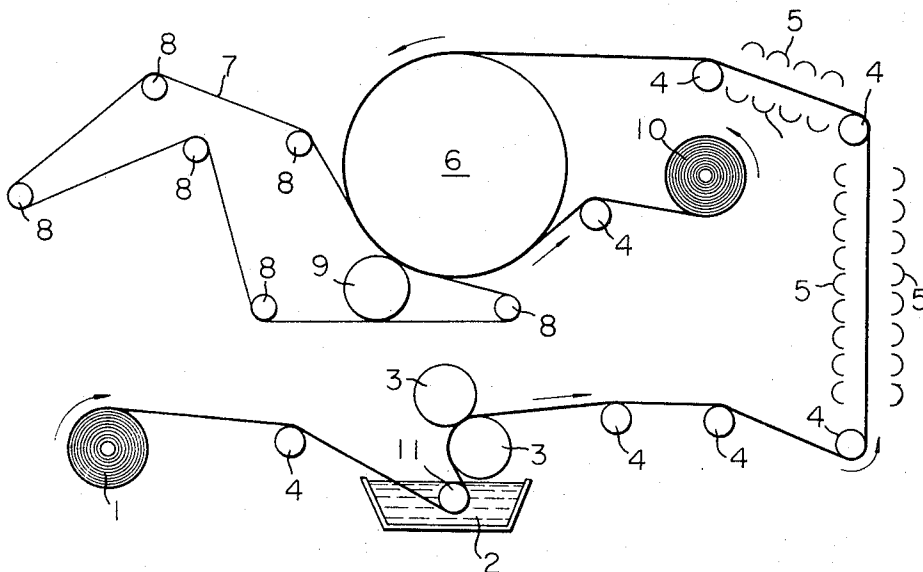


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METHOD OF MAKING PAPER WHICH DISSOLVES IN WATER CONTAINING
PAPERMAKING FIBERS AND FIBROUS CELLULOSE-GLYCOLIC ACID
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3,431,166

METHOD OF MAKING PAPER WHICH DISSOLVES IN WATER CONTAINING PAPERMAKING FIBERS AND FIBROUS CELLULOSE-GLYCOLIC ACID

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2 Claims

ABSTRACT OF THE DISCLOSURE

A method of making paper which dissolves or rapidly disintegrates in water, which comprises (a) heating a paper web comprising fibrous cellulose-glycolic acid having degree of substitution of 0.1 to 0.8, at such a temperature and for such a time as will enable it not to dissolve or disintegrate during the alkali impregnation which follows, (b) impregnating the heat-treated web with an aqueous solution of an alkali selected from the group consisting of sodium compounds and potassium compounds such that the paper web takes greater than that weight of alkali neutralizing equivalent to the cellulose-glycolic acid, and (c) heating the impregnated paper web to dry it.

This invention is a continuation-in-part application of Ser. No. 466,596 filed June 24, 1965, now abandoned.

This invention relates to a process for preparing paper dissolving or rapidly disintegrating in water.

With reference to a process for preparing paper dissolving in water, already in U.S. Patent 3,034,922, one process has been disclosed by Böe. In Böe's process, for binding various kinds of a fiber fleece, a water-soluble film-forming material is used as a binder. As clearly described in U.S. Patent 3,034,922, Böe proposes such a process from the point of view that by an ordinary paper making process, paper dispersing in water cannot be prepared. However, because a film formed by a water-soluble film-forming material is, once dried, unlikely to dissolve in water, a paper-like material prepared by Böe's process, even when thrown into water, takes several minutes until it disintegrates to the individual component. By Böe's process, it is difficult to prepare what disperses in a few seconds. The present inventors have devised a process for preparing paper immediately dissolving or disintegrating in water by an ordinary paper making process by a technology entirely different from that of Böe's.

Namely, this invention uses as material cellulose-glycolic acid (carboxy methylcellulose, hereinafter referred to as CMC—H) singly or in combination with other paper-makable paper making material, at first by an ordinary paper making process, water-insoluble paper is prepared, and by heat-treating, alkali-treating and re-heat-treating said paper as will be mentioned in detail hereinbelow, this invention tries to provide paper dissolving or disintegrating in water.

Originally, a sodium salt or potassium salt of CMC—H, or cellulose-glycolic acid (a sodium salt of potassium salt of carboxy methyl-cellulose, hereinafter referred to as CMC—Na or CMC—K) is used as a binder for increasing water resistance and oil resistance of paper, using the same already many processes have been disclosed, however, a process for preparing paper dissolving or disintegrating in water using CMC—H singly or making

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CMC—H a main component of the material has not been disclosed yet.

