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PROCESS FOR THE PRODUCTION OF CELLULOSE BY DECOMPOSITION OF VEGETABLE FIBERS.

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This invention relates to a process for the production of cellulose by decomposition of vegetable fibers. In order to obtain cellulose by the decomposition of vegetable fibers such for example as red pine wood, straw and the like, it has generally been the custom to boil the fibrous material with alkaline or acid liquids. In the former case the yields are poor and the cellulose obtained is often difficult to bleach, whilst the use of the latter liquids is attended with difficulties owing to their chemical action on the apparatus. In both cases waste liquors are obtained which can not or only with difficulty be further employed. It has been customary to concentrate the waste liquors and to burn them or to empty them into rivers, both of which courses are, however, wasteful because these liquors contain more than half of the raw material.

In addition to the liquids mentioned it has also been proposed to employ other liquids of neutral or slightly acid reaction, such for example as epichlorohydrin, C_3H_5OCl or phenol, C_6H_6O. These substances however have not come into general use owing to their high cost.

For some time grasses have been decomposed by means of chlorine in the gaseous form or by means of chlorine-containing liquids which has generally been done in combination with other processes, but this decomposition process involves a troublesome method of working, requires chlorine resisting apparatus, and could so far only be applied to grasses.

According to the new process forming the subject of the present invention the formation of waste liquors of such a kind that their further treatment on an industrial basis is not economic is avoided. The process enables all the component parts of the vegetable fibers to be utilized and yields a cellulose which without subsequent treatment is of a specially high grade. The yield is almost equal to the actual cellulose content of the vegetable fibers treated. The liquids used for boiling (hereinafter referred to as "boiling lyes") do not attack iron. The reacting chemicals consist of neutral salts which have no action at all or only a slight action on cellulose. Moreover that portion of the vegetable fibers which is dissolved is not decomposed to a great extent and the number of the decomposition products is relatively small and they are moreover easily utilizable. The cellulose obtained is practically free from the other component parts of the vegetable fibers.

Owing to the properties of the boiling lyes utilized according to the invention the most varied kinds of vegetable fibers such for example as those of red pine wood, beech wood, bamboo, straw and also resinous woods, such for example as Scotch fir, can be easily treated so as to yield high grade cellulose.

According to the invention boiling lyes are utilized which necessarily contain one or more soluble oxy-compounds of the isocyclic series, in which at least one hydrogen atom of the oxy group has been replaced by a metal, and I prefer to use for this purpose metals of the alkali group, certain of the alkaline earth metals, and metals of the magnesium group.

The following oxy-compounds of the isocyclic series may be utilized, these being given by way of example only and their international or so called Geneva designations being added in brackets:—

1. Phenols, for example, phenol (oxybenzene) C_6H_6O or cresol (oxytoluene) C_7H_8O;
2. Alcohol phenols for example, phenol alcohol (oxybenzyl alcohol or dioxymethyl benzene) $C_7H_8O_2$;
3. Cyclohexenol (tetrahydrophenol) $C_6H_{10}O$;
4. Hydrated phenols, for example cyclohexanol (hexahydrophenol) $C_6H_{12}O$;
5. Naphthols for example, alpha naphthol (oxynaphthalene) $C_{10}H_8O$;
6. Hydrated naphthols for example oxynaphthalene tetrahydride $C_{10}H_{12}O$ or oxynaphthalene decahydride $C_{10}H_{18}O$;
7. Methylcyclohexanol (hexahydroxytoluene) $C_7H_{14}O$;
8. Polyoxides for example resorcin (dioxybenzene) $C_6H_6O_2$;
9. Oxysulfones for example sulfonoxybenzene $C_{12}H_{10}O_2SO_2$;
10. Sulfo- or carbo-acids of the above substances and the salts of these acids including also metal salts which decompose on heating and form on the one hand oxycompounds and on the other hand sulphites or carbonates, such as for example oxybenezene sulfonic acid $C_6H_4OHSO_3H$, or oxybenezene carbonic acid $O_6H_4OHCO_2H$ and their sodium salts $O_6H_4ONaSO_3Na$ or $C_6H_4ONaCO_2Na$;

11. Functional derivatives of phenol and its homologues and especially such derivatives as contain alkyl or aryl groups which are split off on fusing with alkali provided that such substances contain one or more oxygroups the hydrogen atom of which is replaceable by metal.

The homologues and derivatives of homologues of the substances mentioned may also be utilized. Moreover in the case of the mono- and poly-oxycompounds in addition to the substitution by metal of the hydrogen in the oxy group, chlorine, bromine, iodine, or nitro groups may be substituted either in the ring or in the side chain. Further in the case of dioxycompounds one hydrogen atom and in the case of polyoxycompounds several hydrogen atoms, may be replaced by alkyl, aryl or acetyl groups provided that at least one oxygroup can be provided with a metallic cathion. The molecular constitution of these substances is not material and a plurality of them can be utilized mixed together, thus for example, ortho-, meta-, paracresol can be used either alone or mixed together.

