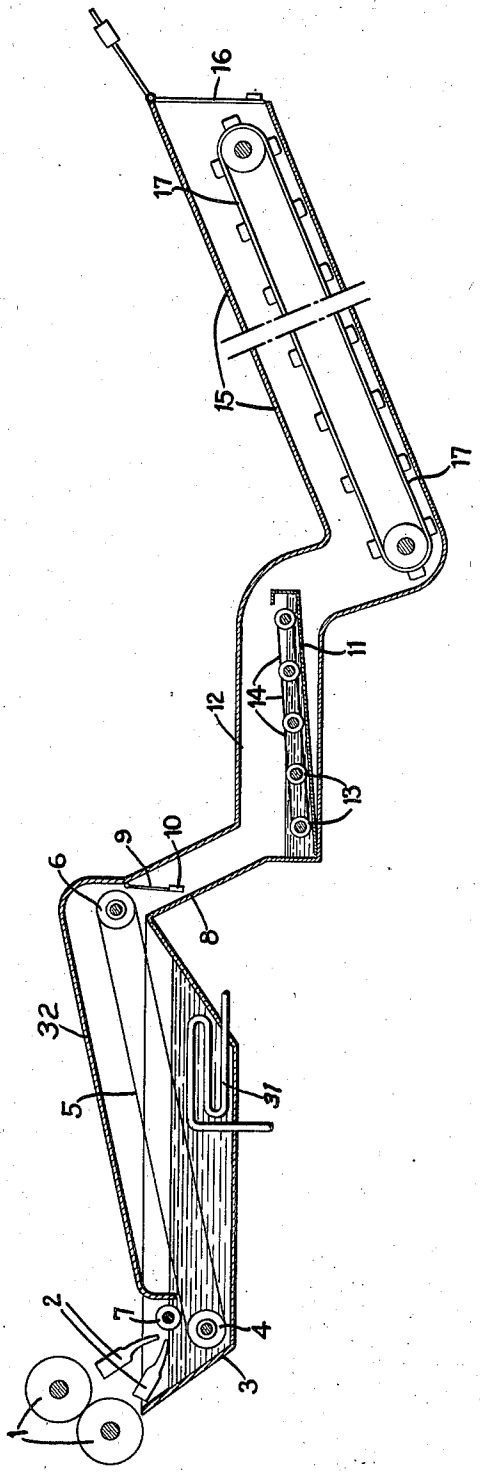
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MANUFACTURE OF SOLUBLE CELLULOSE

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MANUFACTURE OF SOLUBLE CELLULOSE

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Any material containing cellulose in a sufficiently pure form may be used to make a soluble cellulose by treatment with sodium hydroxide and carbon disulphid. Such materials include sulphite, sulphate and soda wood pulps, cotton, rags, ramie, cane fibre, straw, corn stalks, or bamboo. The process described hereafter is not limited to any one basic material and is described with particular reference to woodpulp purely to simplify the explanation and not at all by way of limitation upon the inventive concept.

It has been found that a pulp composed of partially xanthated fibres (that is, fibres having an xanthated exterior surface and an unxanthated core) when mixed with ordinary pulp increases the dry strength of the paper made from such pulp mixture and very greatly increases its wet strength. The xanthated pulp produced in accordance with the present invention may be used to advantage also in the production of cellulose films, artificial silk, in the manufacture of regenerated cellulose, and for a variety of similar purposes. The production of partially xanthated fibres has heretofore been accompanied by serious practical difficulties. If it is attempted to limit the xanthation only to the outer portion of the fibres by adjusting the concentration of the chemical bath, there results a large proportion of completely xanthated fibre and an equally large proportion of virtually unxanthated fibre. The completely xanthated fibres being altogether soluble, there results a pure loss in the papermaking process. Furthermore, the speed of the reaction is retarded by an attempt to control it in this way. It has also been proposed to control the xanthation by limiting the swelling action (which inevitably occurs in this treatment) and thus to limit the penetration of the xanthating solution into the fibre. This is, however, of necessity a batch process, and very slow and cumbersome.

The present invention provides a method, and means for carrying out such method, of continuously treating an indefinite amount of pulp to produce any desired degree of xanthation.

