

(12) **UK Patent Application** (19) **GB** (11) **2 220 881** (13) **A**  
(43) Date of A publication 24.01.1990

(21) Application No 8908940.3  
(22) Date of filing 20.04.1989  
(30) Priority data  
(31) 63105650 (32) 28.04.1988 (33) JP

(71) Applicant  
**Toyo Boseki Kabushiki Kaisha**  
  
(Incorporated in Japan)  
  
No 2-8 Dojima hama 2-chome, Kita-ku, Osaka, Japan  
  
(72) Inventor  
**Syozo Ota**  
  
(74) Agent and/or Address for Service  
**Haseltine Lake & Co**  
**Hazlitt House, 28 Southampton Buildings,**  
**Chancery Lane, London, WC2A 1AT, United Kingdom**

(51) INT CL'  
**B01D 11/02**

(52) UK CL (Edition J)  
**B5B BAE B32Y B901**

(56) Documents cited  
**GB 2009667 A GB 1150832 A GB 1004901 A**  
**GB 0764599 A GB 0527565 A GB 0527328 A**  
**GB 0526553 A GB 0459388 A GB 0453427 A**  
**US 4734239 A**

(58) Field of search  
UK CL (Edition J) **B5B BAE BAH BAJ BAK**  
INT CL' **B01D**

(54) **Improvements in or relating to superabsorbent materials**

(57) A superabsorbent fiber comprises a cellulose fiber substituted with hydrophilic groups such that the degree of substitution is greater than 0.2. The fiber has a coefficient of friction of 0.1 to 0.5 and is treated with a lubricating agent contained in a solvent which does not swell the fiber.

IMPROVEMENTS IN OR RELATING TO  
SUPERABSORBENT MATERIALS

5 The present invention relates to a water-  
insoluble superabsorbent fiber used as a sanitary  
material or in the field of agriculture and civil  
engineering. More particularly, the invention relates  
to a carboxymethyl cellulose fiber which can be  
uniformly blended with other fibers and has an  
10 excellent carding efficiency.

Up to this time, as superabsorbent fibers,  
there have been proposed fibers such as saponified  
polyacrylonitrile fiber (Japanese Patent Kokai No.  
31113/83), regenerated cellulose fiber in which a  
15 water-absorbing substance is dispersed (Japanese Patent  
Kokai No. 61418/74, Japanese Patent Kokai No. 9418/81,  
and carboxymethyl cellulose fiber (Japanese Patent  
Kokai No. 5393/77, Japanese Patent Publication No.  
15641/85, Japanese Patent Kokai No. 2707/85, Japanese  
20 Patent Kokai No. 60101/85). However, the saponified  
polyacrylonitrile fiber has a shortcoming of slow  
water-absorbing speed because of its slow swelling  
speed. The regenerated cellulose fiber in which a  
water-absorbing substance is dispersed lowers its fiber  
25 strength when the degree of etherification becomes  
large, and therefore it is difficult to use it as a  
shaped fiber product such as a woven fabric, a knit  
fabric, a non-woven fabric, etc. In order to use  
carboxymethyl cellulose fiber as a shaped fiber  
30 product, there has been proposed a method of  
carboxymethylation of a non-woven fabric made of  
regenerated cellulose filaments (Japanese Patent Kokai  
No. 15458/81) and a product carboxymethylated after  
forming the fiber into a shaped product (Japanese  
35 Patent Publication No. 43427/81). However, both are

limited in the shape after the carboxymethylation treatment, and it is impossible to form the superabsorbent fiber into a fiber product of an optional shape such as a sheet, by blending it with other fibers: In forming the superabsorbent fiber into a woven fabric, knit fabric, non-woven fabric, or other shaped fiber products, the fiber has to pass through the fiber-opening process, carding process, etc. To make the fiber pass through these processes, the fiber is applied with a lubricating oil which is dissolved or dispersed in water. When this method is applied for the superabsorbent fiber, the fiber swells, and after drying, it becomes stiff or agglutinates.

