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PROCESS FOR TREATING FIBROUS MATERIALS

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Fig. 1.

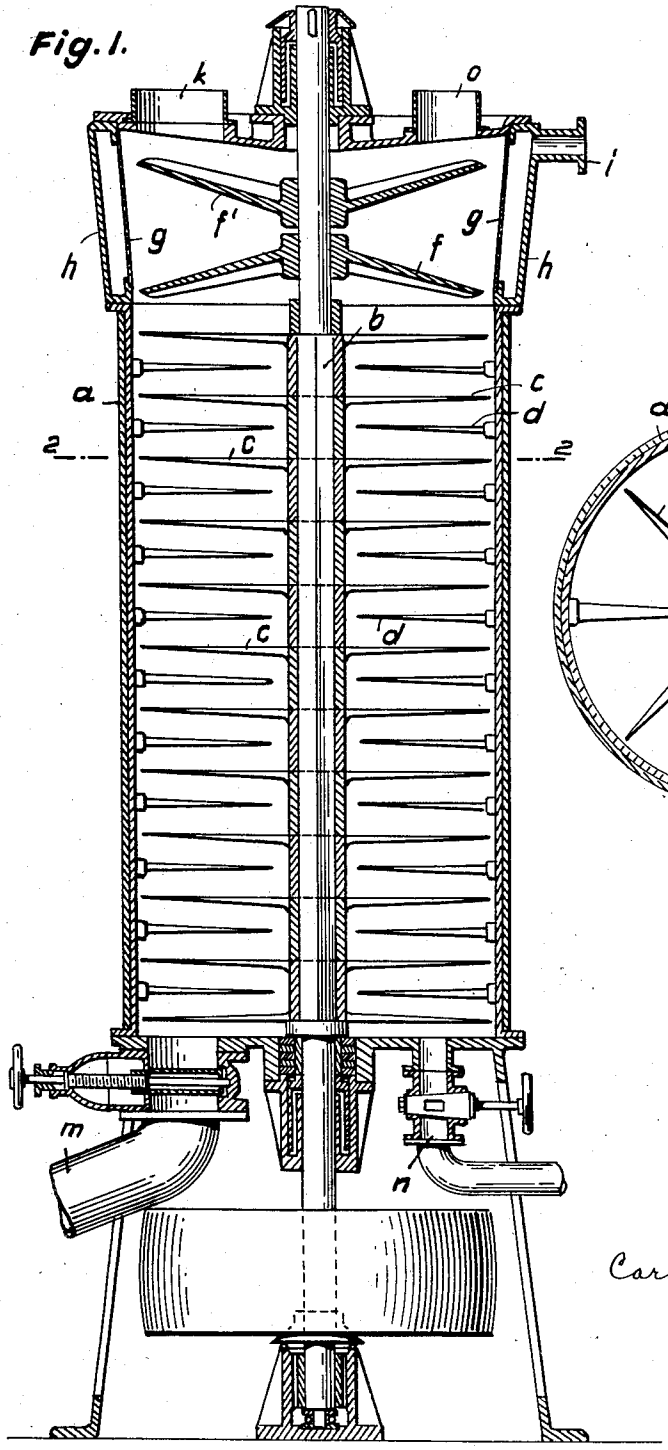
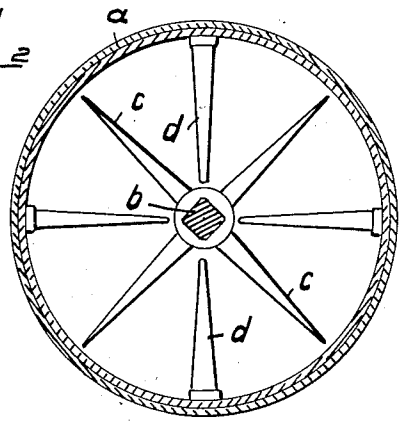


Fig. 2.



