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MANUFACTURE OF SHEETED CELLULOSE
FIBER ADAPTED FOR CONVERSION INTO
CELLULOSE DERIVATIVESGeorge A. Richter, Berlin, N. H., assignor to
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of MaineNo Drawing. Application February 10, 1936,
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This invention relates to the manufacture of sheeted cellulose fiber adapted for conversion into cellulose derivatives of all sorts, including such cellulose esters as the nitrate, acetate, and xanthate, such alkyl ethers as methyl and ethyl cellulose, and such hydroxy alkyl ethers as the hydroxy ethyl ether of cellulose. It deals more particularly with putting cellulose fiber into the form of sheets of such physical and chemical qualities that they can be advantageously converted into the aforementioned cellulose derivatives.

In accordance with the present invention, cellulose fiber or pulp of the appropriate character is formed into a web or felted sheet on a Fourdrinier or other suitable papermaking machine under conditions such that the dry sheet delivered by the machine is of low compactness, whereupon the dry sheet is compressed, as by the action of calender rolls, to a distinctly higher compactness and converted in such compacted sheet form into cellulose derivatives. More particularly, the dry web or felted sheet is formed at a compactness of about 20 to 50 and is then compressed or compacted to a compactness upwards of about 70, for instance, to a compactness ranging from about 70 to about 150. The compactness or density values herein given are determined by dividing the basis weight of the sheet in pounds by its thickness in inches and multiplying by the factor 10^{-2} . The basis weight is the weight in pounds of 480 sheets whose dimensions are $24 \times 36''$. While the basis weight of the sheet material of the present invention is subject to variation, I prefer to form the sheet material at a basis weight commonly possessed by pulpboards or drier sheets, so-called, for instance, at a basis weight ranging from 120 to 500 pounds.

In order to produce the felted fiber sheet of the present invention, it is necessary to depart radically from conventional paper manufacture. To begin with, the cellulose fiber or pulp used as raw material should not be beaten or jordaned to a noteworthy degree, that is, to a degree such that the fibers are appreciably reduced in fiber length, cut into fiber fragments, or hydrated or gelatinized, since cut fibers, fiber fragments, and hydrated or gelatinized cellulose not only tend to increase the compactness or density of the sheet to a value beyond that desired preparatory to the dry-compaction of the sheet, but also to impede penetration into and throughout the dry-compacted sheet of the nitrating, acetylating, or other reagent employed in converting the dry-compacted sheet into cellulose derivatives. Again,

in forming the felted fiber sheet of the present invention, it is necessary to avoid the use of press rolls in partially dewatering the freshly formed or wet sheet before it passes from the wet to the dry end of the papermaking machine, unless provision is made to offset such wet-pressing of the sheet and the resulting undesirable cementation of fiber to fiber during subsequent drying to yield a dried sheet of excessive compactness. A preferred way of offsetting or counteracting wet-pressing of the sheet is to add thereto suitable surface-tension-reducing agent, such as soap, at a suitable stage at the wet end of the papermaking machine, as disclosed in Schur Patent No. 1,986,291, dated January 1, 1935. As described in that patent, the presence of a surface-tension-reducing agent in the sheet during its drying does away with the contractile forces otherwise at play therein and makes possible the attainment of a dried sheet of the compactness value desired herein even when wet-pressing of the sheet is effected before the drying operation.

Once the felted sheet or web hereof has been brought to dryness with the desired bulkiness or low compactness, namely, a compactness of about 20 to 50, the sheet may be markedly compacted or compressed, as by calender rolls, substantially without cementation or bonding of the fibers in the sheet and hence without impeding substantially uniform access of the nitrating, acetylating, or other reagent used in converting the sheeted fiber into cellulose derivatives to substantially all of the fibers in the sheet. The value of the step of dry-compaction resides in the fact that, in making various cellulose derivatives, it is important that excess reagent employed in the reaction productive of the derivative be recovered from the cellulose derivative or reaction product for reuse as completely as possible and in substantially undiluted state. For instance, when sheeted cellulose fiber is nitrated, as in the form of sheet fragments, pieces, or chips, the practice is to centrifuge the nitrated mass while soaked with the mixed nitrating acid for the purpose of separating as much undiluted nitrating acid as possible for reuse before the nitrocellulose is washed and subjected to the other customary after-nitration treatments. When the sheet fragments, pieces, or chips are of high bulkiness, i. e. low compactness, they exhibit what is known as high acid retention. In other words, they retain an excessive amount of nitrating acid even after centrifugation. High acid retention is also experienced when large sheets of low compactness are nitrated by submergence in mixed