The object of the present invention is to remedy such shortcomings of the conventional techniques and to provide a superabsorbent fiber which has a high water-absorbing speed, a large capacity of water absorption and an excellent retention of absorbency and which can be blended with other fibers and can be formed into a fiber product of an optional shape in the subsequent processes.

The present invention relates to a water-swellaible carboxymethyl cellulose fiber of which the degree of etherification is more than 0.2 and the coefficient of friction is from 0.1 to 0.5, and to a method of treating the superabsorbent fiber characterised by applying a lubricating oil to the above-mentioned water swellaible superabsorbent fiber in a non-swelling solvent.

The term "cellulose fiber" as used in the present invention means regenerated cellulose fibers such as viscose rayon, polynosic fiber, cuprammonium rayon, etc. and natural cellulose fibers. In order to obtain a balance between the degree of carboxymethylation and fiber strength, as shown in the

present invention, a regenerated polynosic fiber is desirable which is obtained by spinning a viscose containing cellulose of a degree of polymerization of 450 to 700, coagulating and drawing the resulting filaments in a weak acid bath.

5  
10  
15  
When an ordinary rayon (i.e. a regenerated cellulose fiber obtained by spinning a viscose containing 7 - 10 % cellulose of a degree of polymerization of 250 - 320, coagulating and regenerating the resulting filaments in a strong acid bath, and drawing after crystallization) is carboxymethylated, there occurs a larger drop of fiber strength than in the case of polynosic fiber. It is therefore necessary to pay attention in the subsequent processes for forming fiber products, such as, for example, the carding process.

20  
In natural cellulose fibers, for example cotton, the loss of strength by carboxymethylation is larger than that of polynosic fiber, and therefore attention must be also paid in the subsequent processes.

25  
The term "water-swellable superabsorbent fiber" as used in the present invention means carboxymethyl cellulose fiber of which the absorbency is more than 15 times.

30  
35  
The carboxymethylation may be conducted in the conventional known method which comprises converting cellulose fiber into alkali cellulose fiber with caustic soda, and carboxymethylating the fiber with monochloroacetic acid. In this treatment, it is desirable to use a reaction system in which a solvent is added to suppress the swelling of the resulting carboxymethyl cellulose. At this time, the degree of substitution of carboxymethylation (degree of etherification, hereinafter abbreviated as DS) is

necessary to be more than 0.2, preferably more than 0.25. When it is less than 0.2, the affinity with water is small and the swelling is not sufficient, and therefore it is impossible to obtain an absorbing body  
5 of a high water swelling speed.

In order to obtain a swollen gel fiber quickly with water, it is necessary that the DS should be larger than 0.2, and the larger this value, the more pronounced is this tendency. However, at a DS value  
10 higher than 0.3, carboxymethyl cellulose dissolves partly or completely. Accordingly, it is necessary also in the present invention to conduct insolubilization treatment depending on necessity. The  
15 insolubilization treatment includes various methods such as a method wherein before carboxymethylation treatment, a cross-linked structure is formed in the fiber with formaline, etc.; a method wherein at the same time with or after the carboxymethylation  
20 treatment, a cross-linked structure is formed with a cross-linking agent such as epichlorohydrin, diglycidyl ether, etc.; a method wherein after the carboxymethylation treatment, the fiber is heat-treated for insolubilization. Any of these methods may be  
employed.

25 It is desirable that the fiber strength should be more than 1.8 g/d, preferably more than 2.0 g/d. At a strength lower than 1.8 g/d, there occurs a considerable damage during blending with other fibers, and therefore attention should be paid during each  
30 process.

By the above-mentioned insolubilizing treatment, the superabsorbent fiber can be obtained, and in order to improve fiber-opening and spinnability, oiling treatment is conducted. In this oiling  
35 treatment, it is important to conduct the treatment

with a solvent or a solvent containing a small quantity of water so as not to swell the fiber. Such methods of treatment include the exhaust method, the pad-dry method and the spray method. Any method may be employed, but the exhaust method is desirable.

