

UNITED STATES PATENT OFFICE

2,056,995

CELLULOSIC SUBSTANCES AND PROCESS OF MANUFACTURE THEREOF FROM HEMP FIBERS

Edward Chauncey Worden, I, Millburn, N. J., assignor, by mesne assignments, to Hanson & Orth, New York, N. Y., a firm comprising Charles D. Orth, Sr., Charles D. Orth, Jr., Michael J. Smith, and William Knight, Jr.

No Drawing. Application April 17, 1933, Serial No. 666,541

17 Claims. (Cl. 260—100)

This invention relates to a process for the manufacture of cellulosic substances from hemp fiber used either, alone, or in conjunction with other cellulosic materials such as wood and cotton, and to the product of the process.

This application is a continuation in part of my co-pending application, Serial No. 347,457, filed March 15, 1929 for Manufacture of rayon from hemp fiber and is a continuation in part of my co-pending application, Serial No. 421,069, filed January 15, 1930, and is related to my Patents Nos. 1,814,106, 1,866,917 and 1,899,223 which were co-pending with said applications.

In the practice of this invention there is produced from hemp fibers an intermediate cellulosic product which is, either alone or in admixture with other cellulosic materials, converted into a cellulosic compound which constitutes the final product of the invention or from which the final product of the invention comprising a cellulosic substance is made. Such compounds comprise cellulose esters including cellulose xanthate (viscose) and the acetate and nitrate of cellulose, and cellulose ethers including alkyl cellulose such as ethyl cellulose and aryl cellulose such as benzyl cellulose. The final products of the invention include solutions of such cellulose compounds and products produced therefrom and consisting of or containing a cellulosic substance such as filaments, films, sheets and other objects. In the practice of this invention the final product may comprise one of the compounds above mentioned or such compound transformed into a hydrated cellulose with decomposition of the cellulosic compound, or the product may be deposited from the solution by volatilization of a solvent thereof, or otherwise.

By the practice of this invention in connection with hemp fibers of commerce I have obtained excellent and commercially practicable results in the production of filaments, films and other objects comprising compounds produced from hemp fibers and possessing properties superior to the properties of similar articles composed of cellulosic compounds derived from other types of cellulosic material.

In order to avoid indefiniteness which may result from the loose use of the term "hemp" in literature, hemp useful in this invention includes hemp fibers identified on page 190 of Report No. 9 of the U. S. Department of Agriculture, entitled "A Descriptive Catalogue of Useful Fiber Plants of the World" by Charles Richards Dodge, published by the Government Printing Office, Washington, D. C., 1897. In the practice of this

invention I have found particularly advantageous the use of Manila hems, wild plantain and abacá or Cebu hems, particularly the fibers of the Musa family of which *Musa textilis* and *Musa sapientum* are perhaps best known and of which *Musa basjoo* and *Musa paradisiaca* are members, and other fibers of similar composition used extensively in the manufacture of rope and cordage and to some degree in textiles. I have also obtained excellent results in the use of fibers of *Cannabis sativa* and similar plants. However, it is not now contemplated that fibers of India hemp (*cannabis indica*) shall be employed in the practice of this invention.

The individual fibers or cells of the hemp fibers employed in the practice of this invention have great strength which is of an order different and superior to the strength of the individual fibers or cells of wood and cotton, this being particularly true in a comparison of fibers in a purified state and ready for conversion into a cellulosic compound.

In the production of cellulosic compounds, substances and articles in accordance with this invention, the great strength of the original hemp fibers is conserved and reflected in the product or products of this invention. For example, the treatment in accordance with this invention which is preparatory to esterification or etherification, does not modify or depolymerize hemp fibers of which Musa fibers are an example, to as great a degree as does the preparatory treatment applied to other cellulosic substances used in the manufacture of rayon. Apparently, this is due to the nature and results of that treatment and to the resistivity of such hemp fibers to chemical treatment; and such reduced chemical reactivity requires substantial and critical adjustment of reaction conditions such as concentrations, time factors and temperatures in order that the products derived from hemp fibers shall represent an optimum yield and possess superior qualities obtainable by reason of the superior qualities of the starting material. Thus, in the practice of this invention the hemp fibers employed and the products obtained by the use thereof possess qualities superior to similar qualities of the only cellulosic materials heretofore employed commercially (wood and cotton) and of the cellulosic compounds and articles produced therefrom; and while the steps employed in the practice of this invention possess certain similarities to the steps employed in the treatment of wood and cotton, the differences in those steps are important and critical and upon them—when correctly adjusted—

are predicated the superior qualities of the final product.

