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METHOD OF OBTAINING EASILY-BLEACHED CELLULOSE FIBERS.

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To all whom it may concern:

Be it known that I, BRUNO POSSANNER VON EHRENTHAL, a citizen of Germany, residing at 26 Ecknardstrasse, Cothen, Anhalt, Germany, have invented new and useful Improvements in Methods of Obtaining Easily-Bleached Cellulose Fibers, for which I have filed applications for patents in Germany on August 7, 1919, and November 24, 1919, and of which the following is a specification.

This invention relates to a method of obtaining easily bleached cellulose fibers, as a cotton substitute capable of being directly spun in cotton mills and as raw material for the manufacture of paper, nitro-cellulose, etc., from various vegetable fibers and waste, such as linseed and hemp seed straw, jute, rushes, nettles, agave, potato stems and stalks, willow bark and the like.

The various straw and vegetable stalks of linseed and hemp seed straw, of jute, rushes, nettles, agave, potato stalks, willow bast and the like contain, in addition to short, polygonal parenchypmatous and schlerochymatous cells, which are found in large quantities in these plants, also 10 to 40 per cent fusiform elongated prosenchymatous cells in elongated fibrous bundles or strands, which are generally termed bast fibers. These bast fiber strands, whose length vary up to one metre or more, are however not individual vegetable cells, but bundles of cells which consist of numerous comparatively short fusiform separate cells of 20 to 50 millimetres length joined together in adjacent rows.

The treatment of such bast fiber plants for the production of fibers for spinning purposes is an old problem which it has frequently been attempted to solve. Thus, e. g., it is known (see British patent specification No. 13,642 of 1897) to treat vegetable fibers by treatment under heat with tartaric acid and thereafter with soap and ammonium carbonate to render the fibers useful for industrial purposes. It is also known to boil fibrous plants in slightly acidulated water, then to treat the same with alkalki and finally with soap solutions; it is similarly known to treat duly prepared fibrous substances with soap solutions either in order to wash out the final remains of vegetable matter and the like or to neutralize the acid residues and finally to make the fibers glossy, soft and pliable and thus more suitable for spinning and combing. All these and similar known processes however aim at obtaining these vegetable fibers in the form of long fibers, i. e., in the form of bast strand as long as possible and composed of numerous separate cells in order to use them in long fiber spinning, that is, according to the methods adopted for spinning worsted, flax and jute. In such case, the bast fiber bundles are only treated for the purpose of rendering them soft, pliable and easily bleached while the bast fibers maintain as far as possible their original length and in no case are broken up into separate cells, for the reason that the spinning according to the long fiber method is only possible with long bast fibers and not with short separate cells of only 20 to 50 millimetre length, broken up into single cells.

It is however in practice of the greatest importance to open up such vegetable fibers so that, without being shortened in their natural cell length or weakened in strength, they may be completely split up into single cells so that a fibrous material will be obtained which can be bleached and directly used as a cotton substitute in cotton spinning mills, as the size of the separate cells (20 to 50 millimetres) and their nature are very similar to the cotton cells of 20 to 40 millimetres length and thus a scarcity of cotton can be overcome by utilizing comparatively worthless waste materials.

The present invention has for its object to open up the fibers into their separate cells for spinning in cotton mills. Consequently two requirements must be fulfilled, firstly, as complete splitting-up as possible of the bast bundles into separate cells whilst carefully preserving the strength of such cells and secondly maintaining this condition after drying in such a way that the single fibers, once separated, cannot during drying or felt together again into fibrous bundles. Thus the present invention differs fundamentally from the hereinbefore-mentioned known methods in that, apart from the different chemical opening method, the treatment, (in contra-distinction to the known methods), is extended to breaking up the bundles into separate fiber cells. A further fundamental difference not only from these methods but also from all cellulose treating methods including those which depend on the production of separate cells,

consists in a quite new technical effect, i. e., in the so-called "isolation" hereinafter described. This causes the fibrous mass once split up into the individual cells, to remain in this condition and not stick or felt together again during drying. Without this isolation, this sticking or felting together would again take place with every treated fibrous material, even such perfectly treated fibers as wood cellulose or mechanically digested wood bast, will, during the drying operation, shrink and felt into a firm pulpy mass which presents the greatest mechanical resistance to its reduction into separate fibers.

