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PROCESS FOR MAKING WET WIPES

This invention relates generally to a process for making wet wipes having high water-dispersibility as well as high water-solubility which are used for the purpose of wiping a stool, a toilet flower and the like clean.

The foregoing wet wipes are well known. The articles in the form of water-dispersible or water-dissoluble sheets are also well known, which can be dumped into a flush toilet stool and flushed down the drain. It should be understood that the terms used herein "water-dispersibility" and "water-dissolubility" are synonymous with each other. In the case of water-dispersible wet wipes, two conflicting abilities, i.e., a high wet strength during actual use and a rapid dispersibility after disposal into a large quantity of water must be met by the wet wipes. In order to reconcile these strength and dispersibility, Japanese Laid-Open Patent Application No. Heil-168999 discloses wet wipes comprising water-dissoluble paper mixed with water-insoluble carboxymethyl cellulose, particularly calcium salt thereof during a process of paper making. Japanese Laid-Open Patent Application No. Hei2-149237 discloses wet wipes comprises water-dissoluble paper containing water-soluble binder such

as water-soluble alkali metal salt of carboxymethyl cellulose and impregnated with detergent which contains multivalent metallic ions such as of alkaline-earth metal, manganese or zinc and organic solvent. Japanese laid-Open Patent Application No. Hei5-25792 discloses wet wipes comprising a sheet formed by using water-insoluble but water-swelling alkali metal salt in a process of paper making and impregnated with hydrated organic solvent containing multivalent metallic ions such as of alkaline-earth metal nickel and iron.

As it is well known in the art, carboxymethyl cellulose and/or salts thereof usually used as binders generally change their nature depending on values of degree of substitution (D.S.) and pH. Specifically, carboxymethyl cellulose and/or salts thereof which is initially water-insoluble exhibit water-swelling ability and finally become water-soluble as said values increase. In order that the wet wipes in the form of sheets formed by a process of paper making with use of carboxymethyl cellulose and/or salts thereof as the binder can exhibit a high water-dispersibility, said binder must exhibit a high water-swelling ability or water-solubility. This can be achieved by making the wet wipes using said information obtained from the prior art.

However, the wet wipes made with use of the binder having high swelling ability or water-solubility is accompanied with any apprehension that, during either use or storage, the binder might be swollen or dissolved. Such swelling or dissolution might reduce the wet strength to an unacceptable level for practical use of the wet wipes.

As will be apparent from the previously cited Patent Applications, carboxymethyl cellulose and/or salts thereof having water-swelling ability or water-solubility react with multivalent metallic ions added thereto to form multivalent metallic salt of carboxymethyl cellulose. As a result, water-swelling ability or water-solubility is reduced. This salt producing reaction between carboxymethyl cellulose and/or salts thereof and multivalent metallic ions is accelerated by dissociation of said carboxymethyl cellulose and/or salts thereof. In other words, the higher the values of DS and pH are, in still other words, the higher the swelling ability and the water-solubility are, the more rapidly the reaction progresses. Therefore, the effect provided by addition of multivalent metallic ions is significant when the carboxymethyl cellulose and/or salts thereof have high DS and pH as well as high swelling ability and water-solubility. In consequence, a wet strength of the

wet wipes can be enhanced by this effect compared to the case in which the binder having low DS and pH is employed.

If carboxymethyl cellulose and/or salts thereof used as a binder are water-soluble as in the case disclosed in Japanese Laid-Open Patent Application No. Hei2-149237, it is undesirable to mix the fiber with the binder in water before these components are subjected to a process of sheet making, because a quantity of the binder fixed to the resultant sheet is insufficient to enhance the strength of the sheet as expected from a quantity of actually used binder. Instead of mixing the components before the sheet making, it may be also that the sheet formed without premixing the binder with the fiber is sprayed with the binder. However, aqueous solution of carboxymethyl cellulose and/or salts thereof are relatively viscous and it is difficult to spray the sheet with the binder so as to be uniformly distributed.

If water-insoluble or water-swelling binder is used as in the case disclosed in Japanese Patent Application Disclosure Gazette No. Hei5-25792, the binder is prevented by its high swelling ability from being uniformly mixed with the fibers. If the binder is water-insoluble or has a low swelling ability, a quantity of the binder fixed to the sheet can be increased. However, such binder can not provide a

bonding strength sufficient to maintain the fibers bonded one to another and thereby to achieve a high wet strength of the sheet.