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UNITED STATES PATENT OFFICE

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PROCESS FOR TREATING FIBROUS MATERIALS

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Up to the present all technical procedures for dissolving semi- or full-cellulose stuffs by boiling from ligneous or strawlike raw materials have endeavoured to obtain the digesting results by the following methods:

1. By boiling a slowly rotating mass of raw material in a rotary cooker.

2. By using steam for boiling with the least possible quantity of water and under increased steam pressure.

3. By using steam for boiling stationary raw material in a vertical or horizontal cooker.

4. By boiling effected by a sudden influx of steam into the stuff.

These four procedures are considered scientifically and technically as closed and not improvable. With the exception of slight variations without changing the main principles, apparently no novel procedures are possible.

It is therefore first of all necessary to explain that the errors and deficiencies of these four old procedures, are very considerable, so as to demonstrate comparatively the novel technical principles of hertofore unknown high-speed hydrodynamic disintegrating action and the frictional boiling process.

Using procedure 1, viz, boiling a rotating mass of raw material no higher speed than 15 turns per minute as a maximum can be obtained, owing to the enormous weight of the rotary iron cookers of 10 or more tons. Owing to this limited speed it is impossible to produce a noticeable movement of the raw stuff. Further as the raw stuffs, for instance chaff, bamboo, esparto grass, bagasse or wood chips are generally pressed or stamped as much as possible into the iron cooker, the particles of stuff have no sufficient space inside the boiler, to move effectively one upon the other. What really happens is that the pressed up stuff slowly turns inside the cooker like an enormous cork inside the neck of a bottle, without the pieces sliding over or rubbing against each other. Even if the cooker is only half filled, its speed of 12 to 15 turns p. m. is much too small to produce an effective internal friction in the mass of stuff. When describing the high-speed process involving a hydrodynamic disintegrating motion the importance of a high-speed of 200 to 1200 turns p. m. of the boiling-stuff motion will be demonstrated.

Studies during many years have definitely shown that the boiling process described under 2, employing a slowly rotating or stationary cooking under increased steam-pressure, pressures up to 120 lbs. and even higher, is defective insofar as the high pressure leads to a carbonization of the outside particles of each piece of straw-chaff or wood chips in the iron-cooker in the interior of the mass of raw stuff. This carbonization is proved by the increase of a brown-black colour of the stuff, which becomes darker the longer the steam pressure acts upon the same. But owing to the fact that any corbonization only takes place under superheating, every partial carbonization signifies a production of semi-oxy-cellulose steps. Every fibre, consisting by nature of different steps of growth, changes over, when being super-heated, in the same step of fibre variation into oxy-cellulose or semi-oxy-cellulose, this being a preliminary grade of oxy-cellulose. For the reason that therefore the exterior layers of the boiling stuff are principally exposed to being superheated, the largest quantity of oxy-cellulose is produced in these layers, which, when exposed to the first washing process, is dissolved, causing a certain loss in output, while the semi-oxy-cellulose resisting the first washing, is dissolved during the further procedures in the crushing mills and finishers, thereby further increasing the losses in output. This is, for instance, the reason why cellulose which has been boiled under too high a pressure and then changed to viscose, and after squirting the viscose filament when entering the sulphuric acid bath, suffers excessive rupture of the filament through the dissolution of semi-oxycellulose. This is why up till now only the Swedes are able to produce wood cellulose for artificial silk viscose at low pressure and with careful bleaching. Also the cotton filament which is comparatively much tougher than the cellulose thread, loses considerably in tensile strength under pressure. The investigator Mr. Albert Scheurer has

proved (Theis "Die Breitbleiche" Berlin, published by Krayn, pages 140–142) that cotton filament having a tensile strength of 55 lbs. after boiling 8 hours at 345° F., or at 76 lbs. pressure, drops already to 40 lbs. tensile strength, which signifies that a higher pressure will in any case deteriorate even the strongest filament, always considering, that the natural tensile strength of the cellulose filament is lower than the cotton or hemp filament, thereby deteriorating more quickly under higher pressure.