It is important that the coefficient of fiber-to-fiber static friction (JIS-L-1015, the Röder method) should be 0.1 - 0.5 preferably 0.2 - 0.4. It is desirable that the quantity of application of the oiling agent should be 0.01 - 3 weight %, and a quantity of 0.1 - 1 weight % is especially desirable. At a coefficient of static friction less than 0.1, the draft in the spinning process becomes difficult, and this forms a cause of troubles in the production of yarns. On the other hand, at a value exceeding 0.5, the fiber-opening becomes worse. Also, when an excessive quantity of the oiling agent is applied, the carding efficiency is impaired.

It is important that the oiling agent should be used in the form of a solution or dispersion in a solvent which does not swell the fiber. When the oiling agent is applied as dissolved or dispersed in a solvent which swells the fiber, for example in water, the fiber absorbs water and gels, and after drying, agglutination occurs, and therefore the application of the oiling agent in such a state does not give a favourable coefficient of friction.

The lubricating oil is not particularly limited as far as it dissolves in a non-swelling solvent mentioned later. However, a lubricating oiling containing more than 10 weight % of a nonionic polyethylene oxide adduct is desirable in view of the solubility and the non-impairment of the water absorption of the fiber. It is necessary that the quantity of application of the oiling agent to the

fiber should be 0.01 - 3 weight %, preferably 0.1 - 1.0 weight %, from the point of view of fiber-opening, fiber-bundle condensing, and carding efficiency.

5 The non-swelling solvents are not particularly limited as far as they do not swell the superabsorbent fiber, and such solvents include alcohols such as methanol, ethanol, propanol, etc., ketones such as acetone, methyl ethyl ketone, etc., and aromatic solvents such as benzene, toluene, etc. From the  
10 viewpoint of the solubility of the oiling agent and the drying property of the solvent, it is desirable to use a lower alcohol such as methanol or ethanol in single form or in mixture with water, and the mixing ratio of water to alcohol is 0:100 - 50:50.

15 To apply the oiling agent, there are methods such as a method in which the fiber is immersed in a solution of the oiling agent and then squeezed, a method in which a solution of the oiling agent is circulated in a tank filled with the fiber, a method in  
20 which a solution of the oiling agent is applied by spraying, etc. However, the method is not limited to any particular method.

In the following, the present invention will be explained concretely by Examples, wherein the  
25 absorbency, the degree of substitution and the tensile strength were determined as follows:

(Absorbency)

About 0.5 g of the sample was weighed accurately ( $W_0$ ). The sample was put in a  
30 polypropylene non-woven bag and was immersed in a 500 ml aqueous 0.9% solution of sodium chloride for 30 minutes. After draining water by hanging the bag in air for 30 minutes, it was weighed ( $W_1$ ). The absorbency was obtained by the following formula:

35

$$\text{Absorbency (X)} = \frac{W_1 - W_0 - A}{W_0}$$

wherein A is the weight of the non-woven bag alone  
after absorption of water.

5

(Absorbency under pressure)

The sample after the measurement of absorbency  
was held between two sheets of filter paper (TOYA 5A  
110 mm  $\phi$  ) and was allowed to stand still under a load  
of 500 g for 30 minutes. It was then weighed ( $W_2$ ).  
The absorbency under pressure was obtained by the  
following formula:

10

$$\text{Absorbency under pressure} = \frac{W_2 - W_0 - B}{W_0}$$

15

wherein B is the weight of the non-woven bag alone  
after water absorption and dehydration under pressure.

(Retention of absorbency)

$$R (\%) = \frac{Y}{X} \times 100$$

20

wherein X is the above-mentioned absorbency, and Y is  
the absorbency under pressure.

(Degree of substitution)

After the carboxymethyl cellulose sample was  
converted to the complete acid type, the carboxyl  
groups were obtained by the acid-base titration and the  
degree of etherification was calculated therefrom.  
(Tensile strength)

25

This was obtained according to the method of  
constant rate of extension of JIS-L-1015.

30

(Coefficient of fiber-to-fiber static friction)

This was obtained according to the Roder  
method of JIS-L-1015.