In view of the problems as have been described above, it is a principal object of the invention to provide a process for making wet wipes allowing a desired wet strength and a desired water-dispersibility to be reconciled.

The object set forth above is achieved, according to the invention, by a process for making wet wipes composed of at least carboxymethyl cellulose and/or salts thereof and water-dispersible fibers and impregnated with multivalent metallic ion containing liquid, said process comprising steps of: subjecting a mixture of carboxymethyl cellulose and/or salts thereof which are relatively low in water-swelling ability of water-insoluble and the water-dispersible fibers to a process of sheet making after said mixture has been added with suitable base to obtain a sheet containing a salt of said carboxymethyl cellulose having relatively high water-swelling ability or water-solubility; and impregnating said sheet with multivalent metallic ion containing liquid.

Sodium carbonate is preferably used as said base. Use of such base allows the carboxymethyl cellulose and/or salts

thereof which are relatively low in water-swelling ability or water-insoluble to be modified during the process of sheet making so as to exhibit a relatively high water-swelling ability. In this way, the carboxymethyl cellulose and/or salts thereof having high water-swelling ability or water-solubility is fixed to the sheet. Upon impregnation of this sheet with multivalent metallic ion containing liquid, multivalent metallic salt of carboxymethyl cellulose is produced. The wet wipes obtained in this manner have a desired wet strength owing to the presence of such metallic salt. The multivalent metallic salt of carboxymethyl cellulose is rapidly dissociated, dissolved or swollen immediately after dumped into a flush toilet stool, sanitation tank, drain, etc. Thus, the water-dispersibility of the wet wipes is not practically deteriorated by said multivalent metallic salt.

Raw materials which can be used by the inventive process for making wet wipes include carboxymethyl cellulose and/or salts thereof. Such raw materials include also water-dispersible fibers which can be subjected to the paper making process together with said carboxymethyl cellulose and/or salts thereof to obtain a product in the form of sheets.

While pulp fiber is preferable as one of such water-dispersible fibers, it is also possible to use natural fibers such as linen and wool, regenerated fibers such as rayon, semi-synthetic fibers such as acetate and synthetic fibers such as nylon and polyester.

Suitable materials as binders are carboxymethyl cellulose and/or salts thereof which are water-insoluble or of water-swelling abilities lower than those presented by said fibers and, more preferably, carboxymethyl cellulose and/or salts thereof having D.S. = 0.30 ~ 0.60 and $\text{pH} \geq 5.0$. Binder having D.S. lower than 0.30 is not preferable since no significant improvement of its swelling ability by addition of base can be expected. On the other hand, binder having D.S. higher than 0.60 will be readily swollen or even water-soluble. In consequence, a sheet obtained by the paper making process can not contain necessary and sufficient amount of binder. With pH less than 5.0, an amount of base to be added during the process of paper making will be disadvantageously increased in order to enhance the swelling ability of the binder.

Mixing ratio by weight of the binder to the water-dispersible fiber is 2 : 98 ~ 45 : 55, more preferably, 2 : 98 ~ 20 : 80. If an amount of the binder is below the above-

specified range, the binder may fail of its expected function. On the other hand, if an amount of the binder exceeds the above-specified range, an amount of multivalent metallic ions to be added for temporary suppression of swelling as well as solution of the binder will correspondingly increase. This will necessarily increase a manufacturing cost.

While any kind of base can be added in order to enhance water-swelling ability or water-solubility of the binder, it is preferred to use sodium carbonate from various viewpoints such as a safety during the process of paper making and a manufacturing cost. An amount of sodium carbonate to be added is preferably 10 ~ 400 % by weight of the carboxymethyl cellulose and/or salts thereof. Less than 10 % by weight, addition of the binder can not provides sufficient effect. In excess of 40 % by weight, on the other hand, the water-swelling ability as well as the water-solubility of carboxymethyl cellulose and/or salts thereof will be excessively enhanced. As a result, the process of paper making will become difficult and the environmental burden due to drainage during the process of paper making will become serious.

The mixture of fiber and binder is preferably left for

30 minutes or longer in a stationary condition before subjected to the process of paper making. Starting of the process after the mixture has been left for a period shorter than 30 minutes may result in a trouble. Specifically, such premature starting of the process may cause an apprehension that an expected reaction of base with carboxymethyl cellulose and/or salts thereof might be obstructed.