The boiling process described under heading 3. effected in a vertical or horizontal iron cooker, as, for instance, the sulphite wood-cellulose process, which is carried out in huge digestors having an acid-proof tiled lining, has the following disadvantages. Each layer of boiling stuff has a certain gravity effect which increases from layer to layer. In a cooker 50 feet high and 6 feet in diameter the lower layer up to a height of 6 ft. receives a hydraulic pressure of 31 metrical tons, increasing to 36 tons at the bottom, viz. to 21.5 lbs. per sq. in. This pressure on each layer effects a compression of the fibre particles and therefore a closing up against the resorption or inflow of the lye. This is the reason why the composition of the lye must be much stronger than would appear to be necessary, the strength generally used being 3% sulphurous acid and 1% milk of lime, whereas from consideration of the individual wood chips, it might theoretically be 30% weaker. But owing to the high pressure of the layers a proportional increase of the strength of the lye is necessary to overcome this pressure so as to enter into the interior of the boiling stuff. Hereby too much oxy-cellulose is again formed in the outer layers, diminishing the output. In straw-like stuffs the pressure on each layer increases a sticking-together tendency, viz. an increase of the adhesion. It is therefore practically impossible to boil straw or similar materials in a stationary boiler, so that this stuff is always cooked in turning boilers, whereby the disadvantages explained under heading No. 1 appear over again.

If in the old procedures steam has been the main factor, it is still necessary to describe the disadvantages of a sudden influx of steam as defined under heading 4. All strawlike stuffs absorb up to 200% either in a raw or in a developed state, all timber more or less up to 100%. These absorption phenomena are of great importance in boiling. When the lye can continuously penetrate into the raw stuff, due to this absorption, the latter is more uniformly digested, just as much in the center of the mass as in the exterior layers. A similar absorption process cannot, however, sufficiently take place, if the steam is being suddenly admitted. Many paper manufacturers complain of the fact that inside the cooker socalled "boiling provinces" are formed on a sudden influx of the steam, which signifies that parts in the centre of the boiling mass are formed, which clearly show a distinctly worse boiling effect and which at the end of the process, have not been as thoroughly digested as in the exterior layers. This unfavourable phenomenon is caused by the following. In all strawlike materials a contraction of the cell-canals (lumina) at the sides of the straw takes place due to a too rapid influx. Hot steam being admitted, the pectine crusts which surround the cell canals as protective covers harden at first, soften very slowly as soon as the lye becomes hotter and begins to penetrate. But after this the time of action is very considerably reduced. Taking 5 hours as boiling time, the lye requires, also when steam is suddenly admitted, at first one hour for heating (temperature rise) and more than 1 hour for the osmotic penetration into the boiling mass. But in this case one third of the boiling time, has been used unproductively and has therefore been wasted. Without seeing the biological reasons many paper manufacturers help themselves by a preliminary heating of the cooking lye. In reality the thermo-dynamical transition in the temperature from degree to degree is wanting, which favours the penetration of the lye and which does not come into action in a sufficient manner with a steam influx at 302 degrees F. All straw-like material as well as timber require thermo-dynamical degrees of temperature rise of say 50–68–104–176–212–230–248–266–284–302 degrees F. so as to absorb the lyes as favourably as possible, so that the absorption and swelling, interdepending upon each other in an equal degree may take place from step to step in the shortest possible time. While this absorption of the lye by degrees is handicapped by a sudden influx of steam, it takes place step by step when applying frictional heat developed by a high-speed number of turns of the lye-mixers. It favours and heightens the influx of water and lye exactly in the same space of time into the boiling mass, as this latter permits according to its natural swelling and absorption, as will be explained later on.