In the practice of this invention the critical conditions necessary to the obtainment of superior products, due to the differences in the reactivity and deportment of hemp cellulose as compared with cotton and wood cellulose, will vary somewhat for different kinds, species, varieties or qualities of hemp, for different parts of the plant employed, for fibers grown under different climatic conditions, and for fibers subjected to different kinds or degrees of mechanical and chemical preparatory steps; and when wood or cotton cellulose is mixed with the hemp fibers the variations from the normal procedure will be somewhat in the proportion or percentage in which the hemp fiber is present with the other cellulosic materials.

From the strong and reaction-resisting hemp fibers, there is obtainable cellulosic material which is composed of a high proportion of alpha- or resistant-cellulose and relatively very small proportions of beta- and gamma-cellulose and other inferior cellulosic bodies and non-cellulosic constituents; and in the practice of this invention there is obtained an intermediate product consisting of such cellulosic material. And, the cellulosic material of such intermediate product is produced with a minimum of hydrolysis and of cellulosic degradation and with a maximum of separation of non-cellulosic material and of materials objectionable in further treatment, and the purified cellulosic material is substantially pure alpha-cellulose and contains little or no hemicellulose, water-soluble extractive, fats, waxes or tannins, and the cellulose thereof is in a condition in which it is peculiarly susceptible with marked uniformity to the treatments leading to the intended cellulosic substance. The intermediate cellulosic material possessing such properties responds, in spite of its inherent resistivity to reaction and unusual deportment, to the critical conditions which constitute features of this invention and whereby final cellulosic compounds possessing superior qualities are produced.

For the purpose of further disclosing my invention, I shall describe the application thereof to Musa fibers, with the understanding, however, that the invention is not limited to such fibers or to the specific conditions employed in connection therewith, but relates to the hemp fibers above identified and includes such modifications and variations of conditions as are desirable in connection with those of said hemp fibers other than Musa fibers.

In the treatment of Musa fibers in accordance with this invention, it is immaterial whether the fibers are subjected to an initial mechanical disintegrating treatment or to a chemical treatment for loosening the fibers. For example, it is immaterial whether the fibers are scutched or hackled or subjected to a retting operation, or to a combination of two or more of such operations. I prefer as the first chemical operation (the fiber previously having been placed in physical condition for maximum response to chemical treatment) to boil the fibers or bundles or aggregate thereof at atmospheric pressure with an excess of water containing 5% to 8% of free alkali metal hydroxide such as sodium hydroxide, 1% to 5% of alkali metal silicate and 0.5% to 5% of readily saponifiable non-mineral oil or sulphonated oil, such as cotton seed oil or corn oil or other readily saponifiable or sulphonated vege-

table or animal oil or mixtures thereof, or an equivalent amount of the oil or sulphonated oil in saponified condition. Satisfactory results have been obtained by substituting for the saponified oil, the alkali metal salts of sulphonated oils (i. e., Turkey red oil, alizarin assistant, saponified sulphonated corn oil, etc.). Satisfactory results have been obtained by the omission of alkali metal silicate, and the proportions and nature of the chemicals used may be modified, diminished or increased, by varying the time and pressure factors in subjecting the fibers to heating, the nature and proportion of chemicals and the time being so adjusted and controlled as to insure a maximum of purification with a minimum of reduction of tensile strength, quality and desirability for esterification or etherification, of the treated cellulose-containing fibers. Alkali metal carbonates, bicarbonates or sesqui-carbonates may be substituted for the alkali metal silicate. In general, the purification which comprises removal of non-cellulosic constituents and celluloses inferior to alpha-cellulose is so conducted as to cause a minimum of hydrolysis and of cellulosic degradation and a maximum of removal of non-cellulosic material and material objectionable in subsequent treatment, the intercellular, cementitious products apparently being entirely saponified, emulsified or dissolved. As an alternative, the boiling may be conducted in a pressure kler at a temperature around 110° C. (all temperatures herein being centigrade temperatures), circulation to be aided, if desired, by means of circulatory arrangement for continuously pumping the liquor over the mass of fibers, or the pressure kler may be of the rotatable type. It has been found that the addition of soluble water glass is especially beneficial in the attainment of the maximum removal of intercellular and cementitious materials including fats, oils, waxes and similar encrusting and adhering impurities and tends to leave the fiber in especially porous and absorptive condition for quick, complete and uniform penetration of reagents employed in the production of the cellulosic compounds. The boiling operation is continued for 3 to 8 hours, depending upon the amount of naturally occurring organic silicon compounds and other non-cellulosic materials and the relative refractoriness of the fibers. Toward the close of the boiling operations samples may be withdrawn and washed free from soluble impurities, dried and Soxhlet extracted with ether to obtain an index of the degree of completeness with which the impurities have been removed from the cellulose. The ether extract should not exceed 1% based on the original weight of fiber taken when the purified cellulose is intended for esterification.