In carrying out the splitting up process on a large scale, considerable difficulty in separating the individual fibers is experienced as in the known methods the separation is either incomplete in which case the fiber bundles are not completely split up into individual fibers, or if the treatment is complete, the cells are affected by the chemical reagents and therefore become weaker and brittle. There is also the difficulty arising out of the felting and sticking together during drying, already referred to.

By means of the present invention, these difficulties are overcome and a fiber is obtained from the aforesaid plants in which, whilst fully preserving the natural length and strength of the individual cells, the fiber bundles are completely separated into single cells and these single cells remain always isolated, so that a fibrous material thus produced, after washing and drying still consists of flocculent extremely fine separate cells of 20 to 50 millimetres length and which can therefore be immediately spun on the usual cotton spinning machinery.

The method according to the present invention comprises three different chemical successive operations which effect the gradual loosening, solution and isolation of the cell groups of the vegetable fibers whilst fully preserving the length and strength of the individual cells, viz:

1. Hydrolysis of the incrusting substances.

2. Partial breaking up and solution of the incrusting substances and splitting up of the cell groups into individual cells.

3. Permanent isolation of the separated individual cells.

I. Hydrolysis.—First of all the dried, raw plant stalks and fibers are digested, either without or after mechanical treatment, at ordinary or a higher temperature, with or without pressure, in the presence of dilute aqueous solutions of free acid or acids (inorganic or organic acids) or acid salts of these acids for a few hours up to several days. This effects a partial hydrolysis of the incrusting substances and binding substances of the fibers and cells (lignin substances, pectose, pectinate of lime, pentose, etc.), which in part have the character of salts or esters. Owing to this hydrolytic separation, these incrusting substances dissolve slightly in the hydrolyzing liquid, whilst the greater part is more easily and completely dissolved by the hydrolytic action of the subsequent breaking up operation without the strength of the cellulose suffering thereunder. The time of duration, temperature, pressure and strength of the reagents used in this hydrolytic action depends on the more or less ligneous nature of the raw material, but generally solution of 0.5 to 2% of free acid and temperatures of 40° to 50° C. will be sufficient.

II. Breaking up.—The hydrolyzed material is thoroughly washed and must then go through a chemical opening operation whereby the incrusting and binding auxiliary substances of the cellulose are completely dissolved, whilst the fiber bundles and strands are thus split up into separate cells. For this purpose the fibrous material is treated with dilute alkaline solutions, caustic soda, soda, ammonium compounds, lime-water and the like in suitable digesters at the ordinary or high temperature with or without pressure. The temperature, pressure and strength of the boiling liquid depend on the nature and ligneous nature of the fibrous material and must be such that the fibers are not damaged and do not become brittle, whilst the breaking up into individual cells takes place. It is preferable not to carry out the boiling continuously under high pressure, but only to heat the material for a short time, say 30 to 60 minutes at a pressure of 6 to 10 atmospheres and then to continue boiling at 4 to 6 atmospheres. The necessary boiling period may vary according to the selected raw material from 6 to 12 hours. The purpose of this boiling operation is to effect an extensive splitting up and breaking down of the incrusting and binding substances, which at the same time are dissolved by the alkaline boiling liquors. This dissolving action is substantially increased and the results of the boiling action are improved, by the addition of small quantities (1 to 2%) of suitable organic solvents such as alcohol, carbon bisulphide, acetone, petroleum, hydrocarbons and the like which can be recovered for reuse after the boiling is completed.

By this treatment the fibrous material is completely broken up into the individual cells, i. e., the individual cells are completely separated and the incrusting and binding substances completely dissolved out. After boiling, a very thorough washing must take place in order to completely remove the boiling liquor and dissolved substances from the fibers.