nitrating acid and the acid drained therefrom after nitration has been completed. By dry-compaction of the felted fiber sheets hereof to the desired density upwards of about 70, it is possible to minimize acid retention by the sheets irrespective of the particular size of the sheets during the nitrating operation or the particular way in which the excess nitrating acid is removed from the sheets. That is to say, the principles of the present invention apply to dry-compacted sheets nitrated as large-area sheets or as such small sheets or pieces such as are sometimes termed chips or sheet fragments. By reason of the substantially uncemented relationship of the fibers in the compacted sheets hereof, no trouble is had in realizing uniform and rapid penetration of mixed nitrating, acetylating acids or other chemical reagents throughout the sheets even when they are of such thickness as to fall into the category of pulpboards. As already indicated, the freedom of the sheets from hydrated or gelatinized cellulose, such as is developed during beating or jordaning of cellulose fiber, and the formation of the sheets at initially low dry compactness values make for such desired penetrability of the sheets even after their dry-compaction to markedly greater density; and were one to beat or jordan cellulose fiber and/or wet-press the sheet made therefrom so that the mere drying of the sheet develops at once a dried sheet of the same high compactness as the dry-compacted sheet hereof, he would find that such sheet is not as rapidly or uniformly penetrated by nitrating, acetylating, or other chemical reagents as the dry-compacted sheet hereof on account of the cellulose cementing films between the fibers and their tendency to impede influx of reagent into and throughout the sheet. Indeed, in the case of comparatively thick sheets, these intra-fiber films may give rise to non-uniform reaction on the sheet, for instance, over-treatment of the surfaces of the sheets and under-treatment of their interior fibers or portions. In nitrating or acetylating such sheets, the over-treatment of the surfaces may even be so serious as to be attended by side reaction known as hydrolysis or gelatinization and may further impede penetration of reagent into the inner sheet portions.

In producing the sheets hereof, various kinds of cellulose fiber or pulp may be employed as raw material, including ordinary chemical wood pulps or chemical wood pulps refined to distinctly higher alpha cellulose content, for instance, an alpha cellulose content upwards of about 93%. In the case of ordinary chemical wood pulps such as softwood sulphite, hardwood sulphite, various grades of kraft, etc., it is necessary to control carefully the felting or papermaking operation in order to arrive at sheets of the desired initially low dry-compactness value. Thus, in mixing the pulp with water to produce a uniform dilute fiber suspension such as is requisite for forming a sheet of uniform texture on the papermaking machine, it is necessary to avoid beating, jordaning, or similar manipulation of an intensity such as will hydrate or gelatinize the fibers appreciably or reduce their fiber length appreciably. By using hot water as the suspension medium for such pulp fibers, their hydration may be kept at a minimum so that upon delivery of the hot suspension of fibers to the papermaking machine and upon maintaining the proper conditions at the wet end of the machine, a finished or dried sheet of maximum bulk may be realized. Unless

the pulp suspension contains an appropriate amount of soap or other surface-tension-lowering agent or unless such an agent is added to the wet sheet before it is dried, as described in Schur Patent No. 1,986,291, it is necessary to avoid a wet-pressing of the sheet, that is, while it is traversing the wet end of the papermaking machine, in order to realize a dried sheet having a compactness ranging from about 20 to 50. Accordingly, in the absence of a surface-tension-lowering agent in the wet sheet, substantially no pressing of such sheet is effected before it is dried. The dried sheet of a compactness not exceeding about 50 delivered by the papermaking machine is then compacted, as by passage through the successive pairs of rolls in a calender stack, to a compactness value upwards of about 70, for instance, to a compactness ranging from about 70 to about 150. Because of its increased density or compactness, the sheet is better adapted for conversion into cellulose derivatives and can be stored and shipped more economically.

In making nitrocellulose, not only may the compacted sheets be nitrated as such, but they may be comminuted into flakes or chips which, because of their density, may be nitrated with the desired output of nitrocellulose by the nitrating pots and with the desired low acid retention after having undergone centrifugation. In making other derivatives, such as cellulose acetate, the compacted sheets may also be treated as such or after comminution. Nitrating and acetylating reagents react smoothly and uniformly on all these forms of the interfelted fiber. In making cellulose xanthate from the compacted sheets, they may without difficulty be subjected to the usual processing to which the ordinary drier sheets of pulp are put. Thus, they may be steeped in the usual strong caustic soda solution and excess solution pressed therefrom to yield sheets of alkali-cellulose. The sheets of alkali-cellulose may then be shredded and the shreds aged and xanthated in the customary manner. Again, the compacted sheets hereof may advantageously be xanthated in chip form by the so-called one-step xanthation process disclosed in my application Serial No. 58,539, filed January 10, 1936. In practicing the process of that application, it has been found that chips prepared from the compacted sheets hereof may be quickly and uniformly impregnated with a limited volume of strong caustic soda solution calculated to yield a final xanthate solution of a particular cellulose and caustic soda content, for instance, a cellulose and caustic soda content each about 7% to 10%. In other words, it is unnecessary in such case to soak the chips with an excessive volume of caustic soda solution and then to drain or otherwise remove excess solution in order to produce an alkali-cellulose mixture of the alkali and cellulose concentration and alkali to cellulose ratio requisite for the finished xanthate solution prepared. On the other hand, when the chips are from sheets of a compactness value below 60, it becomes necessary to employ an excessive volume of caustic soda solution in order to attain the desired uniform distribution of caustic soda throughout the chip mass and it further becomes necessary to resort to such steps as draining or squeezing the mass in order to free it of the excess solution. Again, when the chips are prepared from sheets of a compactness value upwards of about 70 but realized by hydration and/or wet-pressing of the fibers thereof, difficulty is experienced in effecting a substantially uniform im-

