrate the improved dielectric qualities of the present product, 10 mil samples of material produced in accordance with the method described in Example 10 were compared with 16 mil samples of an 100 percent cotton content electrical grade paper as to mean value of voltage breakdown in kilovolts for both A.C. and D.C. potential. The second and third samples of the cyanoethylcellulose (C.E.C.) laminate of the present invention had been aged at 300° F., for 48 hours and 216 hours respectively prior to the breakdown tests. Results of these measurements are as follows:

Table.—Mean value of voltage breakdown in kilovolts

	Alternating Current	Direct Current
Paper (16 mil).....	4.0	7.4
Cyanoethylated Cellulose Laminate (10 mil).....	4.3	10.0
C.E.C. Laminate, aged 48 hours at 300° F. (10 mil).....	5.2	8.3
C.E.C. Laminate, aged 216 hours at 300° F. (10 mil).....	4.1	9.3
C.E.C. Laminate, aged 216 hours at 300° F., then 48 hours at 420° F. (10 mil).....	3.5	10.0
C.E.C. Laminate, aged 168 hours at 300° F., then 24 hours at 350° F. (10 mil).....	4.0	10.6

This test illustrates the resistance to aging even at relatively high temperatures of the material. Dielectric sheet material produced in accordance with the process

of the present invention is relatively insoluble in organic solvents. Thus the materials are particularly useful in motors which may be exposed to commercial solvents such as the chloro-fluoro-alkanes. The dielectric materials are similar to paper in their mechanical properties such as resistance to breakage during deformation. The rate of moisture desorption from the material is exceptionally good and qualifies this material for use as an insulating material in hermetically sealed motors, where the insulation must be dehydrated before the motor is sealed. A laminate 10 mils in thickness, made up of 5 sheets of the cyanoethylated cellulose having a D.S. of 1.37 was completely dehydrated in 30 minutes at 300° F.

The process of forming dielectric sheet material is usually applied to heat bonded cyanoethylated cellulose paper webs. It may however be applied to a non-bonded layer of cyanoethylated cellulose fibers passed through at least the first set of rolls on a carrier.

What is claimed is:

1. The method of making a fibrous cyanoethylated cellulose sheet dielectric material which comprises treating cellulose fibers with an aqueous solution of a water soluble strongly basic hydroxide having a 5-10 percent hydroxide concentration, reacting said cellulose fibers contained in said solution with acrylonitrile in an amount 85-300 percent of the weight of the cellulose fibers at a temperature of less than about 50° C., to form cyanoethylated cellulose fibers having a degree of substitution of about 0.5-1.5 cyanoethyl groups per glucose unit of the cellulose, separating the fibers from the solution, forming a layer consisting essentially of the cyanoethylated pulp having a moisture content of at least about 10 percent, heating said layer while supported to convert said layer into a heat bonded self-sustaining paper sheet, passing said sheet having an initial moisture content of at least 15 percent between a resilient roll and a non-resilient roll at a temperature of from about 275° F. to 450° F. under a pressure of at least about 10 pounds per linear inch.

2. A process of forming a cyanoethylated cellulose material having a degree of substitution of about 0.5-1.5 cyanoethyl groups per glucose unit of the cellulose, which comprises treating commercial wood pulp fibers in an aqueous solution of a water soluble strongly basic hydroxide having a hydroxide concentration of about 5-10 percent, then adding acrylonitrile to said solution in an amount of about 85-300 percent of the cellulose present, the major proportion of said solution remaining aqueous after the acrylonitrile addition, reacting the resultant mixture at a temperature less than about 50° C., to a degree of substitution of about 0.5-1.5 cyanoethyl groups per glucose unit of the cellulose, and separating the cyanoethylated cellulose from the mixture.

3. The process of forming a cyanoethylated cellulose sheet which comprises forming a water moistened layer consisting essentially of fibers of cyanoethylated cellulose having a degree of substitution of 0.5-1.5 cyanoethyl groups per glucose unit of the cellulose, having a moisture content of at least about 10 percent, and heating the fibers, whereby the fibers are bonded into a paper sheet.

4. The method of forming a cyanoethylated cellulose

paper sheet from cyanoethylated fibers having a degree of substitution of 0.5-1.5 cyanoethyl groups per glucose unit of the cellulose, which comprises forming a layer of the fibers on a paper forming wire from an aqueous slurry consisting essentially of said fibers, and steaming the layer while retaining a moisture content in said layer of at least 10% by weight, until said fibers are bonded into a sheet.

5. The method of forming a paper dielectric material which comprises passing a fibrous sheet consisting essentially of cyanoethylated cellulose fibers having a moisture content of at least 15 percent and a degree of substitution of 0.5-1.5 cyanoethyl groups per glucose unit of the cellulose between a resilient roll and a non-resilient roll at a temperature of between about 275° F. and 450° F., under a pressure of at least about 10 pounds per linear inch.

6. The method of forming a cyanoethylated cellulose dielectric material which comprises passing a layer of cyanoethylated cellulose fibers having a degree of substitution of 0.5-1.5 cyanoethyl groups per glucose unit of the cellulose and an initial moisture content of at least about 15 percent between a resilient roll and a non-resilient roll under a pressure of at least about 10 pounds per linear inch, and at a temperature of from about 275° F. to 450° F.

7. The method of forming a cyanoethylated cellulose paper dielectric material which comprises assembling a stack of cyanoethylated cellulose paper sheets, the cellulose fibers of said paper having a degree of substitution of 0.5-1.5 cyanoethyl groups per glucose unit of the cellulose, the paper having an initial moisture content of at least 15 percent and passing said stack between a resilient roll and a non-resilient roll at a temperature of from about 275° F. to 450° F., and a pressure of at least about 10 pounds per linear inch, to substantial dryness.

8. The process of forming a bonded fibrous sheet from a mixture of normally non-bonding fibers which comprises the steps of suspending in an aqueous slurry a mixture of fibers consisting essentially of at least 5% cyanoethylated cellulose fibers having a degree of substitution of 0.5-1.5 cyanoethyl groups per glucose unit of the cellulose and non-hydrating fibers from the group consisting of glass, polyacrylonitrile, copolymers of polyvinylidene chloride and polyvinyl chloride, polyethylene terephthalates, nylons, polyurethanes, and the non-hydrating rayons, forming a layer of the fibrous mixture on a foraminous element, and heating the fibrous layer while in moist condition until the fibers are bonded into a self-sustaining sheet.

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