At the completion of the boiling operation the dark aqueous liquor is allowed to drain off and further boiling at atmospheric pressure, if desired, may be effected with an added solution comprising 1% to 2% of alkali hydroxide and .05% to 1% of alkali silicate, the mass preferably having been pressed after the first boiling and before such further addition of alkaline solution. In any event, after the completion of the boiling, clear water is applied to the drained fibers preferably with further application of heat, and such clear water is alternately added and removed until the wash-water is practically colorless and neutral, and a sample of the material, extracted in a Soxhlet or other suitable apparatus, gives practically no extractive and an ash determina-

tion has shown the inorganic residue to be reduced to a minimum. As an alternative the fibers may be tested by boiling in a mixture of alkali metal hydroxide, alkali metal silicate and vegetable or animal oil and are to be considered as sufficiently pure when no soluble extract is thereby produced.

In the treatment of Musa fibers, which are relatively high in siliceous materials, the alkali hydroxide and alkali silicate appear to emulsify and saponify the siliceous material in the presence of the softening effect of the alkali salts of fatty acids, removing the silicate material with a minimum of degradation of the cellulose. The soap in combination with alkali and silicate under the conditions and time of treatment appears to minimize formation of oxycellulose and bodies which lower the stability and other desirable physical characteristics of the cellulose derivatives subsequently formed.

The fibers, still in wet condition, are preferably passed through rollers which break down and disintegrate the fibers, bundles or masses; and the fibers are subjected to an elutriating process in which water removes nonalphacellulose material which was not saponified or emulsified in previous treatment, residual intercellular and encrusting material being disintegrated and removed. The fibers may then be hydroextracted and submitted to a partial bleaching operation, preferably with chlorine rather than with calcium hypochlorite, for example, an electrolytic chlorine bleach, care being taken that the fibers are not exposed to the atmosphere during the bleaching and subsequent acidifying operation, such care minimizing the formation of oxycellulose and other oxidation compounds of cellulose which are deleterious in subsequent ether and ester formation from the purified hemp fiber.

Advantageously, the bleaching may be only a three-quarters bleach, as the resultant cellulosic compound is usually submitted to bleaching unless intended to be dyed full or dark shades.

The fibers which are washed free from reactants are dried, preferably at comparatively low temperatures; and, depending upon the degree of bleaching, will possess a color varying from almost white to faint yellow. The dried fibers will be in the form of a fluffy mass, but for convenience in subsequent treatment may be formed into sheets; and if other cellulosic materials such as those obtained from cotton and wood are to be mixed therewith for subsequent treatment, such admixture is preferably effected prior to the sheeting of the purified fibers.

One or more of the foregoing steps may be varied in duration or repeated or modified and the concentration and proportions of the baths may be changed, depending upon the comparative resistivity or refractoriness of the hemp fiber.

Commercial grades of purified wood cellulose prepared for viscose rayon manufacture seldom exceed 88% to 89% by weight of alpha-cellulose, while many brands are considerably lower in content thereof; and those prepared celluloses usually carry 4% to 5% of hemi-cellulose materials soluble in sodium hydroxide.

By comparison, the intermediate cellulose product obtained from hemp in accordance with this invention, and particularly from Musa, is markedly superior in proportion of alpha- or resistant-cellulose present and in freedom from inferior cellulose constituents and non-cellulose constituents; and the hemp cellulose is practically free of intercellular and cementitious ma-

terials, fats, oil, wax, and similar encrusting and adhering impurities, and the fibers are in an especially porous and absorptive condition for quick, complete and uniform penetration of reagents used in production of cellulosic compounds therefrom.