The most characteristic of this process is that a reaction converting CMC—H constituting said paper to CMC—Na or CMC—K is carried out with water used as a medium. Because CMC—Na or CMC—K has properties of swelling and dissolving in water, it has been customary to practice this reaction with an organic solvent such as alcohol and acetone used as a medium.

This method involves elaborate equipment because of the use of expensive solvents, and the cost of the paper is high.

We have now discovered a method whereby the CMC—H can be converted into its salts using an aqueous alkali solution. The method depends on the discovery that the wet strength of the paper can be greatly increased by a heating step, so that the paper retains its form on treatment with aqueous alkali solution.

The invention includes a method of making paper which dissolves or rapidly disintegrates in water, which comprises (a) heating a paper web comprising fibrous cellulose-glycolic acid at such temperature and for such a time as will enable it not to dissolve or disintegrate during the alkali impregnation which follows, (b) impregnating the heat-treated web with an aqueous solution of an alkali such that the paper web takes up at least that weight of alkali equivalent to the cellulose-glycolic acid, and (c) heating the impregnated paper web to dry it.

The paper product can be used for example in writing paper for confidential use, papers for sanitary use and wrapping paper.

Since no organic solvents are used, the chance of fire is reduced and hazards of toxication are eliminated. Production costs are also lower, not only because of the use of a cheaper solvent, water, but also because there is no need for accessory equipment such as solvent recovery means.

The paper web starting material can be made from CMC—H alone or from a mixture of CMC—H and other fibres, and may for example contain 30–100% CMC—H on a dry basis. These other fibres, e.g. wood pulp or cotton linter pulp, synthetic fibres, e.g. nylon, or inorganic fibres, e.g. asbestos or glass fibre.

As form of CMC—H used in this invention, what is in a fibrous state obtained by a carboxy-methylation of cellulose per se is most suitable and what is obtained by spinning carboxy methyl cellulose or what is in a powder form is unsuitable, because the CMC—H in this invention is not for binding another kind of fibre which constitutes a skeleton such as binder in a non-woven fabric, but forms paper by constituting its skeleton by itself.

Degree of substitution (D.S.) of the CMC—H used in this invention may be within the range of from 0.1 to 0.8, however what is water-insoluble and alkali-soluble is most preferable.

After the paper containing CMC—H has been first formed into a paper web in conventional manner, it is heated for such a time and at such a temperature as will impart to it sufficient strength to enable it to retain its form during the alkali treatment. Providing the condition of the paper is not changed, the heating can be completed in a shorter period of time using a higher temperature. 20 seconds to 12 hours at 50 to 110° C. is conveniently used, though a temperature of 60 to 110° C. is preferred. Further, there are no special limitations as to the method of heat treatment, it being possible to accomplish this for example by a treatment for 20–60 seconds in a dryer at an elevated temperature, e.g. 90–110° C., or by treatment for 1–12 hours in a constant temperature-constant humidity chamber at relatively low temperature, e.g. 50–80° C.

If a paper web without being suitably heat-treated is

dipped in the alkali solution to convert its CMC—H to the sodium or potassium salts, the paper immediately starts to swell and spread, and finally disintegrates. With a suitable heat treatment, the form of the paper is retained. The impregnation with alkali can be carried out for example by dipping, coating or spraying. Usually the alkali is one or more sodium or potassium compounds, preferably one or more of sodium or potassium carbonate, sodium or potassium bicarbonate and sodium or potassium hydroxide. The impregnation is usually conducted at room temperature or above.

The amount of alkali taken up by the paper must be greater than that equivalent to the CMC—H present in the paper web, otherwise the paper retains its form without dissolving in water even after the present method has been completed. Preferably, however, not more than twice the neutralizing equivalent of alkali is taken up, otherwise discoloration and hardening of the paper can occur with such drawbacks as breaking of the paper web and impairment of the appearance quality of the paper product. Convenient concentration of the aqueous alkali solution are, in the case of sodium carbonate or potassium carbonate, 2.3–12.0% by weight; in the case of sodium bicarbonate or potassium bicarbonate, not more than 9.0% by weight; and in the case of sodium hydroxide or potassium hydroxide, not more than 1% by weight.