It has however been found that even with

the most thorough washing, the organic substances dissolved in the liquors cannot be completely washed out of the fibers and that the individual cells after drying, again adhere together and assume more or less a straw character, so that they are only poorly adapted for spinning, because they must be forcibly separated from the cleaning and initial spinning machines and thus become torn and shortened in cell length and in consequence of this disadvantage produce a cellular substance only suitable to a low degree for spinning purposes. This disadvantage can be mitigated by suitable washing, but never can be thoroughly overcome thereby. A further chemical treatment is necessary for this purpose, which will be termed "isolation."

III. Isolation.—The boiled and washed fibrous material is steeped in an isolating solution composed according to the effect to be obtained and left therein for some minutes or up to several hours at ordinary temperature or whilst gently heating (up to say 60° C.), then taken out, washed and dried. The isolating agents may be oleic and fatty acid salts, organic sulpho-acids, amides of fatty and oleic acids, as well as free fatty and oleic acids and the like, which are used in aqueous solutions or emulsions of required strengths. The action of these isolating liquids is probably two-fold, in that the final residue of the boiling liquors is driven out of the fiber which is apparent from the brighter color of the fibrous material, the residues of the liquors passing into the water of the emulsion, whilst on the other hand the individual cells are at the same time saturated by or enclosed in the isolating medium, whereby individual cells are prevented from again sticking together during drying. At the same time the fibers by this treatment are left extremely pliable, smooth and flexible and thus have the properties of a highly valued spinning material which is particularly suitable for spinning on the three-cylinder system of cotton mills, but however also represents a valuable raw material for paper and pulp manufacture, for nitro-cellulose manufacture and the like.

A further advantage of this isolation is that the wood or bark particles, still adhering to the fibers and which otherwise adhere very firmly and must be forcibly torn out by carding engines or similar machines, which in turn give rise to destruction of numerous cells, fall out quite readily by themselves after the aforementioned treatment and after the drying operation, without destroying the fiber cells in any way.

Example.—The raw material such as flax-straw or linseed straw, is subjected in a suitable vessel or tank to the hydrolytic action of a 2% solution of bisulfite of sodium corresponding to about 0.5% of free acid. The material is left in the vessel or tank containing said solution for about three hours at a temperature of 50° C.

The thus prepared fibrous material is then washed with water and thereafter treated with a boiling 1% solution of caustic soda for three to four hours either at ordinary pressure or at a pressure of two to three atmospheres. The said solution of caustic soda is preferably given an addition of ½ to 1% of petroleum or any other suitable organic solvent.

At the termination of the boiling operation the fibrous material is again washed with water and thereafter treated with an insulating liquid, such as an emulsion of 0.1% Turkey red oil in water, by simply dipping the said material into the emulsion whereupon the material is freed from any excess of adhering liquid by removing the latter by squeezing and pressing. The still wet material is then dried without being subjected to any previous washing.

In some cases it will be desirable to modify the breaking-up process in the manner hereinafter described in order to further improve the product and ensure a maximum strength of the separated fibers, especially for the production of fine counts of yarn. In this modification, the process can also be carried out completely at ordinary pressures, using simple open vessels, thus not only increasing the reliability of the method, but also substantially decreasing the cost of plant and the working costs. It also affords a better opportunity for watching the progress of the breaking-up operation and for interrupting the progress of the reaction at the proper moment and before damage to the strength of the fiber or other disadvantages can occur. Cleansing and washing operations are preferably interposed between the various treatments thereby facilitating and accelerating the breaking-up into separate cells, whilst efficiently protecting the fibers.

The modified method is carried out in preferably four operations as follows:—

I. Steeping.—The raw or mechanically prepared vegetable substances are immersed in water in open vats with tilting arrangements or the like, in a similar manner to hemp and flax retting, and are allowed to soak or steep for 3 to 6 days at 30–50° C. until the abundant appearance of gas bubbles indicates the commencement of the retting and the consequent partial breaking away of the incrusting substances. This retting water is then drawn off and may be used again upon fresh raw material. The remaining fibrous material is washed in the vat and afterwards decanted by tilting it into a lower reaction vessel in which the further treatment is effected.