The mean of several determinations from separate lots of purified Musa cellulose, purified as above described, was as follows:

	Maximum	Minimum	Mean
	Percent	Percent	Percent
Moisture (drying at 105° C.).....	8.4	4.2	5.9
Ether extractive.....	0.42	0.08	0.16
Hemicellulose and similar bodies...	3.2	0.7	1.1
Ash (inorganic impurities).....	0.41	0.08	0.2

Hemp cellulose, purified as above described, and especially suitable for esterification, after air-drying contained 5.6% moisture (expelled at 102° C.) and had the following characteristics:

	Per cent
Ether extractive.....	0.07
Hemicellulose	1.1
Alphacellulose	98.1
Ash	0.09
Unaccounted for.....	0.64

Thus, hemp cellulose, and particularly Musa cellulose, obtained in accordance with the foregoing procedure, contains 95% to 99% of alphacellulose, has an ether-extractive usually less than 0.1%, an ash content of about 0.2%, and combined beta-cellulose and gamma-cellulose content under 5%, and is practically insoluble in 17.5% sodium hydroxide solution (the strength normally employed in alkali-cellulose formation for viscose production from wood and cotton), is about 0.3% soluble in 18% sodium hydroxide solution at 18°, is 0.12% soluble in ether (ether extract of Soxhlet extraction), is practically insoluble in water, and is free from tannins. The purified product possesses the great tensile strength and resistance to chemical reaction above mentioned.

Nitration experiments conducted under varying conditions as to time, temperature and relative proportions of water, nitric and sulfuric acids in the esterizing mixture as compared with simultaneously conducted control esterifications with cotton and with wood celluloses, demonstrated superiority of purified hemp cellulose, for fluid and solid nitrocelluloses. The viscosity of nitrated hemp cellulose is usually greater than an equal weight of nitrated wood, wood or cotton celluloses when dissolved in the same solvent or solvent combinations. Nitrated hemp celluloses possess a high thermoplasticity when admixed with camphor and other flexilizers, extensibility-producers and plasticizing agents, and are soluble in acetone, alkyl acetates, diacetone alcohol, and softened by the dihydroxy- and trihydroxy-aliphatic and carbocyclic esters, such as glycol diacetate and resorcinol triacetate. In the production of acetated cellulose from hemp cellulose, the initial acetation progresses more slowly in general, higher temperatures and a larger proportion of energetic catalyst may be used with a minimum of cellulosic degradation, and partial hydration subsequent to acetation requires a longer time to reach the point of solubility represented by complete solution in pure acetone and incipient plasticity and gelatinization in alcohol free chloroform.

The solubility in degree and range of solvents is about the same as with acetated cotton cellulose, but dissolution usually proceeds with less facility. The same generalizations have been found to hold true in the formation of acetated celluloses, and appears to be the same in cellulose ether technology.

The purified cellulosic material obtained from hemp and being peculiarly suited for treatment that produces cellulosic compounds therefrom, produces cellulosic compounds of high strength and possessing other desirable properties; and the production of viscose or rayon from purified Musa fiber cellulose is described herein as an example of such formation. Preferably, the purified fiber is dried to a moisture content of about 1% to 2% (so-called "bone-dry"), and cooled to atmospheric temperature. The dried material (preferably at the temperature of the mercerizing bath) is immersed in an excess of a bath comprising 18.5% to 19.5% sodium hydroxide at a temperature of 19° to 20° C. for four to six hours, the bath being as free as possible from impurities, and especially from iron and sodium chloride.

During this mercerizing treatment with alkali, a gentle circulation of the alkali solution is preferably maintained over and between the sheets of cellulosic material, to remove small amounts of alkali-soluble bodies from the cellulosic material and for other reasons, and to maintain uniform alkali concentration throughout the system during the formation of alkali-cellulose.