The metals mentioned combine as cathions with the oxycompounds referred to as anions to form salt-like compounds, for example, phenolates or phenol alcoholates. The anions can be added to the vegetable fibers either separately or combined in the form of salts and either cold or warm.

For the purpose of decomposition the substances named are preferably utilized in the form of solutions or as permanent emulsions, that is to say, emulsions that will not separate. If the production thereof should be difficult the precipitation of the solutions or the separation of the emulsions may be prevented in any known and/or suitable manner by the addition of certain substances. For this purpose, for example, soaps of castor oil, cyclohexanol $C_6H_{12}O$ and salts of humic acid may be found suitable and these added substances may be so selected as either to increase, reduce or be without effect on the decomposing action of the boiling lye on the vegetable fibers. In every case it is immaterial whether the ions or salts are brought into contact with the vegetable fibers in the form of solutions or emulsions or undissolved in the presence of the solvent or emulsifying agent, and the anion or cathion component may also be present dissolved in slight excess.

For the purpose of assisting a more rapid penetration of the vegetable fibers there may be added alkaline, neutral or slightly acid salts, for instance trisodium phosphate Na_3PO_4, weak acids with basic, slightly alkaline, neutral or acid reaction, metallic bases, aliphatic or aromatic alcohols, phenol alcohol, as well as their homologues and functional derivatives, the latter being phenol derivatives the constitution of which is unknown.

For a similar purpose catalytically acting substances such as barium peroxide BaO_2 may be used.

The time of treatment, i. e. boiling time, depends on the nature and condition of the vegetable fibers to be decomposed, on the nature and strength of the boiling lye, the movement imparted to the boiling lye, or to the mass to be treated, and on the temperature and pressure employed. The decomposition can be materially expedited if before boiling the air which clings to and is contained by the fibers is removed, for example by application of reduced pressure or by replacement by other gases.

Just as most chemical reactions may be expedited by increase of temperature, pressure or both, so the decomposition of the vegetable fibers can be more rapidly effected according to the new process by the employment of higher temperatures or pressures. In the event of this involving any danger of deterioration to the boiling lyes for example as a result of oxidation and of their consequently losing their effect this can be guarded against by adding substances of neutral or alkaline reaction and reducing effect to the boiling lye either before commencing the process or during the boiling. As examples of such substances I refer to neutral salts of sulphurous acid such as Na_2SO_3, salts of formic acid, for example $CHCO_2Na$, alkaline salts of tartaric acid for example $C_4O_6H_4Na_2$, and malic acid $C_4O_5H_5Na_2$, sodium phenyl sulfonate $C_6H_5O_3SNa$, their homologues and substitution products, stannous oxide and the like.

When vegetable fibers are treated with the boiling lyes described the cathionic portion of the lye very rapidly disappears from its compound and it can be shown that acids are formed from the vegetable fibers with which it combines to form salts. If for example the boiling lye consists of an aqueous solution of sodium phenolate C_6H_5ONa produced by the reaction of caustic soda NaOH and phenol (oxybenzene) C_6H_6O in which the latter forms the anion and the former the cathion then a portion of the alkali is used up in combining with the acid and phenol is set free. The boiling lye loses some of its effect due to chemical decomposition and moreover has an undesired effect on the vegetable fibers.

In order to prevent the cathion being completely used up a metal compound is, according to the invention, added to the boiling lye during the boiling operation, the quantity thereof being sufficient approximately to maintain the original alkali content and to prevent the acids from decomposing the lye. As examples of such metal compounds there may be mentioned some of the alkaline bases or alkaline salts which are capable of hydrolytically splitting off alkali, some of the oxyhydrates of alkaline earth metals, such as barium hydrate $Ba(OH)_2+8H_2O$, as well as the

hydroxides of metals of the magnesium group, for example magnesium hydroxide $Mg(OH)_2$. It is preferably to utilize the same metal compound (in this case sodium hydrate NaOH) as that which furnishes the cathion of the boiling lye. In some cases it may be advantageous to allow the alkali content of the boiling lye to become reduced during the boiling operation.

In the course of repeated boiling operations the quantities of acid will then form substantial quantities of neutral salts and these remain present as such even in strong concentrations and generally they do not adversely effect the decomposition of the fibers.

Moreover new substances are formed during the boiling operation which substances are capable of combining with the cathion of the boiling lye, that is to say, of supplementing and increasing or even taking the place of the anion of the original boiling lye—i. e.—phenol in the example mentioned C_6H_6O. The anions of the boiling lye can thus be produced from the vegetable fibers themselves during the progress of the boiling operation owing to their being formed out of certain components of the same. The latter decompose during further treatment with the added cathion substances where desirable in the presence of added catalysts and boiling lyes in accordance with the invention are formed. This reaction already commences during the decomposition of the vegetable fibers.