(Carding efficiency)

35

Ten grams of the fiber was made to pass



through a "Sample Roller Carding Machine" produced by Yamato Kiko Co., Ltd. and the state of the web obtained and the state of fiber entwinement around each roller were judged visually. Also, the ratio of the quantity of the web that passed through the card to the total quantity of the fiber charged (% yield) was obtained.

5

Visual judgement:

◎ : Carding efficiency high; no entwinement around rollers, a good web was obtained.

10

○ : Carding efficiency high; no entwinement around rollers; shaping into the form of web was possible.

15

X : Carding efficiency low; much entwinement around rollers; shaping into the form of web was difficult.

XX : Impossible to pass through the card.  
Production of polynosic fiber

20

The polynosic cellulose fiber which exhibits an excellent effect in the present invention was obtained as follows:

25

A wood pulp having a relative viscosity of 5.1 was steeped in a aqueous 235 g/l caustic soda solution of 58°C, and was compressed to 2.6 times (based on the weight of the pulp). Carbon disulfide was then added and sulfuration was carried out at 28°C for 100 minutes. The resulting cellulose xanthate was dissolved in a aqueous 3.0p g/l dilute caustic soda solution. The resulting solution was filtered, aged, defoamed, and filtered again to obtain a viscose of a cellulose concentration of 4.8 %, an alkali concentration of 2.7 %, a  $\lambda$  value of 75 and a falling ball viscosity of 220 seconds/20 cm. This viscose was spun into a spinning bath of 28°C containing 18.5 g/l sulfuric acid, 0.6 g/l zinc sulfate and 55 g/l sodium sulfate, through a spinneret having 3000 spinning holes

35

whose hole diameter was 0.07 mm. The resulting filaments were drawn out in a 7.5 g/l sulfuric acid bath of 27°C at a draft ratio of 70 %. The filaments were further treated in a 1.8 g/l sulfuric acid bath of 90°C, and was scoured, cut and dried to obtain a polynosic staple fiber of 1.5 d x 38 mm. This fiber was evaluated as Comparative Example 1, and an ordinary rayon fiber sold on the market (1.5 d x 51 mm) was evaluated as Comparative Example 2.

Example 1

The polynosic staple fiber of 1.5 d x 38 mm obtained by the above-mentioned method was carboxymethylated in the following way.

Caustic soda	34 g
Monochloroacetic acid	36 g
Water	180 ml
Ethanol	800 ml

70 grams of the fiber was put into the above bath and was treated at 65°C for 3 hours. The fiber was then washed with methanol and was made to absorb a 25 weight % methanol solution of an oiling agent consisting of 90 parts of oleyl alcohol ethylene oxide adduct (5 moles) and 10 parts of sodium lauryl phosphate so that the quantity of absorbed liquid could become 200 %, and was dried. The quantity of the oiling agent fixed was 0.5 weight %.

Thereafter the fiber was heat-treated at 100°C for 10 minutes.

Examples 2 and 3 and Comparative Example 3

These were carried out in the same way as Example 1 except that the bath composition of Example 1 was changed variously so that carboxymethylation treatment of different degrees of substitution could be conducted.

Example 4

This example was carried out in the same way as Example 1 except that a rayon staple of fiber of 1.5 d x 38 mm was used as the fiber to be  
5 carboxymethylated.

Example 5

This Example was carried out in the same way as Example 4 except that the bath composition of carboxymethylation treatment was changed so that  
10 carboxymethylation treatment of different degrees of substitution could be conducted.

Comparative Example 4

The carboxymethyl cellulose fiber obtained in Examplem 1 was dried before oiling and was used as  
15 Comparative Example 4.

Comparative Example 5

The carboxymethyl cellulose fiber of Comparative Example 4 was subjected to aqueous oiling treatment by spraying an aqueous 0.25 weight % solution  
20 of an oiling agent consisting of 90 parts of oleyl alcohol ethylene oxide adduct (5 moles) and 10 parts of sodium lauryl phosphate.

The characteristics of the fibers obtained in Examples 1 - 5 and Comparative Examples 1 - 5 are shown  
25 in Table 1.