The conditions maintained in this operation and particularly the concentration, temperature and duration are unsuitable to the treatment of cellulose obtained from wood and cotton. Excessive concentration of alkali, temperature and duration of treatment in the mercerizing step tend to reduce wood cellulose and cotton linters to a jelly-like mass, from which solution would not drain. The conditions maintained in this operation are in fact of an order different from the order of the conditions maintained in the treatment of cotton and wood; and they were ascertained only by extensive investigation based on observation of the condition of the material during the mercerizing step and during all of the steps subsequent thereto. Variation of mercerizing conditions above specified may be necessary and such variations are of such kind and degree that necessary conditions and results will be obtained. For example, the mercerization or conversion into alkali-cellulose must be so completed that subsequent xanthation will be complete and all of the xanthated product will go into solution, one indication of incompleteness of mercerization being clogging of filters used prior to spinning, by firm or hard jelly-like particles of unxanthated or insufficiently xanthated cellulose. Again, these conditions are not attained by mere adjustment, one at a time, of duration, temperature and concentration, but by such relative adjustment that mercerization is completed and separateness of particles is preserved.

In the mercerizing operation described, the cellulosic material is not reduced to a jelly-like mass, and at the end of the operation alkaline solution is allowed to flow off by gravity for reuse and the mercerized material is freed of further solution by pressing until the resulting mass weighs approximately 350 to 390 pounds for each 100 pounds of purified cellulosic material originally employed. Excess alkali solution is pressed in such manner that remaining solution

is uniformly distributed through the mercerized cellulose. The alkaline solution removed from hemp cellulose after the mercerizing step is lighter in color than is the alkali discarded after alkali-cellulose is formed from wood pulp, apparently because of the small amount of beta-cellulose and gamma-cellulose soluble in concentrated sodium hydroxide solution present in the purified hemp fiber.

After weighing to insure sufficient removal of alkaline solution, the alkalinized cellulose is promptly disintegrated to "crumbs" in a Werner & Pfleiderer or other masticating machine of the usual enclosed type, preferably brine cooled. The time for producing such "crumbs" is about one-fourth longer than that required in the treatment of alkalinized wood cellulose. The resulting crumbs are then tightly enclosed in receptacles and "ripened" for forty to fifty hours at a temperature between 20° to 30° C. (e. g. 21° C.), preferably with periodic agitation to minimize local preheating.

After ripening until the viscosity is reduced to the desired point, the crumbs are placed in hexagonal or octagonal or round containers adapted to be sealed and mounted for rotation and provided, if desired, with temperature control. The carbon bisulfide in vapor or semi-vapor form is then introduced uniformly into the drum during rotation thereof at 2 to 10 revolutions per minute. During the first 15 or 20 minutes of this operation 13% to 16% by weight on the original purified cellulose of carbon bisulfide is introduced, depending upon the varying refractoriness of the cellulose fiber. The amount of carbon bisulfide must be sufficient to obtain maximum xanthation without waste and is readily determined by preliminary trial. The amount of carbon bisulfide used is substantially greater than the 12% to 12½% used in connection with the treatment of wood or cotton cellulose. At the beginning of the xanthating treatment, the temperature will be in the neighborhood of 21° C. and that temperature rises upon introduction of the carbon bisulfide and should be kept from exceeding 27°-33° C.

After completion of the introduction of carbon bisulfide, rotation of the drums is continued until completion of the xanthation is indicated by the attainment of the desired shade of carrot color by the material in the drums. The completeness of xanthation indicated by color can be confirmed by laboratory test. The total period of xanthation is dependent upon the kind and nature of the fiber used, the degree of initial ripening of the alkali-cellulose, the rate of rotation of the xanthating drum and the percentage of carbon bisulfide employed. Usually xanthating is completed within one to two hours.

After xanthation, the contents of the drum are transferred, with minimum exposure to the air, to a preferably upright receptacle having a stirrer. Therein the mass is thinned with sodium hydroxide solution containing 5% to 7% (e. g., 6.3%) of sodium hydroxide. Stirring is continued until a homogeneous mass, practically a solution, is obtained. Preferably, the dissolving operation is conducted, by use of jackets for circulation of cooling medium, at a temperature between 19° and 21° C. which is as nearly as possible the viscose-ripening temperature. The alkali concentration is preferably above 6% and substantially greater than that employed in the treatment of wood or cotton cellulose.

After the dissolving operation, the solution is

subjected to the second ripening, usually in tanks situated in a room adapted for accurate temperature control, the temperature of which is maintained as near 20° C. as possible.

5 The second ripening operation is continued under standard conditions until the viscosity, combined sulphur content and "salt index" obtained, are considered optimum for spinning. The ripening period in the treatment of wood
10 and cotton cellulose is from 85 to 92 hours but in the treatment of hemp fiber including Musa fiber this period of time exceeds 92 hours and is usually in excess of 100 hours.