Experience has shown that the boiling lye can be reused in a continuous boiling operation without loss of effect. At the conclusion of any boiling operation only a small portion of the lye need be removed. Thereupon the lye is heated further and cathion material and solvent or emulsifying material is added when, as already stated, new substances are formed in place of the phenolate C_6H_5ONa which substances correspond to the phenol of the example mentioned in the original boiling lye and replace the portion removed. This supplementing of, addition to or substitution of the original anions present in the boiling lye is of the greatest practical importance, because the first cost of the commercially obtainable anion material is relatively high and the very large quantities of phenolates which are necessary could not be obtained elsewhere.

The whole of this addition process should be analytically controlled.

Furthermore the waste liquors from previous boilings can be utilized for obtaining the anions therefrom either separately or in combination with cathions for use in the preparation of fresh boiling lyes. Owing to the fact that in this manner new substances are obtained out of the fibers the total amount reclaimed is sufficient not only for the compensation of undesirable losses but the production of oxy-compounds of the isocyclic series and the like from the waste liquors on the largest scale becomes a possibility.

Again the boiling can be started with weak boiling lye because it gradually becomes richer as the material separated during the course of the operation goes to the formation of fresh anions by addition of the cathions until the most suitable concentration of the boiling lye is reached.

There is also the possibility in this method of supplementing the boiling lye, of making continuous use of the heat it holds. At the conclusion of the treatment there is no need to release the pressure on the boiling lye and let it off thus losing the heat units it contains. On the contrary it may be drawn off with retention of the temperature and pressure partially reduced in quantity and the requisite amount of cathion and solvent— or emulsifying agent—added and straightway brought up to strength by anion formation without further heating, or at any rate with less heating. It is then suitable for fu ther use without any deliberate cooling. The solvent—or emulsifying medium—can also be brought up to the necessary quantity after the anion side has been completed.

The process can be even more economically carried out in a boiling vessel capable of being continuously charged and unloaded with vegetable fiber and cellulose respectively, or in a series of boilers connected together into a battery. If for example, the lye be turned over in an uninterrupted stream in a continuously chargeable and unloadable boiler, it can be reclaimed continuously after drawing off from the boiler and re-used again without cooling. The use of boilers connected up one behind the other makes possible the use of fresh lye, by supplementing between the boilers, up to a certain maximum concentration or in similar manner a continuous enriching from boiler to boiler of a primarily weak boiling liquor.

It is not necessary always to use only an exact chemically determined anion. On the other hand however, it is necessary that the anion or the anions should be of phenol character and be chemically combined with a cathion.

For the preparation of the boiling lye a sodium salt of an aromatic phenol, e. g. sodium cresolate C_7H_7ONa, may be used with advantage. 130 parts of sodium cresolate are dissolved in 1000 parts of water or 108 parts of carbolic acid C_7H_8O, light (the commercial cresol mixture) may be used with 40 parts of chemically pure sodium hydroxide NaOH, or correspondingly more of a technical product dissolved in 1000 parts water ($C_7H_8O+NaOH=C_7H_7ONa+H_2O$).

Such soluble alkali salts which break up easily into sodium hydroxide may also be used, e. g. tertiary sodium phosphate Na_3PO_4.

Neutral sodium sulphite Na_2SO_3 can also be added as reducing agent in which case 10 to 20 parts of the salt containing water of crystallization should be used.

The amount of the boiling lye should be sufficient to about cover the vegetable fibers in the boiler. In the following are given a few examples of the new process.

1. 160 parts of straw or Esparto grass are warmed for a considerable time to a temperature of 70 to 100° C. with 1200 parts of lye of the specified strength in an open vessel having a double perforated bottom and a perforated cover below the top rim of the vessel. The lye is circulated by a pump arranged outside the boiler. The composition of the lye is maintained at about the same titer as at the beginning by admixture of alkali.

The decomposition will be completed when the cellulose on examination is found to split up easily into fibers.

2. 160 parts of straw or Esparto grass are warmed with 1200 parts of lye of specified strength in a closed boiler adapted to circulate the lye. The temperature is very slowly raised during about 4 hours to 140° C. and then maintained for 4–6 hours at 150 to 160° C. The replacing of the alkali can be accomplished after determination by titration outside the boiling vessel. The addition can then be made in a solid or liquid form during pumping.

3. 220 parts of wood e. g. red pin wood, are heated with 1300 parts of lye of the specified strength slowly during 5–6 hours to 120° C. in a boiler adapted to circulate the lye. During this time additions of alkali to the extent of about 16 to 18% of the weight of wood are made. The temperature is then quickly raised to 180° C. and this temperature maintained for generally about 4–6 hours.

