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METHOD OF TREATING CELLULOSIC MATTER

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11 Claims. (Cl. 18—54)

The present invention relates to a method of treating cellulose, which is based on a property of cellulose and of some of its derivatives that was not known up to the present time and therefore was never used for practical purposes. This property is the solubility of these bodies in the aqueous solutions of a great number of metallic salts of perchloric acid.

Cellulose, either in one of its natural forms (cotton linters, paper, wood pulp, etc.) or in a form modified by various treatments (cellulose mercerized by an alkali or a mineral salt, cellulose regenerated from xanthogenate, from nitrate, from Schweizer's reagent, etc.), dissolves, either in the cold state, or at a relatively low temperature (from 40 to 60° C.) in concentrated and neutral or basic aqueous solutions of beryllium and aluminium perchlorates. These solutions remain fluid at ordinary temperature if the concentration of cellulose does not exceed from 4 to 6%, according to its origin. The solutions, once they have been obtained, can be diluted with a certain amount of water without precipitating, even if the final concentration of perchlorate in the solution is such that it would be insufficient for the dissolution of the cellulose. A greater amount of water produces a total precipitation. If the solutions of perchlorate do not contain an excess of acid with respect to the amount corresponding to their chemical formula, cellulose thus treated is not altered and in particular does not undergo any appreciable hydrolysis, in opposition to what takes place when cellulose is dissolved in perchloric acid or in sulphuric acid.

The properties that have just been described can be applied in many ways to industrial manufactures or operations. For instance, the solution of cellulose can be forced through pieces provided with fine holes and immersed in a bath of water; the cellulose then coagulates in the form of a thread which, after washing and drying, will furnish artificial silk or artificial horsehair.

The solution of cellulose can also be forced through a narrow slot immersed in water and will thus furnish, after washing and drying, a strong thin sheet, adapted to be used, for instance, for fine wrappings. Or again the solution of cellulose will be poured in the form of an even sheet on a solid surface, either movable or not, and will furnish, after coagulation in a bath of water, a film which can be used as a support for photographic gelatine. Or again a vegetal or metallic fabric can be impregnated with the solution of cellulose and subjected to the action of water, which will produce "ultrafilter" membranes. Ordinary paper or filter paper can also be treated in the same manner. They will thus be strengthened and made watertight, which will make it possible to obtain either reinforced filter paper or parchment paper resisting the action of water. The applications of the process according to the present invention are not limited to the examples above stated.

Such perchlorate solutions may be mixed with one another before coagulation. I may also incorporate with the perchlorated solutions various nitrogenous products, such as gelatine, fibroin, natural silk. These mixed solutions, when coagulated by means of water, according to the examples above stated, yield new products in which the presence of the nitrogenous matter ensures the property of being more easily dyed than purely cellulosic products and nearly as easily dyed as wool or silk, though much less expensive.

Of course, for each particular application, it is advisable to determine the nature of the perchlorate that gives the best results, and also the best conditions or working. The following specific processes will now be given by way of example:

Example 1.—100 kilogrammes of dry cellulose in the form of paper or of wood pulp, are mixed with 2,100 litres of a saturated solution of beryllium perchlorate of the following composition: $5Be(ClO_4)_2$, 2BeO. 100 cubic centimeters of solvent contain 4.96 grammes of Be and 77.9 grammes of ClO_4H.

Cellulose is quickly dissolved and a solution is obtained which precipitates rapidly under the action of water and which can be employed for all of the applications above stated.

Example 2.—88 kilogrammes of a solution of 20% of perchloric acid are mixed with 12.5 kilogrammes of aluminium chloride including $6H_2O$. The solution thus obtained is heated at a temperature of 100° until hydrochloric acid is no longer evolved. Crystals of aluminium perchlorate are thus obtained, which are purified twice by being redissolved in water and crystallized by evaporation. The crystals finally obtained are dissolved in the minimum of water. 5 kilogrammes of cotton linters previously cleaned, bleached and dried are added to 100 kilogrammes of the saturated solution thus obtained. The cellulose thus added quickly swells and after being homogenized in a stirring machine a viscous solution is obtained which may be utilized

for the manufacture of artificial textiles by spinning by means of the known apparatus, use being made of a saturated solution of sodium chloride as coagulation bath.

The diluted solutions of metallic perchlorates that remain after precipitation of the cellulose can be easily concentrated again by evaporation, with extremely low losses, so that they can be reutilized for subsequent operations. Precipitation can also be obtained by utilizing, instead of water, other coagulation baths such as saline or acid solutions which modify the characteristics of the products obtained.