So far as this invention relates to a process, it may be described as follows: The material to be treated, for example, wood pulp produced by the sulfite or the sulfate process, is fabricated into a card, shreddings, or a continuous sheet. It may be produced, for example, on a paper machine or wet machine and is preferably in as loose and bulky a state as possible. The sheet may, for example, conveniently be 1/8" to 3/16" in thickness and should have a water content ranging between, say, 0 and 18%. The web or strip thus formed is fed in a continuous stream into a bath of hot, strong sodium hydroxide solution and is continuously removed from such solution before the cellulose has absorbed and reacted chemically with the quantity of sodium hydroxide which would produce a complete reaction. The duration of immersion, the depth to which the web is immersed, the temperature and strength of the solution, each represents a distinct factor in producing the desired degree or extent of xanthation. It is an important phase of the present process that each of these factors should be accurately and properly controlled.

The sodium hydroxide solution preferably has a concentration of from ten to eighteen parts by weight of sodium hydroxide in 100 parts of solution and it is preferably heated to a temperature of from 35 to 102° C. for this treatment. The duration of immersion, the depth of immersion and the concentration and temperature of the solution will be different for various types of cellulosic material and for various thicknesses of web treated, and will depend upon the particular use to which the xanthated product is to be put, but for any given type of material, thickness of web, and desired degree of xanthation, it will be found desirable to maintain the conditions uniform and substantially constant.

Either previous to the treatment of the material with the sodium hydroxide or after such treatment or both before and after such treatment, the cellulosic material is subjected to a similar, regulated treatment with carbon disulphid. During the carbon disulphid treatment the cellulosic material is run through a closed chamber containing a tank or bath of carbon disulphid. Suitable members transfer the carbon disulphid from the tank or container to the continuously or intermittently moving stream of cellulosic material. After the carbon disulphid treatment the material may be passed into the controlled sodium hydroxide bath previously described. It has been discovered in connection with this invention that pre-treatment with carbon disulphid is satisfactory with all the materials mentioned and is particularly beneficial when a hard, dense, cellulosic material is being treated, since the temperature of the sodium hydroxide bath following the carbon disulphid treatment tends to vaporize the carbon disulphid and disburse it evenly throughout the material treated.

When the carbon disulphid treatment is to follow the sodium hydroxide treatment, the material is subjected to one or a combination of any of the following treatments.

1. The material after passing through the sodium hydroxide bath may be run directly and immediately through just such a carbon disulphid treatment as was above described.

2. The material after the sodium hydroxide bath may be suitably aged for, say, 12 hours or more before being treated with carbon disulphid.

3. The material after the sodium hydroxide bath may be shredded into finely divided pieces

or particles. This may be done in any suitable shredding equipment; many machines suitable for this purpose are well-known in the art. The shredded material is then placed in a wooden or other suitable container and the required quantity of carbon disulphid is poured therein or is otherwise brought into intimate contact with the material.

In approximately one hour the chemical reaction between the carbon disulphid and the pulp is complete. Water or water containing sodium hydroxide is then poured upon the treated material and the whole mixture is violently agitated in a suitable beater until the material is partially or completely dissolved, depending upon the particular purpose of the treatment. The partially dissolved material may, for example, be added to any suitable beater stock for improvement of the strength of the paper made from such beater stock.

It is understood that both the treatments 2 and 3 above mentioned may be used, if desired; that is, the material coming from the sodium hydroxide bath may be aged, then shredded, then treated with carbon disulphid; or it may be shredded, then aged and then treated. In any event, the ultimate pulp produced by treatment with both sodium hydroxide and carbon disulphid is mixed with water or with a sodium hydroxide solution and beaten before being added to ordinary pulp for paper making.

As previously indicated the treatment contemplated by this invention may be arranged to produce not only the partially xanthated fibres for addition to other paper stock but may be utilized in the manufacture of cellulose films, artificial silk, regenerated cellulose and similar products. The extent of the xanthation as determined by the controlled factors above noted may be brought to any desired degree of completion, so that this process is equally applicable to the manufacture of any of the products herein enumerated, in addition to the partially xanthated fibre especially useful in paper making.

The preferred method and apparatus used is as follows, as illustrated in the drawing which is a section in elevation.