The sheet formed in the manner as has been described above may be impregnated with liquid which contains suitable multivalent metallic ions to obtain the wet wipes of the invention. Preferably, bivalent metallic ions, particularly, ions of calcium, magnesium, zinc, etc. are used. Although ions of the other metals such as iron, aluminium and copper can be also used, it is difficult to exactly adjust their amounts to be used, since even extremely small amounts of these metals can make metallic salts of carboxymethyl cellulose water-insoluble or non-swelling in the presence of water.

To obtain the liquid which contains any one of these bivalent metallic ions, water-soluble bivalent metallic salts such as calcium chloride, magnesium sulfate and zinc sulfate may be dissolved in water. These metallic salts preferably have a concentration of 0.1 ~ 10 % by weight. At a

concentration lower than 0.1 % by weight, the wet strength required for the wet wipes can not be obtained. At a concentration higher than 10 % by weight, on the other hand, the water-dispersibility of the wet wipes may be unacceptably reduced.

Said liquid with which the wet wipes is impregnated preferably contains one or more kinds of organic solvent. Such organic solvent functions to further suppress swelling as well as solution of carboxymethyl cellulose and/or salts thereof possibly occurring in actual use of the wet wipes. Examples of the organic solvents include monovalent alcohol such as methanol, ethanol or propanol, polyhydric alcohol such as propylene glycol, isoprene glycol or polyethylene glycol and derivatives of these alcohols. It is also possible to use a mixture of two or more of these organic solvents.

Depending on the particular purpose of use, the liquid containing the bivalent metallic ions may additionally contain one or more of surfactant, disinfectant, antimicrobial, bacteriostatic agent, pH-adjuster, abrasive, colorant, thickener, humectant, perfume, deodorant, and sizing agent.

Details of the process for manufacturing wet wipes according to the invention will be more fully understood from the following description of examples.

Example 1 - 1:

A sample prepared by mixing non-bleached kraft pulp (NBKP) with sodium carboxymethyl cellulose (DS = 0.43, pH = 6.1: manufactured by NICHIRIN CHEMICALS in Japan) at a ratio by dry weight of 87.5/12.5 was mixed and dispersed in a quantity of tap water so as to obtain the sample having a concentration of 1 %. Sodium carbonate of 160 % by dry weight with respect to sodium carboxymethyl cellulose was dissolved in this sample liquid and left for 2 hours in a stationary condition. The sample liquid thus added with sodium carbonate was subjected to a process of paper making by a small-sized testing paper machine, then dried at a temperature of 110 °C for 90 seconds using a dryer of rotary drum type and a dried sheet having a basis weight of 40 g/m² was obtained. Such sheet was spray-impregnated with liquid composed of calcium chloride/propylene glycol/deionized water mixed at a ratio (by weight) of 0.5/30/69.5, a quantity of this liquid being 2.5 times of a dry weight of the sheet, and left at a temperature of 20 °C for 24 hours to obtain the wet

wipes.

Example 1 - 2:

The wet wipes were obtained under the same conditions as in Example 1 - 1 except that the liquid with which the sheet was spray-impregnated was composed of magnesium sulfate/propylene glycol/deionized water mixed at a ratio (by weight) of 0.5/30/69.5.

Example 1 - 3:

The wet wipes were obtained under the same conditions as in Example 1 - 1 except that the liquid with which the sheet was spray-impregnated was composed of zinc sulfate/propylene glycol/deionized water mixed at a ratio (by weight) of 0.5/30/69.5.

Comparative Example 1 - 1:

The wet wipes were obtained under the same conditions as in Example 1 - 1 except that the liquid with which the sheet was spray-impregnated was composed of sodium sulfate/propylene glycol/deionized water mixed at a ratio (by weight) of 0.5/30/69.5.

Comparative Example 1 - 2:

The wet wipes were obtained under the same conditions as in Example 1 - 1 except that the liquid with which the sheet was spray-impregnated was composed of propylene glycol/deionized water mixed at a ratio (by weight) of 30/70.

