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This paper comprises:

*	Letter from the applicant	2011/A(Ch)/EN/1-6
*	Document D1	2011/A(Ch)/EN/7-9
*	Document D2	2011/A(Ch)/EN/10-11

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LETTER FROM THE APPLICANT

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Dear Sirs,

We would like you to file a European patent application covering our invention as described in this letter. All matter worth patenting should be covered. You should however note that for financial reasons we are not able to pay claim fees for this application. In order to assist you in drafting the application, documents D1 and D2, which in our opinion best represent the state of the art, are enclosed with this letter.

As you know our company has been active in the field of absorbent products for many years. In particular we are interested in products for absorbing bodily fluids such as baby diapers, adult incontinence items, female hygiene products and bandages. These products always comprise a liquid-impermeable first layer, a second layer made from a non-woven material and an absorbent core between these two layers. The absorbent core is usually a mixture of a superabsorbent polymer and fibres. It is also possible to use a superabsorbent polymer on its own, but this is less preferred. Superabsorbent polymers are polymers able to absorb a large quantity of liquid.

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The superabsorbent polymers currently available on the market are almost exclus acrylic-based products such as acrylic acid grafted onto a carrier or cross-linked polyacrylic acid. These polyacrylic superabsorbent polymers are not readily biodegradable. It would be very desirable for environmental reasons to provide biodegradable superabsorbent polymers with properties similar to those of the traditional polyacrylic superabsorbent polymers.

Our research has now led to the development of superabsorbent polymers resulting from the cross-linking of sodium carboxymethylcellulose (CMCNa) and hydroxyethylcellulose (HEC) with a carbodiimide as cross-linking agent. These polymers are biodegradable.

Carbodiimides are unconventional cross-linking agents. They induce the formation of ester bonds between CMCNa and HEC without participating in a bond themselves. The carbodiimides are transformed into urea derivatives during the cross-linking reaction. It has been confirmed experimentally that no trace of carbodiimide remains in the final product. A particularly preferred carbodiimide is 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC).

The method we use for preparing these superabsorbent polymers comprises the following steps:

(i) reacting an aqueous solution of sodium carboxymethylcellulose (CMCNa) and hydroxyethylcellulose (HEC) with a carbodiimide cross-linking agent in the presence of an acid catalyst to produce a polymer gel;

(ii) washing the gel with water, deionised water being preferred, as this results in polymers with higher absorption capacity;

(iii) drying the gel by phase inversion.

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The pH in step (i) is usually from 3 to 6, preferably from 3.5 to 4.5. There is no res on the acid to be used as the acid catalyst. It is typically citric acid. The sum of the concentrations of CMCNa and HEC in the aqueous solution must be from 3 to 10 wt.%. The sum of the concentrations of CMCNa and HEC in the aqueous solution is usually from 4 to 9 wt.%. It has been shown experimentally that concentrations below 3 wt.% or above 10 wt.% impede cross-linking. The weight ratio of CMCNa to HEC has to be from 0.5 to 5.0, preferably from 0.6 to 3.2. It is essential that the concentration of carbodiimide in the solution is from 5 to 15 wt.%, otherwise a gel with very poor mechanical properties is obtained. The concentration of carbodiimide is usually from 5 to 10 wt.%.

In the phase inversion drying step the gel is contacted with a liquid which does not dissolve the polymer but will absorb water. The polymer gel is contacted with the liquid until it precipitates as white granules. The liquid used in this step is usually acetone. Drying the superabsorbent polymer by phase inversion results in a much higher absorption capacity than air drying. It is however also possible to use air drying if necessary.

The conditions described above result in a degree of cross-linking of from 2 to 10%. This degree of cross-linking is essential for a useful superabsorbent polymer. The degree of cross-linking is measured according to Italian Standard ITNA0011 published in 1990.

The superabsorbent polymer made by the method described above is in the form of white granules. This product is formed into an absorbent product by conventional methods. The granules are mixed with fibres in hot air in a rotating vacuum drum to make the absorbent core. The absorbent core is laminated between the first layer and the second layer as it leaves the drum in order to make the absorbent product.

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Example 1:

A number of superabsorbent polymers have been made and compared with Superwet A1000, a commercially available polyacrylic superabsorbent polymer. The polymers were evaluated by measuring their absorption capacity, water retention and shear modulus in accordance with the test methods published in US-A-3 000 000. The absorption capacity is a measure of the amount of liquid that can be absorbed. The water retention measures how much of the liquid is retained under moderate load. The shear modulus is an indication of how likely it is that the polymer granules will break. Acceptable products require an absorption capacity of at least 25 g H_2O per g of polymer, a water retention of at least 60 % and a shear modulus of at least 2 MPa.