In order to avoid oxidation of the boiling lye 20 parts of crystallized sodium sulphite Na_2SO_3 or any alkali sulphite may be added, keeping the relative amount of lye the same, or other sulphites may be added which do not interfere with the reaction.

4. The relative amounts and method of working are the same as in 3, except that instead of sodium hydroxide, trisodium phosphate (Na_3PO_4) is added. The alkalinity will not suffer by this because one of the three sodium atoms in the phosphoric acid salt is split off by the tertiary alcohol and in this way phenolate is again formed, whilst disodium phosphate Na_2HPO_4 reacts alkaline. The amount is then 44% of the weight of the wood, and the 18% of sodium hydroxide can also be only partly replaced by an aliquot part of phosphate. Similarly for example, tri-potassium phosphate K_3PO_4 can also be used.

Ammonia and ammoniacal derivatives are formed in the boiling of grasses. Decomposition products of plant albumen are also present which when boiled with a weak soda solution about 2 to 3% are dissolved.

The process may be carried out without circulation of the lye and without replacement of the alkalis, but in this case larger amounts of lye and bigger boiling space must be employed. The purpose of the boiling is then fulfilled when the crude cellolose is the only undissolved constituent of the reaction material. A wash with a 0.5% soda solution followed by a 0.2% hydrochloric acid solution is recommended.

The waste liquor after letting off a part and dilution with water and addition of alkali is regenerated again by boiling until the prescribed strength of 40 per thousand of phenol combined sodium hydroxide is approximately attained. Care must be taken to find out that the sodium hydroxide is completely combined with phenol for which special testing methods are available.

Having now particularly described and ascertained the nature of my said invention and in what manner the same is to be performed, I declare that what I claim is:—

1. A process for the production of cellulose which comprises decomposing vegetable fibers by boiling the said fibers in a solution comprising a metallic compound of a soluable hydroxy-compound of the iso-cyclic series.

2. A process for the production of cellulose which comprises digesting vegetable fibers in a hot water solution of a soluble alkaline metal derivative of a soluble hydroxy-compound of the iso-cylic series.

3. A process for the production of cellulose which comprises digesting vegetable fibers in a hot aqueous solution of a metallic derivative of a water-soluble hydroxy-compound of the iso-cyclic series in the presence of a phenolic body and an acidic derivative having the property of yielding a hydroxy-compound.

4. A process according to claim 1 wherein substances are added to the boiling solution to cause the formation of stable solutions or permanent emulsions.

5. A process according to claim 1 wherein the ions are brought together with the vegetable fibers.

6. A process according to claim 1 characterized by the feature that a metal compound is added as cathion during the boiling step and in sufficient quantity to convert the metallic compound into a salt which will not injure the cellulose and wherein the acids split off from the vegetable fibers are utilized to hinder the decomposition of the boiling lyes by the acids formed during boiling.

7. A process according to claim 1 characterized by the feature that the necessary anions for the preparation of the boiling solution are obtained from the vegetable fibers themselves in the course of the boiling operation.

8. A process according to claim 1 wherein a portion of the boiling solution is separated after each use and is brought up to the concentration and quantity necessary for the next boiling by the sole addition of cathion and solvent agent and heating.

9. A process according to claim 1 wherein the anions in the free state or combined in the form of a compound with the cathion are separated and recovered out of the constituents of the vegetable fiber in the waste liquor after having been used and are used in the preparation of a fresh boiling solution.

10. A process for the production of cellulose which comprises decomposing vegetable fibers by boiling the said fibers in a solution comprising a metallic compound of a soluble hydroxy-compound of the iso-cylic series, and adding to the boiling solution a hydrolyzable salt and an alcohol.

11. A process for the production of cellulose which comprises decomposing vegetable fibers in a solution comprising a metallic derivative of a soluble hydroxy-compound of the iso-cyclic series, and adding to the boiling solution a hydrolyzable salt, an alcohol and a catalyst.

12. A process for the production of cellulose which comprises decomposing vegetable fibers in a solution comprising a metallic derivative of a soluble hydroxy-compound of the iso-cyclic series, and adding to the boiling solution a hydrolyzable salt, an alcohol, a catalyst, and a reducing agent.

13. A process for the production of cellulose which comprises decomposing vegetable fibers in a solution comprising a metallic derivative of a soluble hydroxy-compound, and adding thereto a metallic compound capable of forming a metallic cathion in the boiling solution.

14. A process for the production of cellulose which comprises decomposing vegetable fibers in a solution comprising a metallic compound of a soluble hydroxy-compound of the iso-cyclic series, boiling the fibers in the said solution, and recovering the solution for re-use.

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