pregnation of the chips throughout with caustic soda solution even in the presence of an excessive volume of solution, unless soaking of the chips in the excess solution is continued for an undesirably long period of time. It is thus seen that chips prepared from the compacted sheets hereof are advantageous in that they are quickly and uniformly penetrated by a limited volume of caustic soda solution, such as may be desired in a one-step xanthation process. This holds true even when such chips are of greater than normal thickness or basis weight. Moreover, in a one-step xanthation process, the matter of volume or space in the xanthating vessel occupied by the chips is of importance; and by virtue of the density or compactness of the chips prepared from the compacted sheets hereof, it is possible to realize satisfactory conversion of such chips into alkali-cellulose while getting maximum output or capacity from the xanthating vessel.

In some instances, the addition of soap as a surface-tension-reducing agent to the web or sheet before it is dried may be quite advantageous, as when the dry-compacted sheet is to be formed into xanthate by a one-step xanthating process such as is disclosed in application Serial No. 63,876, filed Feb. 14, 1936, by Harold P. Vannah and myself.

According to that application, soap may advantageously serve the purpose of quickly inducing fine particle size emulsification of the liquid carbon bisulphide added as the xanthating reagent to the mixture of alkali and cellulose; and, when soap is employed as herein indicated as a surface-tension-lowering agent, it may subsequently additionally serve to promote fine particle size emulsification of the liquid carbon bisulphide as disclosed in the last-named application. On the other hand, the presence of soap in the dry-compacted sheet may be undesirable, as when the sheet is to be converted into cellulose nitrate or cellulose acetate, in which case the use of soap should, of course, be avoided. Suitable volatile surface-tension-lowering agents might in such case be used in lieu of soap; or no surface-lowering agents at all need be used and the conditions of sheet manufacture may, as already described, be such as to lead to a dried sheet of the appropriate initial compactness.

As already indicated, various kinds of cellulose fiber or pulp may be used as raw material in producing the compacted sheets hereof, the particular fiber employed depending upon the cellulose derivative into which it is to be converted. For the purpose of making xanthate, it may be desirable to use ordinary bleached sulphite pulp or suitably bleached kraft pulp. If desired, however, white wood pulps of high alpha cellulose content may be employed, for instance, wood pulps of an alpha cellulose content upwards of about 93%. In the event that the compacted sheets hereof are to be nitrated or acetylated, it is particularly desirable that the cellulose fiber used therein be a white fiber of high alpha cellulose content, say, bleached wood pulp of an alpha cellulose content upwards of about 93%. In any one of these instances, the cellulose fiber may be prepared in such a way as to exhibit high or low solution viscosity, depending upon the cellulose derivative or ultimate product to be realized therefrom. The present invention extends also to the use as raw material of mercerized cellulose fiber or wood pulp of the appropriate whiteness, purity or alpha cellulose content, solution viscosity, and other characteristics, even though it

is preferable to use as raw material for the compacted sheets hereof substantially unmercerized cellulose fiber or wood pulps by reason of the fact that it is more difficult to prepare uniformly textured sheets from mercerized pulps unless the mercerized pulps are well beaten or jordaned and delivered at very dilute consistencies to the paper-making machine, in which latter case the finished sheets will contain fiber fragments and short fibers such as are avoided in the compacted sheets hereof.