II. Hydrolysis.—The steeped fibrous ma-

terial is subjected to the action of dilute aqueous solutions of free organic or inorganic acids or acid salts for a few hours up to two days at ordinary temperature or up to a maximum of 30° to 40° C. This and the subsequent operations may be carried out alternatively in rotary or shaking boilers of the kind commonly used in paper and cellulose factories.

If the hydrolysis is effected at an elevated temperature the slight heat necessary therefor may be obtained by combustion of the large quantities of waste scrapings or beards which are separated during the mechanical treatment.

When the hydrolytic treatment is completed, the acid liquid is drawn off and used for hydrolytically breaking up fresh steeped material, whilst the residual fibrous material is washed in the boiler under the continuous supply of fresh water and if necessary whilst simultaneously and slowly rotating the boiler, until the wash water no longer gives any acid reaction.

If very fine and completely isolated fibers are to be produced, it is desirable to subject the hydrolyzed and washed fibrous material for a few hours up to two days to the action of an organic solvent between the hydrolysis and breaking-up stage, adopting also higher temperatures, since such solvents have no deleterious effect upon the fibers. The partially hydrolyzed and loosened incrusting substances are to a large extent brought into solution by the organic solvents, whilst to some extent they only separate from the fibers and remain in suspension, or settle as a muddy deposit. When the treatment is complete, the solvent is drawn off, and recovered in suitable vessels by distillation, and purified, whilst the dissolved and suspended substances remain as a deposit. The solvent still adhering to the fibers after the drawing off operation is recovered from the liquor and may be used in the subsequent opening-up operation, either by precipitation or distillation, so that practically very little solvent is lost. Suitable organic solvents are, for example, ether, petroleum ether, alcohols, carbon disulphide, acetone, carbon tetrachloride, petroleum distillates and the like.

III. Breaking-up.—The hydrolyzed and thoroughly washed fibrous material (purified in certain cases by treatment with organic solvents) is now subjected to an operation which effects the breaking up and the complete removal of all of the incrusting substances completely from the fibers by dissolving them, whilst simultaneously separating the fibrous bundles and strands completely into individual cells. For this purpose the fibrous material is treated in the same boiler with dilute alkaline solutions (caustic soda, soda, ammonium compounds, lime-water and the like) at ordinary temperature or gently heated (30 to 50° C.). The temperature, strength and duration of this opening up operation depends on the nature of the fibrous material. They must be so selected that the fibers are not damaged and do not become brittle, whilst effecting separation into individual cells. The time required for this purpose varies from one to several days. The action of these alkaline liquors may be accelerated by the addition of small quantities of suitable organic solvents (alcohol, carbon disulphide, acetone, petroleum or other hydrocarbons and the like) which may be separated and recovered from the final liquors of this process. The alkaline liquors can be repeatedly used.

By slowly and periodically rotating the boiler, the action can be increased, and a better and more uniform penetration of the liquor into the fibrous material can be thereby obtained. By this treatment, the fibrous material will be thoroughly broken up into the individual cells and the latter completely separated and the incrusting and binding substances completely dissolved out.

The use of lower temperatures and ordinary afmospheric pressure enables one to superintend the process and to interrupt it at the time when the necessary degree of breaking up is attained, so that an excessive chemical action and consequent damage of the fiber can readily be obviated.

The thus treated fibrous material must be thoroughly rinsed by a suitable washing process after decanting the alkaline liquors. The splitting-up into individual cells is thus thereby facilitated. By using a current of wash water flowing contrary to the material, the cleansing water becomes so alkaline that it can be used again for the breaking-up process.

It may be desirable or necessary to vary the sequence of the chemical actions hereinbefore described and thus vary the resulting effect.