These disadvantages of the four old procedures are almost entirely removed by the novel cooking, milling and digesting process using a high speed motion of the raw-stuff mixtures involving a hydrodynamic disintegrating action producing frictional heat. This combinative invention worked out after many years of study depends upon the following novel technical ideas and effects. A universal machine, provided with a vertical shaft fixed to which are long sharpened revolving swords, is filled with a certain amount of cold water together with wood chips or strawlike chaff or similar materials. In the drawing a constructional example of

the device used in carrying out the new process is represented. My universal-engine consists first of an acid resisting cast-iron drum *a* which also may be produced of wrought iron. In the middle of the drum is a vertical four cornered-shaft *b* on which is fixed distances of 70–180 mm. from sword to sword (in specially cases to 220 mm.) rotary steel swords or knives *c* with sharp edges are fastened. On the inside of the drum *a* are fastened a certain number of stationary steel swords or knives *d* with sharp edges, each stationary sword *d* standing midway between two of the sharpened swords *c*. In an upper chamber enclosed by a sieve-basket *g—h* are two propellers *f* and *f'*. The downwardly bent propeller *f* holds the dancing stuff down while the upwardly bent propeller *f'* draws the dirty water or assortable stuff toward the top past a sieve-basket *g—h* in the putout-hole *i*. Similarly two upwardly bent propellers can be arranged on the bottom.

If the stuff is ready milled or washed or bleached, the outlet hole *m* is opened, whereupon the two lowermost swords *c* sweep out the stuff automatically. When dirty stuff is to be washed, a considerable surplus of fresh water is running in at the inlet hole *n* and the rotation diminished to half-speed, whereupon automatically the dirty water is drawn out at the headsieves *g—h*. The same headsieves serve also for the first preliminary assorting after insertion of suitable assorting-sieves. The first assortable stuff can be assorted within half an hour. If the stuff is to be bleached, the engine is filled through the inlet hole *k* at the top, the charging of the stuff being followed by running in the chloride of lime liquor. During the bleaching the rotation is diminished and specially here is shown the importance of the exact long swords for avoidance of dangerous stuffnests. After the first preliminary bleaching, the first thinner bleaching liquor may be drained, followed by washing and then finish bleaching but it is also possible to carry through a perfect bleaching of two hours in one stage of manufacture. After finishing the bleaching the engine automatically is washed. The washing water again is run in at the bottom at *n* and led out again at the top *g—h*. The bleached stuff can—because the engine consists preferably of acid-sure founding and for bleaching-purposes is equipped with wooden movers and with a shaft covered with wood—the neutralizing also can be expected. Therewith the washing water at *g—h* flows off lighter, the propeller f^1 on the top is formed a little upwards. In this way the propeller *f* of the upper propellers presses the stuff downwards; the upper propeller f^1 the washing water or the swimming assortable stuff upwards, therewith the stepping-out by the sieve-baskets *g—h* is lightened. For strengthening the effect in the whirl-zone the rotary and stationary swords can be equipped with smaller swords. For insuring complete bleaching cloride of lime can be forced into the drum at each whirl-zone by compressed air or chlorine gas. If the highest white colour is not required, but only a yellow-white colour, also SO_2 can be run in upwards, downwards or lateral by entrance-valves. *o* is a canal to conduct away steam.

The sharp rotary swords *c* are revolved at a speed which may run as high as 1500 turns per minute, whereby firstly the water is slung against the fixed sharpened counter-current swords or knives *d*, fastened radially to the inside of the iron drum. Through the velocity of the revolving water thrown against the fixed swords or knives a sudden back-flow comes into action, which, similar to water acting under a high head of pressure, acts upon the material contained in the water, helping to disintegrate the same.

At the same time an internal friction takes place between the water, the raw material and both together between the revolving and fixed swords *c* and *d*, owing to the high speed of turns. This friction develops heat by degrees, reaching inside of an hour a temperature up to 212 degrees F. equal to the boiling point.