Table 1

	Original fiber	Degree of etherification	Tensile strength (g/d)	Absorbency	Retention of absorbency (%)	Oiling agent fixed (%)
Example 1	Polynosic	0.45	2.4	25	72	0.5
"	Polynosic	0.30	2.8	23	61	0.5
"	Polynosic	0.22	3.4	21	48	0.5
"	Rayon	0.43	1.4	24	71	0.5
"	Rayon	0.21	1.7	20	50	0.5
Comparative						
Example 1	Polynosic	0.0	3.5	11	30	0.0
"	Rayon	0.0	2.9	12	25	0.0
"	Polynosic	0.18	3.5	18	35	0.5
"	Polynosic	0.45	2.4	25	72	0.0
"	Polynosic	0.45	Measurement impossible*	Measurement impossible*	Measurement impossible*	Measurement impossible*

(\*) Since the oiling agent was applied in aqueous form, the fiber surface became sticky. This made the handling of the fiber impossible and consequently the measurement was impossible.

/Cont...

Table 1 /Cont....

	Original fiber	Coefficient of friction ( $\mu$ s)	Fiber-opening property
Example 1	Polynosic	0.26	○
" 2	Polynosic	0.25	○
" 3	Polynosic	0.27	○
" 4	Rayon	0.25	○
" 5	Rayon	0.25	○
Comparative Example 1	Polynosic	0.47	△
" 2	Rayon	0.55	×
" 3	Polynosic	0.25	○
" 4	Polynosic	0.70	×
" 5	Polynosic	Measurement impossible*	×

(\*) Since the oiling agent was applied in aqueous form, the fiber surface became sticky. This made the handling of the fiber impossible and consequently the measurement was impossible.

Examples 6 - 9

After a polyinosic fiber of 1.5 d x 38 mm was  
carboxymethylated in an ethanol/water solution of  
5 monochloroacetic acid and caustic soda, it was cross-  
linked under heat to obtain a superabsorbent fiber.  
The degree of substitution of the thus-obtained  
carboxymethyl cellulose fiber was 0.45 and its  
absorbency was 29 times.

10 An oiling agent containing the following  
components was then dissolved in methanol in a quantity  
of 1.5 - 10 weight %, and was applied to the fiber by  
spraying in a quantity of 20 weight % based on the  
fiber.

15 Oleyl alcohol ethylene oxide adduct (5 moles) 90 parts  
Sodium lauryl phosphate 10 parts

The characteristics of the thus-obtained fiber  
is shown in Table 2.

Example 10

20 The carboxylated cellulose fiber used in  
Example 6 was immersed in a 1 weight % methanol  
solution of the oiling agent shown in the following to  
apply the oiling agent, and was then dehydrated to a  
squeeze ratio of 50 %.

25 Oleyl alcohol ethylene oxide adduct (5 moles) 25 parts  
Vegetable fat 45 parts  
Polypropylene/polypropylene glycol ether 30 parts

Comparative Examples 8 and 9

30 When an aqueous 2.5 weight % solution of the  
oiling agent shown in Example 6 was spray-applied in a  
quantity of 20 weight % to the superabsorbent fiber  
shown in Example 1, the fiber swelled, and after  
drying, agglutination occurred among the filaments.

35 Also, when a water/ethanol (80/20) 2.5 weight  
% solution of the oiling agent shown in Example 6 was

spray-applied in a quantity of 20 weight % to the superabsorbent fiber shown in Example 1, the fiber swelled, and after drying, agglutination occurred partly among the filaments.

5 Comparative Example 10

When the following oiling agent was mixed with methanol in a quantity of 2.5 weight %, it did not dissolve or disperse uniformly. When this mixture was spray-applied to the fiber shown in Example 6, uniform application of the oiling agent was impossible. Consequently, the carding efficiency was low.