The subsequent treatment consists of:

IV. Isolation.—Which is effected in the manner hereinbefore described.

This isolating process can also be used for fibrous materials which have been broken and split into individual cells by any other process, that is, already split up into the individual cells, in order to prevent the adhesion and felting together of the individual cells of the material. Complete breaking-up and isolation whilst preserving the strength of the fiber is only possible however by using the opening up process hereinbefore described. Complete splitting up into the individual cells without the individual cells being damaged in strength and length, so

that a really useful substitute for cotton with equal staple and spinning qualities is obtained is possible only by this process.

After treatment with the isolating liquid, the fibrous materials is freed from the excess liquid by draining, siphoning off or the like, and then dried at low temperatures in loose fleeces.

Example.—The raw fibrous material such as flax-straw or linseed-straw is retted or soaked in water for three to four days at a temperature of about 40° C. The thus preliminarily treated material is then subjected, just as in the hereinbefore described example, to the hydrolyzing action of a solution of bisulfite of sodium corresponding to about 0.5% of free acid, say for about 24 hours at a temperature of 35° C. After that the fibrous material is separated from the solution and washed with pure water in order to be properly prepared for the subsequent operation. The latter consists in treating the washed material with a 5% solution of caustic soda heated to a temperature of 50° C. The material is left in the said solution for several hours, and if desired or required, 0.5 to 1% of an organic solvent may be added to the solution prior to use.

Subsequently the fibrous material is removed from the caustic solution and washed with water just as in the above described example, whereupon it is soaked in an insulating liquid, pressed and dried with any further intermediate washing operation.

A very light and flocculent fibrous material is thus obtained, as the degree of breaking up can be varied and interrupted as desired. A fibrous material material is obtained by this process which can be spun in flax and worsted spinning mills and particularly in cotton mills on the three-cylinder system, as a complete substitute for the usual fibers, but which naturally constitutes also a valuable raw material for paper manufacture and for the production of nitrocellulose and other cellulose esters.

The fibrous material produced is characterized by its particular strength and uniform staple length. Furthermore, owing to the careful treatment at ordinary temperature or at a gentle heat, the cellulose of the fibers is not attacked at all so that the highest yield of spinning material is thus obtained, which is again of great practical importance. It may be emphasized that at the temperatures employed, the waste wood particles (scrapings and beards) from the mechanical treatment are sufficient to be used as fuel to provide the necessary heat, so that this process involves only slight or no consumption of coal.

Finally it may be mentioned that for carrying out this process satisfactorily, the utensils and their arrangement may and must be such that practically no manual labour will be necessary, the whole process of treating the boiled material, raw material, liquors, waste, etc., taking place mechanically and automatically.

I claim—

1. Method of obtaining easily bleached cellulose fibers from vegetable fibers and waste which consists in subjecting the raw material to an acidic hydrolytic action, treating the hydrolyzed material with dilute alkaline solutions and finally isolating the cells of the fibers by means of an oleic or fatty reagent, substantially as described.

2. Method of obtaining cellulose fibers as specified in claim 1 in which an organic solvent is added to the alkaline solution, substantially as described.

3. Method of obtaining cellulose fibers as specified in claim 1 in which the acidic action is effected by means of dilute solutions of acid salts substantially as described.

4. Method of obtaining cellulose fibers as specified in claim 1 in which the isolating reagent consists of an oleic or fatty emulsion substantially as described.

5. Method of obtaining cellulose fibers as specified in claim 1 in which the isolating reagent consists of a fatty acid compound substantially as described.

6. Method of obtaining cellulose fibers as specified in claim 1 in which the raw material is subjected to a preliminary water retting process substantially as described.

7. Method of obtaining cellulose fibers as specified in claim 1 in which the sequence of operations is varied as required substantially as described.

In witness whereof I affix my signature.

Dr. BRUNO POSSANNER von EHRENTHAL.

Witnesses:

ARTHUR SCHOLZ,
ROBERT SCHAPER.