15 The ripened solution is spun into a coagulating or settling bath of usual composition containing free sulphuric acid, acid sodium sulphate and other components. The viscose remains in solution mainly because of the free alkali present, and neutralization and decomposition in the acid setting or coagulating bath proceeds in the individual resulting filaments from the surface toward
20 the core. The resistivity of hemp fiber or its density or lower porosity results in lower coagulation rate and requires higher concentration of acidity and salts, by about one-fourth, or a longer contact with the coagulating solution, to effect complete coagulation. A filament or film so produced by precipitation or coagulation from a solution of the xanthate in an alkaline solution is
30 hydrated cellulose from substantially pure hemp alpha-cellulose and is sharply distinguished from hydrated cellulose from cotton or wood cellulose that is relatively weak, short-fibered, and non-resistant.

35 In the practice of this invention the coagulating bath may have a temperature between 40° and 42° C. in which case the free sulphuric acid is increased to about 8.5%. Increase of acidity may be avoided to some extent by raising the
40 temperature of the bath to 45° C.

The resulting filaments are washed to neutrality, desulphurized and bleached in accordance with the usual practice, it being necessary in connection with hemp cellulose, because of the resultant resistivity to chemical and physical action,
45 to make certain that the successive steps are complete. For example, desulphurization and bleaching require respectively greater quantities of sodium sulphide and bleaching agent or more prolonged treatment. It is also to be noted that in
50 chlorine bleaching of the product of hemp fiber, exclusion of air is desirable to avoid formation of oxycellulose, apparently because of the purity of the product produced in accordance with this
55 invention.

The rayon filaments thus produced from hemp fiber often require a more thorough or prolonged softening treatment with natural, emulsified, saponified or sulphonated oil in order to impart
60 desired degree of pliability and softness. The filaments produced from hemp fiber are distinguished from filaments obtained from wood and cotton, the only cellulose now commercially employed, in possessing greatly increased tensile
65 strength in both the dry and the wet states, and greater uniformity in dyeing, giving full shades from standing baths although color penetration is slower but more uniform. As a result of the increased strength and resistance to abrasion
70 there results from this process a larger proportion of A grade of finished filament, as compared to the proportion of B and other inferior grades, than is obtainable from wood and cotton cellulose.

75 The marked superior properties of artificial filaments obtained from hemp over similar filaments

obtained from other cellulose is indicated by the following table of the properties of viscose rayon obtained from Musa in accordance with this invention and rayon produced in a rayon plant producing several tons daily of rayon, the comparison being made between 24 filament 150 denier material which had passed inspection as A grade:

	Musa rayon	Factory rayon
Ash.....	0.02%	0.09%
Dry strength, grams per denier.....	2.10	1.80
Wet strength, grams per denier.....	1.05	0.72
Extensibility.....	21%	16%

15 The above values are the average of twenty-five determinations made on the rayon tested, the factory rayon being made from a mixture of 50% Kipawa high-alpha wood pulp and 50% Buckeye cotton linters pulp, the alpha content
20 of the latter being 98% or better.

Other tests of rayon made from Musa fiber in accordance herewith, give as the average of ten tests the following:

Dry strength, grams per denier.....	2.35
Wet strength, grams per denier.....	1.45
Extensibility.....	18% to 22%

25 As an example of the employment of a mixture of purified hemp cellulose and cellulose obtained from other sources, purified Musa fiber in a proportion of 25% by weight was mixed with 75% by weight of purified wood cellulose having 88.4% alpha cellulose and 4.9% of hemicelluloses. Sheets of the mixture containing 5.8%
30 moisture were treated with 19.3% sodium hydroxide solution at 19.5° for four hours. After pressing, the mass weighed three times as much as the original cellulose. The crumbs of disintegrated material were matured for forty hours
40 at 25° C., plus or minus 5° C., and then xanthated in sixty-five minutes, employing 8% more carbon bisulfid than would be used with cellulose obtained from wood or cotton alone. The resulting carrot colored product of xanthation was
45 thinned with 6.3% caustic soda solution and ripened for ninety-two hours and then spun into filaments. The resulting filaments showed greater strength and diminished porosity as compared with filaments made from Musa fiber
50 alone. Increase of the percentage of hemp fiber to wood fiber or cotton fiber in the mixture requires increase of mercerizing time and possibly some further increase in concentration of caustic soda in the mercerizing bath, extension of
55 xanthating time, extension of ripening periods, and increase of alkalinity of the solvent for the product of xanthation.