The cross-linked carboxymethylcellulose/hydroxyethylcellulose superabsorbent polymers were made using the following method:
An aqueous solution containing CMCNa and HEC was prepared. The sum of the concentrations of these two components was set to be 5 wt.%. The weight ratio of CMCNa to HEC is as indicated in Table 1. The carbodiimide (EDC) cross-linking agent was added until its concentration was 7 wt.% in the aqueous solution. Citric acid was then added as a catalyst giving rise to a solution of a pH of 4.0. The gel obtained was washed with deionised water and then dried by phase inversion in acetone until it precipitated as white granules.

The properties of Superwet A1000, a commercially-available polyacrylic superabsorbent polymer, were also determined: an absorption capacity of 45 g H_2O /g polymer, a water retention of 65 % and a shear modulus of 3.0 MPa were the measurements obtained.

The CMCNa/HEC polymers of the invention all have a degree of cross-linking of 5%. The results for the CMCNa/HEC superabsorbent polymers are presented in Table 1:

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Table 1

Sample Number	CMCNa to HEC wt. Ratio	Absorption Capacity g $H_2$0 per g polymer	Water retention %	Shear Modulus MPa
1	0.6	32	71	2.4
2	0.8	36	60	3.2
3	1.0	34	61	3.1
4	1.2	39	65	3.0
5	1.4	36	77	2.9
6	1.6	38	75	3.1
7	1.8	36	69	3.2
8	2.0	60	70	3.0
9	2.2	59	69	2.9
10	2.4	69	72	2.8
11	2.6	72	67	3.3
12	2.8	70	69	3.2
13	3.0	73	61	3.1
14	3.2	34	65	2.4

The CMCNa/HEC superabsorbent polymers all exhibit excellent properties and are all very useful. The choice of superabsorbent polymer to use will depend on the precise product being made.

Example 2:

Absorbent products were prepared using the CMCNa/HEC superabsorbent polymers of sample 4 and sample 11 from example 1, and using Superwet A1000
(a polyacrylic superabsorbent polymer).

A stream of cotton fibres in hot air was fed into a rotating vacuum drum. Superabsorbent polymer granules were fed into the stream. The absorbent core obtained is laminated between a liquid-impermeable first layer and a second layer made from a non-woven material.

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The absorbent core contains 30 wt.% of superabsorbent polymer. The absorption capacity and water retention of the absorbent product were measured as described in US-A-3 000 000. The perceived softness is evaluated by a group of testers on a scale of 1 to 100. The higher the value the better and the more comfortable the absorbent product will feel to the user. The test results are presented in Table 2:

Table 2

Superabsorbent polymer used	CMCNa/HEC superabsorbent polymer of Sample 4	CMCNa/HEC superabsorbent polymer of Sample 11	Polyacrylic superabsorbent polymer Superwet A1000
Absorption Capacity g H_2O per g polymer	65	95	80
Perceived Softness	80	72	31
Water retention %	65	70	72

We have repeated these experiments with the sole difference that the cotton fibres were replaced by other cellulosic fibres, namely flax fibres and rayon fibres. Similar results were obtained. Although the granules of superabsorbent polymer are located within the core of the absorbent product, the nature of the polymer used appears to significantly affect the perceived softness.

In a further series of experiments the cellulosic fibres were replaced by the synthetic fibres made from polypropylene or polyamide. In this case the perceived softness for all three superabsorbent polymers was very similar.

Yours sincerely

Pietro Pannolino
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DOCUMENT D1 (state of the art):

Biodegradable superabsorbent polymer and soil-improving composition containing the polymer

[001] In arid climates, agricultural yields are often limited by the inability of the soil to store water. Thus even where irrigation water is available, it is used inefficiently. It has been proposed to add a superabsorbent polymer to the soil to improve its water-retaining capacity. A significant problem with this proposal is that the superabsorbent polymers available on the market are polyacrylics and thus only biodegrade very slowly. It is not permitted to include non-biodegradable materials in soil-improving compositions in many countries.