Lauryl alcohol sulfuric acid ester	60 parts
Oleyl oleate	20 parts
Sodium lauryl phosphate	20 parts

Table 2

	Kind of fiber	Absorbency (g/g)	Retention of absorbency (%)	% conc. in the bath		Oiling agent fixed (%)	Coefficient of friction ( $\mu$ s)
				oiling agent	water		
Example 6	CM Cellulose	29	72	1.5	0	0.3	0.28
" 7	"	"	"	2.5	0	0.5	0.26
" 8	"	"	"	5.0	0	1.0	0.24
" 9	"	"	"	10.0	0	2.0	0.20
Comparative Example 6	"	"	"	0.25	0	0.05	0.38
" 7	"	"	"	17.5	0	3.5	0.15
Example 10	"	"	"	1.0	0	0.5	0.27
Comparative Example 8	"	"	"	2.5	100	"	-*
" 9	"	"	"	2.5	80	"	-*
" 10	"	"	"	2.5	0	"	Large fluctuation

/Cont....

\* Measurement was impossible because of agglutination of fibers.



Table 2 /Cont...

	Kind of fiber	Carding efficiency		General evaluation
		Ratio of card passage (%)	State of card passage	
Example 6	CM Cellulose	95	Good	⊙
" 7	"	95	Good	⊙
" 8	"	98	Good	⊙
" 9	"	85	Good	○
Comparative Example 6	"	60	Much entwinement around rollers	×
" 7	"	80	Web breakage	×
Example 10	"	93	Good	⊙
Comparative Example 8	"	-*	Passage impossible	×
" 9	"	-*	Passage impossible	×
" 10	"	60	Much entwinement around rollers	×

\* Measurement was impossible because of agglutination of fibers.

From these results, the following can be acknowledged:

5 (1) At a value less than 0.2 of the degree of substitution (degree of carboxymethylation), even if the absorbency reaches a satisfactory value, the retention of absorbency is insufficient. Therefore such a fiber is not suitable for actual use as an absorbing body.

10 (2) By carboxymethylation, the coefficient of friction of the fiber drops to a large extent, and therefore it is impossible to retain a fiber-opening property of a level of practical use.

15 (3) Even though an oiling agent is applied to the fiber to improve the opening property, if the oiling agent is an aqueous form, the fiber surface becomes sticky. This makes the fiber stick together to form masses and makes it impossible to handle them as fibers.

20 (4) Application of the oiling agent in the form of a solvent solution makes it possible to attain the aimed coefficient of friction of 0.1 - 0.5, whereby the problems in the fiber-opening process can be solved.

25 By the present invention, it became possible to obtain a superabsorbent fiber having an absorbency more than 20 times and having a fiber strength that allows the fiber to pass through the subsequent processes.

CLAIMS:

1. A superabsorbent cellulose fiber in which hydrophilic groups are introduced, of which the degree of substitution is greater than 0.2 and the coefficient of friction is 0.1 to 0.5.

2. The superabsorbent fiber as claimed in Claim 1 wherein the hydrophilic groups are carboxymethyl groups.

3. The superabsorbent fiber as claimed in Claim 1 or 2 wherein the cellulose fiber is a polynosic fiber.

4. The superabsorbent fiber as claimed in any of Claims 1, 2 and 3 wherein the fibre is applied with a lubricating oil.

5. A superabsorbent carboxymethyl cellulose fiber having a degree of substitution of 0.2 to 0.8, and being applied with a lubricating oil, and having a coefficient of friction of 0.1 to 0.5.

6. A method of treatment of the superabsorbent fiber in which hydrophilic groups are introduced wherein said superabsorbent fiber is applied with a solution of a lubricating oil dissolved in a solvent which does not swell the fiber.

7. The method of treatment as claimed in Claim 6 wherein the hydrophilic groups are carboxymethyl groups.

8. The method of treatment as claimed in Claim 6 wherein the lubricating oil is a nonionic surface-active agent of the polyalkylene oxide type.

9. The method of treatment as claimed in Claim 6 wherein the non-swelling solvent is an organic solvent system consisting of 100 % methanol and/or ethanol, or a system containing 0 - 50 % water.

10. A superabsorbent fiber substantially as described in any of Examples 1 to 10.