Example 2 - 1:

A sample prepared by mixing non-bleached kraft pulp (NBKP) with sodium carboxymethyl cellulose (DS = 0.43, pH = 6.1: manufactured by NICHIRIN CHEMICALS in Japan) at a ratio by dry weight of 87.5/12.5 was mixed and dispersed in a quantity of tap water so as to obtain the sample having a concentration of 1 %. Sodium carbonate of 160 % by dry weight with respect to said sodium carboxymethyl cellulose was dissolved in the sample liquid and left for 2 hours in a stationary condition. The sample liquid thus added with sodium carbonate was subjected to a small-sized testing paper machine, then dried at a temperature of 110 °C for 90 seconds using a dryer of rotary drum type and a dried sheet having a basis weight of 40 g/m². This sheet was spray-impregnated with liquid composed of calcium chloride/isoprene glycol/deionized water mixed at a ratio (by weight) of 3/10/87, a quantity of this liquid being 2.5 times of a dry

weight of the sheet, and left at a temperature of 20 °C for 24 hours to obtain the wet wipes.

Example 2 - 2:

The wet wipes were obtained under the same conditions as in Example 2 - 1 except that the liquid with which the sheet was impregnated was composed of magnesium sulfate/isoprene glycol/deionized water mixed at a ratio (by weight) of 3/10/87.

Example 2 - 3:

The wet wipes were obtained under the same conditions as in Example 2 - 1 except that the liquid with which the sheet was impregnated was composed of zinc sulfate/isoprene glycol/deionized water mixed at a ratio (by weight) of 3/10/87.

Comparative Example 2 - 1:

The wet wipes were obtained under the same conditions as in Example 2 - 1 except that the liquid with which the sheet was impregnated was composed of sodium sulfate/isoprene glycol/deionized water mixed at a ratio (by weight) of 3/10/87.

Comparative Example 2 - 2:

The wet wipes were obtained under the same conditions as in Example 2 - 1 except that the liquid with which the sheet was impregnated was composed of isoprene glycol/deionized water mixed at a ratio (by weight) of 10/90.

Example 3 - 1:

A sample prepared by mixing non-bleached kraft pulp (NBKP) with sodium carboxymethyl cellulose (DS = 0.43, pH = 6.1: manufactured by NICHIRIN CHEMICALS in Japan) at a ratio by dry weight of 87.5/12.5 was mixed and dispersed in a quantity of tap water so as to obtain the sample having a concentration of 1 %. Sodium carbonate of 160 % by dry weight with respect to said sodium carboxymethyl cellulose was dissolved in this sample liquid and left for 2 hours in a stationary condition. The sample liquid thus added with sodium carbonate was subjected to a small-sized testing paper machine, then dried at a temperature of 110 °C for 90 seconds using a drier of rotary drum type and a dried sheet having a basis weight of 40 g/m². Such sheet was spray-impregnated with liquid composed of calcium chloride/propylene glycol/deionized water mixed at a ratio (by weight) of 0.5/30/69.5, a quantity of said liquid being 2.5 times of a

dry weight of the sheet, and left at a temperature of 20 °C for 24 hours to obtain the wet wipes.

Example 3 - 2:

The wet wipes were obtained under the same conditions as in Example 3 - 1 except that a quantity of sodium carbonate dissolved in the sample liquid is 80 % or higher with respect to a dry weight of sodium carboxymethyl cellulose.

Comparative Example 3 - 1:

The wet wipes were obtained under the same conditions as in Example 3 - 1 except that the sample liquid was left for 2 hours in without dissolving sodium carbonate therein.

The wet wipes obtained in these Examples and Comparative Examples were evaluated as will be described below.

(1) Evaluation of water-dispersibility:

Sample pieces of wet wipes each dimensioned 10 cm x 10 cm were successively thrown into a 300 ml glass beaker filled with 300 ml of deionized water and stirred with a magnetic

stirrer (600 rpm) to observe how the dispersion of wet wipes progresses with the passage of time. Observations were evaluated as A, B and C on the basis of the period within which the sample pieces were broken into parts.

A: the sample piece was broken into parts within 100 seconds.

B: the sample piece was broken into parts within 200 seconds.

C: the sample piece was not broken into parts within 200 seconds.

(2) Evaluation of wet tensile strength:

Sample pieces of 25 mm (width) x 150 mm (length) were placed under the tension at a rate of 100 mm/min and a chuck spacing of 100 mm to determine break strength of the respective sample pieces. It was found that a break strength of 300 g or higher is sufficient for practical use of the wet wipes.