Owing to this frictional heat a hydrolytical dissolving effect results which combines with the primary disintegrating factor, the motion of the water, and the action of the sharpened edges of the knives.

Through the combined action of these factors a semi-cellulose is developed from the raw material introduced into the drum without an addition of chemicals or any external heat, semi-cellulose from which a large part of the lignone and incrusting matter has been already dissolved. Upon adding alkaline matter, or acids or neutral salts full cellulose is developed, the time of milling being increased, the cellulose which may be bleached, attaining a high degree of tensile strength and other good qualities. The bleaching process may be carried out when the work is finished in the same "Universal-machine".

All these factors and novel technical effects take place in one and the same "Universal-machine, Leyst system", so that according to the old system the iron-cooker, the beating-engine besides the stuffchest, the finisher, the refiner and bleaching finisher altogether six units of the old system become superfluous. This necessitates at the same time only a part of the supervision required by the old system, besides economizing a large part of the countershafting, the power transmission, and the factory space, thereby extraordinarily simplifying the entire plant.

I now have to present some proofs and explanations which will demonstrate these novel effects. First of all many paper manu-

facturers are of a practical opinion—viz. the periodical "Papierfabrikant" No. 8 of 1909, page 2861—that every fine milling process with water has a hydrolytic effect. "Schwalbe" writes in this respect: (Chemie der Zellulose, page 15) "By hydrolytic effect very frequently the process of hydratization is understood. According to Gross (Cross & Bevan, 'Researches') cotton slime for example is an hydrate." Schwalbe, without indicating the novel process appertaining thereto, counts among the hydro cellulose stuffs those that develop: "by mechanical disintegration in the presence of water." In connection herewith it must be clear that Schwalbe means hereby the formation of oxy-cellulose resulting from a mechanical disintegration of cellulose stuffs in water, and not from raw stuffs. It is a well known scientific fact, and experience shows, that cellulose stirred in water just the same if milled or stirred, is partially dissolved forming slimes. This knowledge is standard for cellulose hydration, but it is a novel fact in connection with the present invention as a hydrolytic effect on raw materials from which semi-cellulose is to be produced through a high-speed motion with frictional heat. But this hydrolytic action is only possible without an addition of chemicals if—and this is the important factor—when stirring the raw material a high speed of 200 to 1200 and even more turns per minute is applied, thereby producing frictional heat. In this case effects are however produced, which can be attained either with a revolving or stationary boiling under pressure without chemicals, nor with a crusher mill, a finisher, or with a refiner unless chemicals are added during the boiling process. Even in this case the effect of a genuine semi-cellulose production does not take place if a stationary or revolving boiling process without the addition of chemicals and the combinative effect of beating-engine, finisher and refiner one after another has been applied. In the best case a hard, brittle stuff is always produced without having the qualities of semi-cellulose stuff. On the contrary genuine semi-cellulose is produced from which 20 to 25% of the lignone and incrusting matter have been extracted without the use of steam and without adding chemicals if ligneous materials are milled by sharpened knives rotating at a high speed, in a triple amount of water, for 2 hours, thereby economizing a boiling process of 5 hours, a consecutive treatment in a beating-engine of 1 hour, in a finisher of 1 hour and a refiner of 1 hour or a total of 8 hours as against 2 hours in the Leyst process.

This shows therefore that the high speed turns of the sharpened stirring devices in combination with the frictional heat developed has an up to now quite unknown extraordinary effect, but also that the high speed does not at the same time mill the stuff so much as to kill it or to produce an inferior product such as mechanical wood pulp. On the contrary, it saves the fibres, recovering them in their natural length, so that they can, in an increasing measure, be easily and economically manufactured into full-cellulose, which in the case of white mechanical wood pulp is economically quite impossible.