After being impregnated with alkali, the paper web is heated to be dried and converts the CMC—H to the sodium or potassium salts. The temperature to which the paper is heated must of course be such as will not render the paper web hard and brittle like keratin. A preferred temperature is 50–110° C. The heating means can be for example a drum dryer, a hot-air dryer or an infrared dryer.

The invention is illustrated by the accompanying drawing whose sole figure illustrates a particular method according to the invention.

In the drawing, 1 is a paper web which has been wound up into a roll after having been heated and prior to alkali impregnation; 2, a bath for impregnating the paper web; 3, a pair of squeezing rolls consisting of one rubber and one ebonite roll; 4, paper rolls; 5, an infrared lamp for application of heat; 6, a drum for drying the paper (dryer); 7, a dryer felt for effecting the uniform intimate contact of the paper web without imparting any creases in the paper web; 8, felt rolls for the dryer felt; 9, a pressure roll for pressing the impregnated paper web and dryer felt against the dryer; 10, converted paper which has been wound into a roll; and 11, an applicator roll in the bath for impregnating the paper web with the alkali solution.

The paper web from paper web roll 1 first passes over roll 4 to enter impregnation bath 2 which is filled with the alkali solution, which is continuously replenished as it is consumed. The paper web, after passing under applicator roll 11 and becoming saturated with the treatment liquid, is squeezed between a pair of squeezing rolls 3 which are disposed above the bath to remove excess liquid. These two squeezing rolls, one of which is made of rubber and the other of ebonite, are pressed together by means of a lever weight. The content of the treatment liquid in the paper web after having passed between these squeezing rolls amounts to about 1.2–1.8 times the weight of the dried paper web. The amount of treatment liquid retained in the paper web is not critical, it being possible to increase or decrease the number of the squeezing rolls or, at times, even to eliminate them. When the paper web is immersed in the treatment liquid and squeezing rolls are not used, the content of the liquid in the paper web is generally about 2–3 times the dried weight of the paper web, though it differs depending on for example the density and porosity of the paper. It is preferred, however, to retain only a small amount of treat-

ment liquid in the paper web, in view of the fact that the next step is to dry it.

The wet paper web from between the squeezing rolls 3 passes over paper rolls 4 and then enters an infrared dryer equipped with a plurality of infrared lamps 5, where it is pre-dried, losing the majority of its water. The paper web then comes in contact with the drying surface of drum dryer 6 and is completely dried and flattened between dryer 6 and dryer felt 7 by means of the action of presser roll 9, following which it is wound up in the form of a roll as converted paper 10.

Although the infrared dryer and the drum dryer may be at any temperature, the temperature of the paper itself must not be such as will render the paper hard and brittle. Preferred is a temperature of 50–110° C.

The invention is further illustrated by the following examples, in which parts and percentages are by weight unless otherwise indicated.

Example 1

The equipment illustrated in the accompanying drawing was employed. As the paper web, a roll of paper web 45 cm. in width was made in the following manner. 70 parts of commercially available pulp were beaten to a freeness of 70° S-R, then 1 part of a rosin soap was added and the pH was adjusted to 4.5 with aluminum sulphate, after which to the foregoing stock was thoroughly mixed 30 parts of dried, fibrous CMC—H of a degree of substitution of 0.3 after the latter had been well macerated. The paper stock so obtained was formed into a 30 gram per square metre web in conventional manner. After heating this roll of paper web by placing it in a constant temperature-constant humidity chamber at 50° C. for 12 hours, the paper web was impregnated in a bath, 60 cm. in width, 30 cm. in length and 20 cm. in depth, containing 30 litres of 4% sodium bicarbonate solution which was continuously replenished as it was consumed. The paper web, after impregnation, was squeezed and dried. In the drying section, the infrared dryer was one in which were disposed six infrared lamps, each of 375 watts, in its upper part, while ten lamps, each of 1,500 watts, were disposed on each of the two sides in the lower part. As the drum dryer, an iron drum 60 cm. in width and 122 cm. in diameter, was used, and the dryer felt thickness was 3 mm.

The paper web was immersed in the bath at room temperature by feeding it from the aforementioned roll of paper web, 45 cm. in width, its alkali-solution content being so adjusted as to be 1.63 times the dry weight of the paper web upon emerging from between the squeezing rolls. This treated paper web was then passed through the infrared dryer and, after being completely dried on the drum dryer, heated to 80° C. with steam, and wound up on a roll for the converted paper. All of the foregoing operations were carried out continuously. It was possible to write, print or type on the converted paper as on conventional paper. However, when a 3 cm. square piece of the converted paper was introduced into 300 cc. of water at room temperature and gently stirred for several seconds, is dispersed in the water and lost all its original form.