Unbleached sulphite or sulphate pulp is formed into a continuous sheet upon the wire of a paper machine and run directly from the couch roll into dryers. The sheet thus formed, containing about 8% moisture and being from $\frac{1}{8}$ to $\frac{3}{16}$ of an inch thick, is cut into a continuous strip about 15'' wide and wound into a roll weighing, say, 60 lbs. The roll is strongly clamped onto a bar passing through its center. Each end of the bar is supported on suitable journals, in a manner well understood, so that the roll of pulp may unwind freely. Referring to the drawing, one end of the sheet of pulp is fed between two steel rollers **1**. These rollers are placed directly in front of the roll of pulp, are geared together and are driven by any suitable source of power, preferably a variable speed slip ring motor. The rollers draw the pulp from the roll and direct the sheet between wooden guide fingers **2**. The sheet passes over the guide fingers and into a tank **3** containing a solution of sodium hydroxide, preferably a 15% by weight solution. Submerged in the solution is a roller **4** over which passes a monel-metal, wire-mesh **5**. The wire-mesh forms a continuous band which at the end opposite that passing around the roller **4** passes over a roller **6**. The sheet of pulp coming from the rollers **1** between the guide fingers **2** rests upon and is carried by the screen **5**. A small, substantially floating roller **7** rests upon the pulp to keep it in contact with the screen. This roller is adapted to rotate freely and engages the pulp sheet lightly substantially at the point of deepest immersion. Due to its free rotation and the fact that it nearly floats in the solution it will not exert any objectionable pressure upon the sheet of pulp. The solution of sodium hydroxide is maintained preferably at 50° C. For this purpose there may be provided a heating coil **31** in the bottom of the tank **3** supplied with steam or the like from any suitable source under thermostatic control. The linear speed of the screen **5** corresponds exactly with the linear speed of the rollers **1** so that the pulp is removed from the solution by the screen **5** at exactly the rate at which it enters the solution from the rollers **1**. For this purpose the roller **4** may be driven through suitable gearing (not shown) from the same source as the rollers **1**. The depth of the solution in the tank **3** is regulated by any suitable device, preferably some constant head weir. By regulating the speed of the rollers **1** and the wire-mesh **5**, the temperature and depth of the solution in the tank **3**, all of the factors previously discussed are rigidly controlled and any desired degree of xanthation may be procured. The conditions are preferably such that each pound of the pulp containing 8% moisture absorbs approximately three pounds of the sodium hydroxide solution, although the conditions may be varied so that the solution absorbed may range between two and five times by weight the quantity of dry cellulose treated. I have found it desirable to maintain a maximum depth of two inches of the hot caustic soda solution above the sheet of pulp in its travel on the wire-mesh. I have also found that by maintaining the pulp immersed for a distance of about 11 inches along the wire-mesh and by advancing the sheet at the appropriate speed, a desirable degree of absorption of the solution may be made to take place. An advance of the sheet at the rate of a foot per second will be found appropriate under the conditions mentioned to produce partial xanthation to a desirable degree.

The pulp leaves the wire **5** as it runs over the upper roller **6**. The pulp then descends into a closed duct **8**. This duct is equipped at its upper end with a flexible door **9** weighted at its lower edge **10**. This door normally remains shut but as the sheet of pulp enters the duct the sheet presses against the lower edge of the door swinging it back and allowing the sheet to pass down through the duct or chamber. The swinging of this door is to minimize the quantity of carbon disulphid escaping from the equipment. If desired the escape of carbon disulphid may be further reduced or substantially eliminated by the provision of a hood **32** over the tank **3** and connected with the upper end of the duct **8** as shown. The forward end of this hood may dip into the caustic soda solution adjacent the roller **7** and thus provide an effective seal. At the bottom of the duct is placed a tank or tray **11** in a closed horizontal chamber **12**. The tank or tray **11** is tilted preferably at an angle of between 10 and 30° to the horizontal, the forward end resting on the bottom of the chamber **12** directly under the duct **8**. A series of, say, from two to five iron rollers **13**, journaled at their ends, are mounted adjacent the bottom of the tank or tray and serve, upon rotation, to transfer the carbon disulphid to the under sur-

face of the pulp sheet. All of these rollers are geared together and are synchronized with the rollers 1 and the screen 5. The space between these rollers in the tray is bridged across by suitable endless chain conveyor units 14 which carry the pulp from one roller to the next. Any desired device, such as a constant head weir, may be used to maintain constant the desired level of carbon disulphid in the tilted tray or tank. It will be apparent that due to the tilting of the tray the first roller will be immersed to a greater degree than the succeeding rollers and each succeeding roller will accordingly transfer less of the carbon disulphid to the pulp than the one ahead. The level of the carbon disulphid in the tray may be such, if desired, that the first roller will be completely immersed and the sheet of pulp thus permitted to come in direct contact with the liquid. One or more of the final rollers may, under certain conditions, be completely out of contact with the carbon disulphid. If desired the raised end of the tray may be adjustably retained so as to permit variation in its angle of inclination. Normally the total quantity of carbon disulphid employed should be, say, between 25% and 50% of the weight of the dry cellulose treated.