The compacted sheets hereof may be described or characterized not only as being made up of interfelted fibers in substantially uncemented relationship but as containing the fibers at substantially their original or preliberated average fiber length. Thus, in the case of wood pulps initially liberated at an average fiber length of, say, about 1.2 to 1.5 millimeters, such average fiber length is substantially preserved or carried through to the finished or dry-compacted sheets hereof. The substantial preservation of fiber length from the time of fiber-liberation and the substantially uncemented interfelted relationship of the fibers in the finished sheets renders such sheets valuable as bases for the production of various binder-impregnated products. Thus, the sheets hereof may advantageously be impregnated with rubber latex compositions, bitumens, resins, and many other binders by virtue of their quick and substantially uniform penetrability by such binders and the toughness of the resulting binder-impregnated products. The quick and uniform penetrability of such sheets is a reflection of the absence thereof of intra-fibrous cementing films and the toughness of the impregnated products is a reflection of the high average fiber length of the fibers constituting their bases. The step of dry-compaction necessary to the production of the sheets hereof strengthens such sheets so that they do not tend to disintegrate or break when passed continuously and under tension through baths of liquid or liquefied binders of the character mentioned in the production of binder-impregnated products.

I claim:

1. A process which comprises wet-felting into a sheet preliberated cellulose fibers at an average fiber length substantially as liberated, dewatering the sheet to dryness while maintaining its fibers in substantially uncemented relationship so as to produce a dried sheet having a compactness ranging from about 20 to 50, and compacting the dried sheet to a compactness upwards of about 70.

2. A process which comprises wet-felting into a sheet preliberated cellulose fibers at an average fiber length substantially as liberated, dewatering the sheet to dryness while maintaining its fibers in substantially uncemented relationship so as to produce a dried sheet having a compactness ranging from about 20 to 50, and compacting the dried sheet to a compactness of about 70 to 150.

3. A process which comprises wet-felting into a sheet preliberated wood pulp fibers in substantially unhydrated condition and at an average fiber length substantially as liberated from wood, dewatering the sheet to dryness while maintaining its fibers in substantially uncemented relationship so as to produce a dried sheet having a compactness ranging from about 20 to 50, and compacting the dried sheet to a compactness upwards of about 70.

4. A process which comprises wet-felting into a sheet preliberated wood pulp fibers in substantially unhydrated condition and an average fiber length substantially as liberated from wood, dewatering the sheet to dryness while maintaining its fibers in substantially uncemented relationship so as to produce a dried sheet having a compactness ranging from about 20 to 50, and compacting the dried sheet to a compactness of about 70 to 150.

5. A process which comprises wet-felting into a sheet preliberated cellulose fibers at an average fiber length substantially as liberated, dewatering the sheet to dryness while maintaining its fibers in substantially uncemented relationship so as to produce a dried sheet having a compactness ranging from about 20 to 50, compacting the dried sheet to a compactness upwards of about 70, and converting the dry-compacted sheet into cellulose derivatives.

6. A process which comprises wet-felting into a sheet preliberated cellulose fibers at an average fiber length substantially as liberated, dewatering the sheet to dryness while maintaining its fibers in substantially uncemented relationship so as to produce a dried sheet having a compactness ranging from about 20 to 50, compacting the dried sheet to a compactness of about 70 to 150, comminuting the dry-compacted sheet into chips, and converting the chips into cellulose derivatives.

7. A process which comprises wet-felting into a sheet preliberated wood pulp fibers in substantially unhydrated condition and at an average fiber length substantially as liberated from wood, dewatering the sheet to dryness while maintaining its fibers in substantially uncemented relationship so as to produce a dried sheet having a compactness ranging from about 20 to 50, compacting the dried sheet to a compactness up-

wards of about 70, converting the dry-compacted sheet into cellulose derivatives.

8. A process which comprises wet-felting into a sheet preliberated wood pulp fibers in substantially unhydrated condition and an average fiber length substantially as liberated from wood, dewatering the sheet to dryness while maintaining its fibers in substantially uncemented relationship so as to produce a dried sheet having a compactness ranging from about 20 to 50, compacting the dried sheet to a compactness of about 70 to 150, comminuting the dry-compacted sheet into chips, and converting the chips into cellulose derivatives.

9. A dried, wet-felted sheet of preliberated cellulose fibers existing in such sheet in substantially uncemented interfelted relationship at an average fiber length substantially as liberated, said sheet being of a compactness of at least about 70.

10. A dried, wet-felted sheet of preliberated cellulose fibers existing in such sheet in substantially uncemented interfelted relationship at an average fiber length substantially as liberated, said sheet being of a compactness ranging from about 70 to 150.

11. A dried, wet-felted sheet of preliberated wood pulp fibers existing in such sheet in substantially uncemented interfelted relationship at an average fiber length substantially as liberated from wood, said sheet being of a compactness of at least about 70.

12. A dried, wet-felted sheet of preliberated wood pulp fibers existing in such sheet in substantially uncemented interfelted relationship at an average fiber length substantially as liberated from wood, said sheet being of a compactness ranging from 70 to 150.

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