[002] In order to solve this problem, a new superabsorbent polymer is proposed which is a cross-linked mixture of sodium carboxymethylcellulose (CMCNa) and hydroxyethylcellulose (HEC). The weight ratio between CMCNa and HEC may be from 0.1 to 5.0 and is preferably from 0.8 to 1.6. This weight ratio ensures that the polymer is able to absorb a large quantity of water and release it to plants. The cross-linking is performed in aqueous solution and any known cross-linking agent such as epichlorohydrin, formaldehyde, carbodiimides and divinylsulphone may be used. The gel obtained in this step is washed with deionised water and dried by phase inversion. The polymer is obtained as white granules.

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[003] The granules of superabsorbent polymer can be applied to soil by conventional means such as by spreading or dispersing in a liquid carrier and spraying. However, in one preferred embodiment the granules are placed in a bag made from biodegradable cellulosic fibres. The bag may also contain fertilizer or pesticides mixed with the superabsorbent granules. The bag must obviously allow water to pass through it unhindered. This embodiment is very useful as it ensures that the superabsorbent polymer can be accurately located to provide water only to the roots of the plant.

Example 1:

[004] An aqueous solution of CMCNa and HEC was prepared. The overall concentration of CMCNa and HEC was 5 wt.%. 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC) as cross-linking agent was added until its concentration in the aqueous solution was 7 wt.%. Citric acid was then added as an acid catalyst giving rise to a solution of pH 4.0. The gel obtained was washed with deionised water and dried by phase inversion in acetone. The absorption capacity was measured in accordance with the method described in US-A-3 000 000. The water release capacity was measured by absorbing 20 g of deionised water into 1 g of the polymer and then drying it in a flow of dry air at 30°C for 3 hours. The percentage water remaining in the polymer is then measured. Values of from 38 to 50% are ideal for superabsorbent polymer for conditioning soil.

[005] The results are presented in Table 1:

CMCNa to HEC weight ratio	Absorption capacity g H_2O per g polymer	Water release capacity (%)
0.8	36	40
1.0	34	42
1.2	39	43
1.4	36	45
1.6	38	51

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Example 2:

[006] Granules with a weight ratio of CMCNa to HEC of 1.2 manufactured in accordance with example 1 were used in a practical test in a field used to grow lettuce in southern Spain. The granules were spread on one half of the field and the other half was left untreated.

[007] Lettuces were planted in the field and irrigated according to the standard procedure. Once the plants were established, each half of the field was only watered upon the first sign of wilting. The half of the field treated with the granules required 30% less water. The quality of the lettuces grown on each half of the field was identical.

[008] In order to test for biodegradability, a sample of soil from the field was investigated one year after the initial treatment with the polymer. No traces of the polymer could be detected, demonstrating that the polymer was completely biodegraded.

Claims

1. Superabsorbent polymer consisting of a cross-linked mixture of sodium carboxymethylcellulose (CMCNa) and hydroxyethylcellulose (HEC).

2. Superabsorbent polymer according to claim 1 where the weight ratio of CMCNa to HEC is from 0.8 to 1.6

3. The use of the superabsorbent polymer of claims 1 or 2 as a soil conditioner.

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DOCUMENT D2 (state of the art):

Soft absorbent products based on fibres and polyacrylics:

[001] Absorbent products for absorbing bodily fluids such as baby diapers are widely used. These products comprise an absorbent core arranged between a water-impermeable first layer and a non-woven second layer. Consumer feedback has indicated that these products often feel rough against the skin. We have surprisingly found that this is related to the composition of the absorbent core.

[002] In order to solve this problem, an absorbent structure is proposed with a core comprising polyacrylic superabsorbent polymers and cellulosic fibres. The preferred cellulosic fibres are cotton fibres. The preferred polyacrylic superabsorbent polymer is Superwet A1000.

[003] The absorbent products are made by conveying the fibres in a stream of hot air to a rotating vacuum drum. Superabsorbent polymer granules are fed into the stream of fibres thereby mixing them with the fibres and forming the absorbent core. The absorbent core is then laminated with the first layer and second layer to form the absorbent product.

[004] Two absorbent products were made: one (product A) with a core consisting of 15% Superwet A1000, and the rest being cotton fibres; the second one (product B) had a core consisting of 30% Superwet A1000, and the rest being cotton fibres. These products were given to a testing panel and their softness was rated from 1-100, with a higher value being better. Product A had a perceived softness value of 50 and product B had a perceived softness of 31. These products are thus much softer than products commercially available today which all have a perceived softness of between 10 and 20.

[005] The tests were repeated with other cellulosic fibres and identical results were obtained.

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Claim

1. An absorbent product comprising an absorbent core comprising cellulosic fibres and polyacrylic superabsorbent polymer granules.

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