It is only a seaming contradiction, that the high turns are opposed by the stationary counter-current arms *d*. If these counter-current arms were absent, practically the whole mass of stuff would turn inside of the apparatus. But because stuff and water form one mixture which contains the stuff as a body giving material, the water as well as the stuff are slung against the sharpened counter-current arms. At or above 200 turns per minute the sling-effect is so great, that the increased water-pressure against wood has the effect of a water-cutting. This water-cutting is so effective that it does the work of grounding-engine, beating-engine and refiner, and does it better because these engines of the old system work too forcibly and too coarse by, impairing the organic structure of the paper-fibres. The water-cutting, which results from the rapid water-current, works so intensively that in connection with the frictional heat, it dissolves the material more and more and in this stage of the process also parts of resin will be dissolved, and the sharp rotary knives and counter-knives assist and multiply these effects. During the course of one and the same stage of manufacturing a technical combination between hydrolytic action water-cutting, and frictional heat is developed. This process can be assisted by a small percentage of all oils which contain hydrocarbon.

A very important factor is the increasing frictional heating of the water, which I now have to consider, rising to 212 degrees F. inside of an hour. As this frictional heating is a steadily rising one the raw stuff has time to fully imbibe without any reactive closing up of the cell canals. The stuff becomes saturated in all its pores up to the center with water and the increasing heat up to 212 degrees F. heightens the hydrolyte effect. Schwalbe judges that: (Chemie der Zellulose, page 20) "if boiling water does not effect a dissolution of the cellulose, the boiling itself produces certain changes." Scheurer has discovered (Theis: Die Breitbleiche, page 141) that steaming alone during 60 hours diminishes the tensile strength of woven matter about 20% and after 360 hours even to 70%. Danish and German inventors even want to digest straw stuff without using chemicals, but under pressure and with boiling. If however they have up to the present obtained only a very inferior stuff, which has to be treated too long in the crusher mill and which

has to pass through the beating-engine and all the other auxiliary machinery of the old system, it is scientifically generaly known that a boiling process without chemicals produces certain changes not only in meat, fish, fruit, vegetables but especially also in paper pulp, which cannot exclusively be obtained in a cold process. This is the reason why the action of frictional heat is much more advantageous than steam boiling, the latter having besides all the other disadvantages already described due to the sudden influx of steam.

The high speed number of turns generates a hydrodynamical disintegrating action and frictional heat. In parallel therewith these effects are heightened by the sharp edges of the revolving and fixed counter-current knives, in such a manner that by the united action of these novel technical factors semi-cellulose without the addition of chemicals can be manufactured from all cellulose-containing wood- and straw-stuffs, including bamboo and bagasse (pressed out sugar cane) palm tree, palm leaves, esparto grass or alfa, lorio, saboi and all other grasses in one and the same "Universal"-machine according to the Leyst system and in one and the same process of manufacture in 2 to 3 hours. If corresponding alkaline matter, acids or neutral salts are further added to the mass of pulp, the result with a slightly prolonged time of manufacture will be a highly qualified bleachable cellulose in one and the same "Universal-machine" of the Leyst system, in one and the same process of manufacture. In case these bleachable pulp stuffs are to be further bleached this is effected by adding bleaching matter in the same way in the same Universal-machine and the same working process in 2 hours.

The method of working is therefore the following: The prepared and broken up raw material is filled into the Universal-machine including at the same time three times and in some single instances of raw material up to four times their quantity of cold water without adding any chemicals whatever. According to the stuff, milling sets in with a speed of 200–300–400 up to 1200 turns per minute, during a period of 2 to 4 hours. After 1 hour's working frictional heating takes place and from 2 hours upwards ready finished semi-cellulose may be sorted off. If full-cellulose is to be furnished caustic soda, lime or other alkalin matter or neutral salts are added (from the beginning). When using acids, the Universal-machine is covered in the interior with an acid-proof material. After 6 to 7 hours work the cellulose is finished and can in the same working process, be washed and bleached by adding bleaching materials, then washed again and neutralized.

