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METHODS OF TREATING CELLULOSE

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The present invention relates to a method of treating cellulose with borohydride.

The main object of this invention is to improve the result of the treatment of cellulose with borohydride.

It is known that it is possible by a reduction of cellulose with borohydrides to achieve a number of advantageous effects in particular a decreased yellowing on heating and a reduced solubility in hot aqueous alkali as well as a higher viscosity. The accepted explanation of these effects is that the number of carbonyl groups present in the cellulose is decreased by a reduction thereof to hydroxyl groups. This explanation is confirmed by the fact that the reducing power of the cellulose, as measured by a determination of the copper number is decreased. A reduction of the tendency for yellowing is particularly desirable in cellulose pulp intended to be used in paper-making as well as in cellulose pulp intended to be used as a filler in plastic materials. A lower solubility in hot alkali is particularly desirable in pulp which is to be used in the manufacture of viscose rayon and cellulose derivatives, such as cellulose ethers and esters.

The treatment with borohydride is suitably carried out with the cellulose suspended in water. The amount of borohydride to be used may vary depending on the type of cellulose and the desired effect and will generally be between about 0.01% and 20% based on the weight of the cellulose. Since borohydrides, however, are expensive chemicals it would be very advantageous to be able to lessen the quantity of borohydride required to achieve a desired effect. A specific object of this invention, therefore, is to provide a method whereby it is possible to achieve a desired improvement of the cellulose by the aid of a quantity of borohydride which is smaller than that necessary to achieve a similar improvement by prior art methods of treating cellulose with borohydride.

It has now been discovered that the presence of salts of lithium, magnesium, calcium, strontium and barium when treating cellulose in aqueous suspension with an alkali metal borohydride enhances the effect of the treatment, so that a smaller amount of borohydride can be used to attain a desired effect or the same amount of borohydride provides a more marked effect in the presence of said salts than in the absence of them.

The term "alkali metal borohydride" as used herein includes the borohydrides of sodium, potassium, rubidium and cesium. For economical reasons, however, sodium borohydride and potassium borohydride will preferably be used in practice, since the borohydrides of rubidium and cesium are very expensive.

It will be noted that some salts are known to have an effect-enhancing action when certain organic substances, such as esters, lactones and carboxylic acids, are reduced with borohydrides in organic solvents. It is to be observed, however, that the present invention comprising reduction of cellulose in aqueous suspension, involves a phenomenon different in character from that observed in such known reductions, which is borne out by the fact

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that e.g. aluminum salts have been stated to have a favorable action in such reductions in organic solvents, while aluminum salts in the present case have shown an opposite action in that the result is impaired by the presence of aluminum ions. This shows that the advantageous action of the salts referred to hereinbefore could not be predicted on the knowledge of the action of salts in connection with reductions carried out in organic solvents.

Salts of lithium, magnesium, calcium, strontium and barium which can be used in accordance with this invention, include all water-soluble salts of these metals, e.g. barium nitrate, barium chloride, barium bromide, calcium chloride, calcium bromide, lithium bromide, lithium chloride, lithium iodide, magnesium chloride, magnesium sulfate, strontium chloride, strontium nitrate etc. Since the results obtained so far indicate that it is the metal ion of the salt which is active in the process of this invention, the anion of the salt is immaterial as long as it does not result in such a low solubility in water of the salt that it is impossible to obtain a sufficient concentration of the salt to achieve the effect desired and as long as the anion does not interfere with the reduction of the cellulose carbonyl groups by the borohydride. To achieve a positive effect it is in general necessary that the salt is present in an amount of at least 0.1% of the weight of dry cellulose. With increasing amounts of the salts an increased effect will be obtained up to a certain limit above which no further improvement is achieved. Although it is possible to utilize practically unlimited amounts of the salts, it is therefore preferred to use not above 10% based on the weight of dry cellulose. For a given salt a definite upper limit is established by the solubility in water of the salt at the reaction temperature involved, since it is obviously useless to add the salt in amounts exceeding the maximum solubility thereof. The amount of borohydride is preferably 0.1–5%, based on the weight of dry cellulose.

The reaction will preferably be carried out at a temperature between room temperature and 100° C. The temperature is not critical, however, and higher or lower temperatures may be used, if desired. It is preferable to have a high concentration of cellulose in the suspension, since it has been found that the action of the borohydride is more efficient when the concentration of cellulose is increased. The concentration of cellulose will generally be at least 2% and preferably at least 10% by weight, based on the suspension.

The cellulose used in this process may be any type of cellulose such as cotton, cotton linters or chemical pulp prepared by the soda, sulfate or sulfite process from wood, straw, esparto, bagasse or other vegetable cellulosic raw materials.