Connected to the horizontal closed chamber 12 is a third closed chamber or duct 15. The forward end of this chamber is placed below the discharge end of the second chamber 12 and the duct is tilted upwardly so that the end or exit is at substantially the same level as the entrance to or inlet of the second chamber 12. The exit of the third chamber 15 is closed by a door 16 similar to the door 9. Within the third chamber is driven a suitable endless conveyor 17, which moves at a comparatively slow speed. The pulp which has received both the caustic soda and the carbon disulphid is deposited on the conveyor 17 and, due to the slow movement of the latter, is caused to bunch up to a certain extent. The conveyor should be of sufficient length and should be moved at such speed as to allow a suitable period of reaction of, say, an hour within the chamber 15. It should be capable under the particular conditions mentioned of retaining about 3,600 feet of the pulp sheet. If desired several conveyors could be arranged in parallel and each adapted to receive a quantity of treated pulp in turn. If the conveyor capacity is limited the apparatus may be operated in a semi-intermittent way. For example, a desired quantity of the pulp sheet, up to the capacity of the conveyor, may be run in a continuous way through the caustic soda and carbon disulphid treating stages at the appropriate speed and may be accumulated on the conveyor 17. When this is loaded to capacity, after say 15 minutes, the feeding of the material may be stopped and the pulp may remain in the chamber 15 for the desired reaction period. After the reaction is substantially completed the material may be discharged from chamber 15 and a new quantity may be run in, in the same way. By employing a somewhat thicker pulp sheet and limiting the immersion in the caustic soda to a distance of say 5 inches the speed of the feed may be considerably reduced so that the conveyor 15 would then need to accommodate only say, 900 feet of the pulp even though the apparatus is operated continuously.

The operation of the entire equipment is as follows: The sheet of pulp is immersed in the bath of sodium hydroxide in the tank 3 and is permitted to absorb a desired amount of the solution. The pulp is carried out of the sodium hydroxide solution by the wire 5 and leaves the wire at the roller 6 to enter the first chamber 8 of the closed series through the door 9 and travels by gravity into the tank or tray 11 containing carbon disulphid. The pulp rides over the rollers 13 in the tray 11 which act to transfer carbon disulphid to the pulp. It will be understood that the pulp, due to its immersion in the hot sodium hydroxide solution, is still quite warm when it arrives in the chamber 12. This warmth volatilizes the carbon disulphid and results in the thorough penetration of the carbon disulphid through the pulp. The iron rollers 13 each act to transfer a limited amount of carbon disulphid directly to the pulp and the quantity transferred is controlled and limited by the level of carbon disulphid maintained in the treating tray. By regulating this depth the material can be subjected to a treatment ranging anywhere from complete immersion in carbon disulphid to a mere transfer by one or two of the rollers. If desired, the material may be shredded and aged upon leaving the sodium hydroxide bath and prior to the carbon disulphid treatment.

After the carbon disulphid treatment the pulp falls by gravity into the third chamber 15 coming to rest upon the slowly moving conveyor 16. The rate of travel of this conveyor is so regulated both as to its speed and as to its length as to give time for the required chemical reaction with carbon disulphid to make the material wholly or partly soluble as desired. When the desired reaction is completed the material is brought into contact with a quantity of water, with or without caustic soda, and is violently agitated in a beater or any suitable mixer until the material is partially dissolved. This partially dissolved material may then be added, if desired, to any suitable beater furnish for improvement of the strength of the paper to be made therefrom.

While a particular manner of conducting the process has been pointed out in considerable detail and certain speeds of movement and reaction, etc., have been mentioned, it will be understood that these are illustrative only and designed to produce a particular type of product. Numerous variations may be made in the operating conditions and in the form of equipment disclosed without departing from the principles and scope of the invention as defined by the claims.

I claim:

1. Apparatus for the treatment of cellulosic material which comprises a treating tank adapted to retain a liquid, a conveyor arranged at an angle within said tank, and means for directing a sheet of said material onto said conveyor, said conveyor being adapted to retain the material within the liquid during a portion of its travel and to carry the material out of the liquid.

2. Apparatus for the treatment of cellulosic material which comprises a plurality of connected closed treating chambers, means within one of said chambers for applying a treating fluid to said material, and a conveyor within another of said chambers for slowly transporting the material during reaction with said treating fluid.

3. A method for the production of cellulose fibres having a xanthated exterior surface soluble in water and having an unxanthated core, comprising, in combination, the steps of passing cellulose fibres through a hot aqueous solu-

tion of caustic soda, removing the fibres from said solution before complete penetration, treating said fibres with carbon disulphide and removing said fibres from contact with the carbon disulphide after the same has reacted with only that portion of the fibres treated with the caustic soda solution.