On the other hand, paper made from the same pulp but without having CMC—H added to it, using the same treatment and the same equipment, retained its original form even after being immersed in water for 6 hours.

Example 2

50 parts of fibrous CMC—H of a degree of substitution of 0.8 were thoroughly mixed in 50 parts of commercially available dissolving pulp, then beaten to a freeness of 20° S-R, following which the paper stock was formed into a sanitary paper at 30 g./m.² and dried in conventional manner. Thereafter, it was passed for 30 seconds through a dryer having a surface temperature of 110° C., followed by alkali impregnation as in Example 1 employing the same equipment and procedures, except

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that as the treatment liquid was used a mixed aqueous solution of 0.1% sodium hydroxide, 2.5% potassium carbonate and 4% sodium bicarbonate, a processing speed of 8 metres per minute was employed, and the temperature of the aqueous alkali solution was maintained at 65° C. The appearance and strength of the paper so obtained hardly differed from conventional sanitary paper, but when it was introduced into water, it dispersed in about 10 seconds.

Example 3

80 parts of dried, fibrous CMC—H of a degree of substitution of 0.1–0.2 were mixed thoroughly with 20 parts of commercially available dissolving pulp beaten to a freeness of 30° S-R. This paper stock was then formed into paper and dried in conventional manner, yielding a paper 60 g./m.² and 0.1 mm. in thickness. After the paper so obtained had been heated for 30 minutes at 80° C., it was treated using the same equipment and procedures as described in Example 1, except that a mixed aqueous alkali solution of 0.3% potassium hydroxide and 4% sodium carbonate was used and the treatment was carried out with the solution at room temperature and at a speed of 8.8 metres per minute. The paper so obtained dissolved immediately when introduced into water.

When in this experiment the concentration of the sodium hydroxide in the solution was reduced to 0.15% and that of the sodium carbonate of 2% and the same treatment was given, the paper so obtained retained its original form even after one hour when introduced into water under identical conditions.

Example 4

Fibrous CMC—H having a degree of substitution of 0.4 was used as a material, and by an ordinary paper making step, paper for teletype of 80 g./m.² was prepared.

After heat treating said paper inside a constant temperature chamber at 60° C. for 12 hours, using the apparatus shown in the accompanying drawing, said paper was passed through and immersed in an aqueous solution of potassium carbonate colored to blue of a concentration of 6% by dyestuff, thereafter said paper was squeezed so that its weight might become 1.5 times that

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of the original paper, dried by being passed through a two-stage drier, having surface temperatures of 110° C., thereafter it was wound. Subsequently, the surface of said paper was made smooth by a 10-stage supercalender to obtain water-dissoluble blue-colored paper for teletype.

Throughout this step, said paper retained its original shape, sufficiently usable as ordinary paper for teletype, moreover, when said paper was thrown into water, it completely dissolved within 30 seconds without retaining the original shape.

What we claim is:

1. A method of making paper which dissolves or rapidly disintegrates in water, which comprises (a) forming a slurry of a mixture of papermaking fibers 30–100% of fibrous cellulose-glycolic acid having a degree of substitution of 0.1 to 0.8, (b) forming a web, (c) heating the web at 50 to 110° C. for 20 seconds to 12 hours to obtain sufficient strength so that said web will not disintegrate during the following alkali impregnation step, (d) impregnating the heat-treated web with an aqueous solution of an alkali selected from the group consisting of sodium- and potassium-carbonates, bicarbonates and hydroxides such that the paper web takes up from 1 to 2 times the weight of alkali equivalent to the cellulose-glycolic acid, and (e) heating the impregnated paper web to dry it.

2. A method according to claim 1 wherein the impregnated web is heated in step (e) at 50° to 110° C.

References Cited

UNITED STATES PATENTS

2,184,312	12/1939	Merrill	162—135
2,766,137	10/1956	Ashton	162—177 X
3,034,922	5/1962	Böe	162—158 X
3,288,631	11/1966	Jorder	117—62.1

FOREIGN PATENTS

803,670 10/1958 Great Britain.

S. LEON BASHORE, Primary Examiner.

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117—62.1; 162—146, 184