The invention is illustrated by the following working examples.

EXAMPLES 1–11

A series of experiments was carried out with various salts and varying amounts thereof, and with varying amounts of sodium borohydride, as set forth in the table below. In each experiment the salt and the borohydride were dissolved in 100 g. of water, whereupon 2 g. of cellulose were slurried in the solution and this was left for 3 hours at 50° C. with slow stirring. Thereafter the cellulose was separated from the liquid on a suction filter, washed with water and dried, whereupon the copper number was determined. In each experiment, the starting cellulose was a dissolving type cellulose made from spruce and having an alpha cellulose content of 90%, a viscosity in 1% cuprammonium solution at 20° C. of 22 centipoises, measured according to TAPPI's standard method, and a copper number of 1.6.

For comparison, the table below includes an experiment

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made with an aluminum salt in addition to experiments with salts coming within the scope of this invention.

The amounts of salts and borohydride set forth in the table are given in percent based on the weight of dry cellulose. "Reduction of copper number" refers to reduction in relation to the copper number of the starting cellulose.

Table

Ex. No.	Salt	Amount of salt, percent	Amount of NaBH ₄ , percent	Copper number	Reduction of copper number
1.			2.0	1.2	0.4
2.			1.0	1.5	0.1
3.	Ba(NO ₃) ₂	4.0	2.0	0.6	1.0
4.	Ba(NO ₃) ₂	50.0	2.0	0.6	1.0
5.	Ba(NO ₃) ₂	250.0	2.0	0.6	1.0
6.	CaBr ₂	2.0	2.0	0.8	0.8
7.	CaBr ₂	2.0	1.0	1.1	0.5
8.	LiCl	0.2	2.0	1.0	0.6
9.	MgCl ₂	1.0	2.0	0.8	0.8
10.	SrCl ₂	0.5	2.0	1.1	0.5
11.	Al ₂ (SO ₄) ₃	4.0	2.0	1.6	0.0

In a similar series of experiments in which potassium borohydride was used instead of sodium borohydride, similar results were obtained.

EXAMPLE 12

A strong sulphite pulp of the type suitable for paper-making, made from spruce with alpha content 86%, viscosity in 1% cuprammonium solution according to the TAPPI standard method 100 centipoises and copper number 1.60 was defibrated in water. The pulp suspension was sucked off on a Büchner funnel and dried. The loose pad of pulp obtained was then impregnated with four times its own weight of a water solution containing sodium borohydride and magnesium chloride; temperature 50° C. The wet pad was kneaded slightly to ensure that the water had penetrated to all parts of it and then kept at 50° C. for one hour. After washing and drying the copper number was determined. The result of a series of experiments is given below. The amounts of magnesium chloride and sodium borohydride are calculated on the dry weight of the pulp.

Run No.	Amount of MgCl ₂ , percent	Amount of NaBH ₄ , percent	Copper number
Original pulp			1.6
1.	0	0.1	1.5
2.	2	0.1	1.2
3.	0	0.3	0.8
4.	2	0.3	0.5
5.	0	1.0	0.3
6.	2	1.0	0.1

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EXAMPLE 13

The same pulp as in Example 12 was slurried in a water solution containing varying amounts of sodium borohydride and magnesium chloride. Concentration of pulp in the suspension 2%, temperature 50° C., duration of treatment 3 hours with slow stirring. The pulp was then sucked off on a suction filter, washed with water and dried. Determination of the copper number gave the results shown in the table below. The amounts of sodium borohydride and magnesium chloride are calculated on dry pulp.

Run No.	Amount of MgCl ₂ , percent	Amount of NaBH ₄ , percent	Copper number
Original pulp			1.6
1.	0	0.5	1.5
2.	2	0.5	1.3
3.	0	1.0	1.3
4.	2	1.0	0.8
5.	0	2.0	0.7
6.	2	2.0	0.4

I claim:

1. A method of improving cellulose, which comprises reacting cellulose suspended in an aqueous medium with an alkali metal borohydride in the presence of a water-soluble salt of a metal in the group consisting of lithium, magnesium, calcium, strontium and barium.

2. A method as in claim 2 in which said alkali metal borohydride is sodium borohydride.

3. A method as in claim 1 in which said water-soluble salt is used in an amount of about 0.1% to 10% based on the weight of the cellulose.

4. A method as in claim 2 in which said cellulose is pulp suitable for use in papermaking.

5. A method as in claim 1 in which said cellulose is dissolving pulp.

6. A method as in claim 1 in which said cellulose is pulp suitable for use as a filler in plastic materials.

No references cited.