Evaluations of Examples and Comparative Examples based

on the observations will be seen from Table 1 given hereunder. As will be apparent from comparison of Examples 1 - 1 ~ 1 - 3 with Comparative Examples 1 - 1 ~ 1 - 2 as well as from comparison of Examples 2 - 1 ~ 2 - 3 with Comparative Examples 2 - 1 ~ 2 - 2, the wet wipes impregnated with the multivalent metallic ion containing liquid exhibit not only significantly enhanced wet strengths but also adequately high water-dispersibilities. On the contrary, the wet wipes impregnated with the liquid which contains monovalent metallic ions alone or none of metallic ions are short of the wet strengths.

Furthermore, comparison of Examples 3 - 1 ~ 3 - 2 with Comparative Example 3 - 1 suggests that the sheet obtained by the process of paper making without addition of sodium carbonate exhibit no significantly enhanced wet strength and its water-dispersibility is rather reduced even after such sheet has been impregnated with said multivalent metallic ion containing liquid.

Table 1

	added Na ₂ CO ₃ (wt %)	composition of impregnation liquid (ratio by weight)	water dispersion	wet tensile strength (gf/25mm width)
Example 1-1	160	calcium chloride/propylene glycol/water=0.5/30/69.5	A	704
Example 1-2	160	magnesium sulfate/propylene glycol/water=0.5/30/69.5	A	515
Example 1-3	160	zinc sulfate/propylene glycol/water=0.5/30/69.5	B	816
Comp-Ex 1-1	160	sodium sulfate/propylene glycol/water=0.5/30/69.5	A	284
Comp-Ex 1-2	160	propylene glycol/water=30/70	A	275
Example 2-1	160	calcium chloride/isoprene glycol/water=3/10/87	B	477
Example 2-2	160	magnesium sulfate/isoprene glycol/water=3/10/87	A	318
Example 2-3	160	zinc sulfate/isoprene glycol/water=3/10/87	B	503
Comp-Ex 2-1	160	sodium sulfate/isoprene glycol/water=3/10/87	A	92
Comp-Ex 2-2	160	isoprene glycol/water=10/90	A	75
Example 3-1	160	calcium chloride/propylene glycol/water=0.5/30/69.5	A	704
Example 3-2	80	calcium chloride/propylene glycol/water=0.5/30/69.5	B	466
Comp-Ex 3-1	0	calcium chloride/propylene glycol/water=0.5/30/69.5	C	326

Note: Comp-Ex means Comparative Example.

The process for making the wet wipes according to the invention facilitates a desired quantity of binder to conglutinate to a sheet obtained by a process of paper making since carboxymethyl cellulose and/or salts thereof which are relatively low in water-swelling ability or even water-insoluble are mixed as a binder in water-dispersible fiber. During a process of sheet forming, addition of suitable base enhances water-swelling ability as well as water-solubility of this water-dispersible fiber. Addition of suitable base thereby allows the wet wipes to be rapidly dissolved or dispersed in water. When the sheet containing such binder added with the base is then impregnated with multivalent metallic ion containing liquid, the binder reacts with the multivalent metallic ions to produce a salt. This salt temporarily enhances a wet strength of the wet wipes in actual use thereof.

The entire disclosure of Japanese Patent Application No. 8-197423 filed on July 26, 1996 including specification, claims and abstract are incorporated herein by reference in its entirety.



WHAT IS CLAIMED IS:

1. A process for making wet wipes composed of at least carboxymethyl cellulose and/or salts thereof and water-dispersible fiber and impregnated with multivalent metallic ion containing liquid, said process comprising the steps of:

subjecting a mixture of carboxymethyl cellulose and/or salts thereof which are relatively low in water-swelling ability or water-insoluble and the water-dispersible fiber to a process of paper making after said mixture has been added with suitable base to obtain a sheet containing a salt of said carboxymethyl cellulose having relatively high water-swelling ability or water-solubility; and

impregnating said sheet with multivalent metallic ion containing liquid.

2. The process according to Claim 1, wherein said base is sodium carbonate and said multivalent metallic ion is bivalent metallic ion.

3. The process according to Claim 1 or 2, wherein said multivalent metallic ion containing liquid is aqueous solution of multivalent metallic salt.



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4. The process according to any one of Claims 1 through 3,
wherein said liquid contains organic solvent.