4. A method for the production of cellulosic fibres having a xanthated exterior surface soluble in water and having an unxanthated core, comprising, in combination, the steps of passing a sheet of cellulosic material through a hot aqueous solution containing from 15 to 18 per cent by weight of caustic soda, removing the sheet from said solution before the solution has penetrated therethrough, treating said sheet with a solution of carbon disulphide and removing said sheet from the solution after the carbon disulphide has reacted with only that portion of the sheet treated with the caustic soda solution.

5. A method for the production of cellulosic fibres having a xanthated exterior surface soluble in water and having an unxanthated core, comprising, in combination, the steps of passing a sheet of cellulosic material through an aqueous solution containing from 15 to 18 per cent by weight of caustic soda maintained at a temperature of from 40° to 50° C., removing the sheet from said solution before the solution has penetrated therethrough, treating said sheet with a solution of carbon disulphide and removing said sheet from the solution after the carbon disulphide has reacted with only that portion of the sheet treated with the caustic soda solution.

6. A continuous method for the production of cellulosic fibres having a xanthated exterior surface and unxanthated core, comprising in combination, the steps of passing fibrous material through an aqueous solution of caustic soda, maintaining the material in the solution until the outer surfaces of the fibres comprising the material are coated with from 3 to 5 parts by weight of caustic solution to one part by weight of the fibrous material, and thereafter bringing the material into contact with a solution of carbon disulphide.

7. A continuous method for the production of cellulosic fibres having a xanthated exterior surface and unxanthated core, comprising, in combination, the steps of passing fibrous material through an aqueous solution of caustic soda, maintaining the material in the solution until the outer surfaces of the fibres comprising the material are coated with from 3 to 5 parts by weight of caustic solution to one part by weight of the fibrous material, immersing said material in a solution of carbon disulphide, and maintaining said material in said solution until those surfaces treated with the caustic soda solution have become xanthated.

8. A continuous method for the production of cellulosic fibres having a xanthated exterior surface and an unxanthated core, comprising, in combination, the steps of passing fibrous material through an aqueous solution of caustic soda, maintaining the material in the solution until the outer surfaces of the fibres comprising the material are coated with from 3 to 5 parts by weight of caustic solution to one part by weight of the fibrous material, immersing said material in a solution of carbon disulphide, regulating the time of immersion until the surfaces of the material previously treated with caustic soda have absorbed an amount of the carbon disulphide solution from 25 to 50 per cent by weight of the untreated portion of the fibrous material.

9. A continuous method for the production of a binding material for use in the manufacture of paper and the like, comprising, in combination, the steps of passing fibrous material through a solution of caustic soda, confining said material in said solution until the outer surfaces only of the fibres of said material have reacted with the caustic soda, thereafter passing said material through carbon disulphide, maintaining said material in contact with the carbon disulphide until the treated surfaces of the fibres have reacted with the carbon disulphide and thence, after complete xanthation of the treated surfaces of the fibres immersing said material in water.

10. A continuous method for the production of a binding material for use in the manufacture of paper and the like, comprising, in combination, the steps of passing fibrous material through a solution of caustic soda, confining said material in said solution until the outer surfaces only of the fibres of said material have reacted with from 3 to 5 parts by weight of caustic soda to one per cent by weight of material treated, thereafter passing said material through carbon disulphide, maintaining said material in contact with the carbon disulphide until the treated surfaces of the fibres have reacted with the carbon disulphide and thence, after complete xanthation of the treated surfaces of the fibres immersing said material in water.

11. A continuous method for the production of a binding material for use in the manufacture of paper and the like, comprising, in combination, the steps of passing fibrous material through a solution of caustic soda, confining said material in said solution until the outer surfaces only of the fibres of said material have reacted with from 3 to 5 parts by weight of caustic soda to one per cent by weight of material treated, thereafter passing said material through carbon disulphide, maintaining said material in contact with the carbon disulphide until the treated surfaces of the fibres have reacted with the carbon disulphide to the extent of from 25 to 50 per cent by weight of the untreated material, and thence, after complete xanthation of the treated surfaces of the fibres immersing said material in water.

12. As a new article of manufacture, cellulose material comprising a plurality of fibres, each having an unxanthated core covered with xanthated cellulose.

13. A product of the class described comprising a fibre treated with xanthating solutions characterized by the fact that the core thereof consists of unxanthated cellulose and is surrounded by a body of xanthated cellulose.

14. A product of the class described comprising a fibre treated with xanthating solutions characterized by the fact that the core thereof consists of unxanthated cellulose surrounded by a body of xanthated cellulose, and which is soluble in water or in water containing alkali.

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