60 Due to the resistance of hemp fibers to chemical and physical conditions of the order of those employed in connection with wood and cotton fibers, the production of inorganic cellulose esters, such as nitro-cellulose from the purified cellulose obtained from hemp fiber, requires a higher nitration temperature and an increase in
65 the proportion of nitric acid over sulphuric acid in the esterifying bath. Also, acid elimination and stabilization require a longer period to obtain a product meeting the heat test and other stability requirements. Solution of the nitric
70 ester in such solvents as ethyl, butyl and amyl acetates and acetone is slower but complete. The viscosity of the solutions is considerably higher than that of ordinary solutions of nitro-cotton but the viscosity is reducible in the usual ways.
75

Nitro-cellulose from hemp is as completely, but not as quickly, de-nitrated as is nitro-cotton and the resulting rayon is stronger in both the wet and dry conditions.

5 From the foregoing it will be apparent that while hemp cellulose does not respond properly or completely or effectively to conditions of the same order as the conditions under which cotton and wood cellulose are treated, conditions of
10 the order specified herein will produce a high yield of markedly superior products from hemp fibers and particularly Musa fibers. Moreover, conditions of the order herein specified are unsuitable for the treatment of cotton or wood
15 cellulose and produce therefrom products greatly inferior to the products produced by the conditions usually maintained in the treatment of wood and cotton. Apparently the steps described herein for the purification of hemp fiber by re-
20 moval of non-cellulosic substances and of inferior cellulose, bring the hemp fiber into a condition in which, in spite of its resistance to chemical and physical forces and its low porosity, it can nevertheless be converted into valuable cel-
25 lulosic substances without destruction. In this connection, it is to be noted that the conditions in the mercerizing operation are such as would convert cotton or wood cellulose into undesirable or useless condition, and care must be ob-
30 served that hemp fibers are not thereby improperly converted or destroyed; and if the intensity of the conditions during mercerizing is so reduced, in an effort to avoid such destruc-
35 tion, that firm and jelly-like particles clog the filter used prior to spinning, the time or temperature or concentration in the mercerizing operation must be so adjusted without injuring the fibers that xanthation will be complete and the occurrence of such particles avoided.

40 From the foregoing it also appears that the removal from crude hemp fibers, including particularly Musa fibers, of non-cellulosic material and cellulose other than alpha-cellulose, renders possible mercerization of the hemp and Musa
45 alpha-cellulose, the removal of undesirable constituents rendering the pure cellulose sufficiently susceptible to the reagents subsequently used that the reagents may exert their proper effect without undesirable alteration or destruction of
50 the valuable fiber. In the conditioning of the hemp fibers for production therefrom of hydrated cellulose, the intensity of the purifying causes, such as strength and concentration of reagents and duration and temperature of treatment,
55 must be such as to remove the undesirable constituents and produce a maximum yield of commercially pure alpha-cellulose from hemp without degradation of the alpha-cellulose which might cause some part of it to become soluble and to be lost or to lose its superior qualities. The dried and purified cellulose is peculiarly porous and penetrable and makes possible complete mercerization without degradation and
60 without such gelation as would impair or prevent removal of excess alkali. The dryness of the material subjected to mercerization ensures the porosity and penetrability thereof and ensures treatment of inner as well as outer portions of the fibers with the same concentration
70 of mercerizing solution. The degree to which the advantages of this invention are attained is dependent upon the careful attainment and preservation of these conditions.

I claim:

75 1. In the process for producing cellulosic sub-

stances from hemp fiber (not of Indian hemp origin), the step comprising mercerizing substantially pure alpha-cellulose from such fiber by treatment with a sodium hydroxide solution containing within 0.5% of 19% of sodium hydroxide
5 at a temperature between 19° C. and 20° C. for four to six hours.

2. In the process for producing cellulosic substances from Musa fiber, the steps comprising mercerizing substantially pure Musa alpha-cellulose by treatment with a strong aqueous solution of sodium hydroxide at a low temperature, ageing the mercerized product, and subjecting the aged product to treatment for one to two hours with
10 13% to 16%, by weight on the purified cellulose, of carbon disulphide at a temperature between
15 27° and 33° C.