The dissolving or plastifying action of perchlorates can also be utilized in another manner, without forming a true solution. For instance, paper subjected for a short time to the action of a solution of perchlorate and subsequently washed becomes much stronger due to the swelling of the fibers, which are welded together without being dissolved. This action, which is improved by a rise of temperature, by a pressure exerted on the paper, or by rolling, can be utilized for the industrial manufacture of parchment paper or of paper for wrapping butter. I may also, according to the present invention, immerse the cellulosic masses (wood pulp, paper paste, etc.) in these solutions of perchlorates diluted with a small amount of water, drive out the excess of water, and compress at a relatively low temperature, for instance 60° C. The fibers, swelling under the action of the perchlorate, become welded together so as to form a coherent mass, which will be freed from the salt employed, by washing. Such agglomerated masses have insulating properties and can therefore be utilized in electric machines or apparatus of any kind whatever.

The swelling and the dissolution of the cellulose thus subjected to the action of perchlorates can be utilized for rendering cellulose more sensitive to the action of reagents; these reagents will be either added directly to the solution or caused to act on cellulose regenerated by precipitation. As a matter of fact, regenerated cellulose, due to its fine state of division, is very sensitive to the action of reagents. This word is here used in its more general meaning, that is to say includes not only chemical compounds, but also physical actions, such as catalysis, electrolysis, action of radiations, or dyes which will form lacquers with cellulose regenerated by precipitation. The properties of this finely divided cellulose will be further improved by the addition of nitrogenous matters, as above stated.

The expression "derivatives of cellulose" used in the claims hereafter, is taken to include cellulose either in its natural state or in a form modified by various treatments, as hereinbefore described at the beginning of the specification.

What I claim is:

1. A process of treating cellulosic matter, which comprises subjecting the same to the dissolving action of a concentrated aqueous solution of a metallic perchlorate, and treating with a liquid adapted to produce the separation of the cellulose from the perchlorate.

2. A process of treating cellulosic matter, which comprises substantially dissolving the same by the action of a concentrated aqueous solution of a metallic perchlorate, and precipitating the cellulosic matter by means of a liquid from the solution thus obtained.

3. A process of treating cellulosic matter, which comprises substantially dissolving the same by the action of a concentrated aqueous solution of beryllium perchlorate, and precipitating the cellulosic matter by means of a liquid from the solution thus obtained.

4. A process of treating cellulosic matter, which comprises substantially dissolving the same by the action of a concentrated aqueous solution of aluminum perchlorate, and precipitating the cellulosic matter by means of a liquid from the solution thus obtained.

5. A process of treating cellulosic matter, which comprises substantially dissolving the same by the action of a concentrated aqueous solution of a mixture of metallic perchlorates, and precipitating the cellulosic matter by means of a liquid from the solution thus obtained.

6. A process of treating cellulosic matter, which comprises substantially dissolving the same by the action of a concentrated aqueous solution of a metallic perchlorate, and precipitating the cellulosic matter by means of water from the solution thus obtained.

7. A process of treating cellulosic matter, which comprises substantially dissolving the same by the action of a concentrated aqueous solution of a metallic perchlorate, and precipitating the cellulosic matter by means of a liquid from the solution thus obtained, and regenerating the initial solution of metallic perchlorate by merely concentrating the liquid used for the precipitation of the cellulosic matter.

8. A process of treating cellulosic matter, which comprises substantially dissolving the same by the action of a concentrated aqueous solution of a metallic perchlorate, adding to the solution nitrogenous products, and precipitating the cellulosic matter by means of a liquid from the solution thus obtained.

9. A process of treating cellulosic matter, which comprises substantially dissolving the same by the action of a concentrated aqueous solution of a metallic perchlorate, adding to the solution proteic matters, and precepitating the cellulosic matter by means of a liquid from the solution thus obtained.

10. In a process as claimed in claim 1, the step consisting of subjecting the cellulosic matter, treated with a concentrated aqueous solution of a metallic perchlorate, to the action of reagents adapted to modify the properties of the said cellulosic matter.

11. In a process as claimed in claim 1, the step consisting of subjecting the cellulosic matter, treated with a concentrated aqueous solution of a metallic perchlorate and separated from the said perchlorate, to the action of reagents adapted to modify the properties of the said cellulosic matter.

ALMA DOBRY.

CERTIFICATE OF CORRECTION.

Patent No. 2,022,589. November 26, 1935.

ALMA DOBRY.

It is hereby certified that the name of the assignee in the above numbered patent was erroneously written and printed as "Compagnie de Produits Chimiques et Electrometallurgiques Olais, Froges et Camargue" whereas said name should have been written and printed as Compagnie de Produits Chimiques et Electrometallurgiques Alais, Froges et Camargue, Paris, France, a corporation of France, as shown by the records of assignments in this office; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 18th day of February, A. D. 1936.

Leslie Frazer
Acting Commissioner of Patents.

(Seal)