In this manner an entire cellulose manufacturing plant is simplified by this novel boiling, milling and bleaching procedure with frictional heat; the service, the countershafting and factory space is diminished; the cost of production is economized and an entire revolution of the old procedures involving a large economy of capital has been practically achieved.

By means of the novel high-speed and frictional heating process nowadays all cellulose-containing woods in the Tropics, of the American, African, Asiatic and all other primeval forests, which up till now it has not been possible to utilize owing to the enormous costs, can be manufactured into semi-cellulose by means of economical plants, excluding all cookers, grounding-engines, beating-engines, refiners and all import of chemicals, even in the middle of the primeval forests themselves. Further all sorts of straw stuffs can be gathered in the farthest countries and utilized as highly qualified products at low shipping rates.

On the other side now it is possible to transform such semi-cellulose with great savings of chemicals into finished cellulose. Exact experiments have shown that with 3½% caustic soda liquor and a proportion of dry stuff to liquor of 1 to 7.6, six hours boiling of the semi-cellulose has resulted in a finished cellulose capable of making paper having 6075 metre solidity. Since large factories always use a ratio of water to wood (dry weight) of only 3.3 to 1, practically the 3½% caustic soda is reduced to 1.52%, from which results a saving of more than 50% in chemicals, regeneration, coal, and labor.

I claim:

1. Process of working up raw cellulosic materials into semi-cellulose, which comprises subjecting the raw material to a combined hydrodynamic and frictional heating treatment.

2. Process of working up raw cellulosic materials into semi-cellulose, which comprises mixing the raw material with a greater quantity of water, and subjecting the mixture to the action of high-speed whirling swords and interdigitated stationary swords.

3. Process of working up raw cellulosic materials into semi-cellulose, which comprises mixing the raw material with a 2.5 to 7.6 fold quantity of water, and subjecting the mixture to the action of high-speed whirling swords and interdigitated stationary swords.

4. Process of working up raw cellulosic materials into semi-cellulose, which comprises mixing the raw material with a greater quantity of water, and subjecting the mixture to the action of interdigitated stationary and whirling swords, the latter having a rotational speed of at least 150 turns per minute.

5. Process of working up raw cellulosic materials into semi-cellulose, which comprises mixing the raw material with a greater

quantity of water and a small proportion of mineral oil, and subjecting the mixture to the action of high-speed whirling swords and interdigitated stationary swords.

6. Process of converting raw cellulosic materials into perfect cellulose, which comprises mixing the raw material with a greater quantity of a chemical liquor, and subjecting the mixture to the action of high-speed whirling swords and interdigitated stationary swords.

7. Process of treating raw cellulosic stuff which comprises mixing the stuff in a drum with a greater quantity of water, subjecting the mixture in the drum to the action of high-speed whirling swords and interdigitated stationary swords until the stuff is disintegrated, and then adding a bleaching agent to the material in the drum.

8. Process of converting raw cellulosic material into semi-cellulose, which comprises mixing the raw material with a greater quantity of water and subjecting the mixture to a combined hydrodynamic and frictional heating process produced by the action of interdigitated high-speed whirling swords and stationary swords.

9. Process of producing high quality cellulose from raw cellulosic materials, which comprises mixing the raw materials with a greater quantity of water, subjecting the mixture to the disintegrating action of high-speed whirling swords and interdigitated stationary swords until a considerable proportion of the incrusted substances have been removed, and then adding a chemical liquor and continuing the disintegrating action.

10. Process of producing high quality cellulose from raw cellulosic materials, which comprises mixing the raw material in a drum with a greater quantity of water, subjecting the mixture in the drum to the disintegrating action of interdigitated high-speed whirling swords and stationary swords until a considerable proportion of the incrusting substances have been removed, then adding a chemical liquor and continuing the disintegrating action until a bleachable cellulose has been produced, and then washing and bleaching the cellulose in the same drum by adding a bleaching agent.

In testimony whereof I affix my signature.

CARL LEYST-KÜCHENMEISTER.