3. As an article of manufacture, the hydrated cellulose precipitate from an alkali solution of the xanthate of hemp (not of Indian hemp origin)
20 alpha-cellulose.

4. As an article of manufacture, viscose solution comprising an alkaline solution of the xanthate of hemp (not of Indian hemp origin)
25 alpha-cellulose.

5. As an article of manufacture, the hydrated cellulose precipitate from an alkali solution of the xanthate of Musa cellulose.

6. As an article of manufacture, viscose solution comprising an alkaline solution of the xanthate
30 of Musa cellulose.

7. In the process for producing cellulosic substances from hemp fibre (not of Indian hemp origin), the steps comprising mercerizing substantially pure alpha-cellulose from such fiber by
35 treatment with a sodium hydroxide solution containing within 0.5% of 19% sodium hydroxide at a temperature between 19° and 20° C. for four to six hours and subjecting the mercerized product to treatment with 13% to 16%, by weight on the
40 purified cellulose, of carbon disulphide at a temperature between 27° and 33° C.

8. In the process for producing cellulosic substances from Musa fiber, the step comprising mercerizing substantially pure Musa alpha-cellulose
45 by treatment with a sodium hydroxide solution containing within 0.5% of 19% of sodium hydroxide at a temperature between 19° and 20° C. for four to six hours.

9. In the process for producing cellulosic sub-
50 stances from Musa fiber, the steps comprising mercerizing substantially pure Musa alpha-cellulose by treatment with a sodium hydroxide solution containing within 0.5% of 19% of sodium hydroxide at a temperature between 19° and 20° C.
55 for four to six hours, and subjecting the mercerized product to treatment for one to two hours with 13% to 16%, by weight on the purified cellulose, of carbon disulphide at a temperature between 27° and 33° C.

10. In the production of cellulosic substances, the steps comprising, by treatment with an aqueous solution of sodium hydroxide containing within 0.5% of 19% thereof, mercerizing hemp fiber (not of Indian hemp origin) substantially freed
60 of non-cellulosic and hemi-cellulosic compounds, and then xanthating the alkali cellulose thus formed with carbon disulfide.

11. In the production of cellulosic substances, the steps of mercerizing, by treatment with an aqueous solution of sodium hydroxide containing within 0.5% of 19% thereof at a temperature between 19° and 20° C., hemp fiber (not of Indian hemp origin) substantially freed of non-cellulosic and hemi-cellulosic compounds, ageing the
75

mercerized product and subjecting the aged product for one to two hours with 13% to 16% by weight on the purified cellulose of carbon disulphide, at a temperature between 27° and 33° C.

5 12. In the production of cellulosic substances from hemp fiber, the step of mercerizing, by treatment with an aqueous solution of sodium hydroxide containing within 0.5% of 19% of sodium hydroxide, hemp fibre other than of Indian hemp
10 origin substantially freed of non-cellulosic and hemi-cellulosic compounds.

13. In the production of cellulosic substances, the step comprising mercerizing substantially pure alpha-cellulose of hemp fiber of other than
15 Indian hemp origin by treatment with an aqueous solution of sodium hydroxide containing within 0.5% of 19% of sodium hydroxide and subjecting the mercerized product to treatment with 13% to 16% by weight on the cellulose, of carbon disulfide.

20 14. In the production of cellulosic substances, the step of mercerizing, by treatment with an

aqueous solution of sodium hydroxide containing within 0.5% of 19% of sodium hydroxide, Musa cellulose substantially freed of non-cellulosic and hemi-cellulosic compounds.

15. In the production of cellulosic substances, 5 the steps of mercerizing, by treatment with an aqueous solution of sodium hydroxide containing within 0.5% of 19% of sodium hydroxide, Musa cellulose substantially freed of non-cellulosic and hemi-cellulosic compounds, and then xanthating
10 the resultant alkali-cellulose with carbon bisulphide.

16. An article according to claim 3 in which the cellulose precipitate has a tensile strength of 2.10 to 2.35 grams per denier in the dry state and 1.05
15 to 1.45 grams per denier in the wet state.

17. An article according to claim 5 in which the cellulose precipitate has a tensile strength of 2.10 to 2.35 grams per denier in the dry state and 1.05
20 to 1.45 grams per denier in the wet state.

EDWARD CHAUNCEY WORDEN, I.