

ABSORBENT MATERIAL

The present invention relates to an absorbent material,
5 more particularly a material of the type commonly referred to
as a "superabsorbent".

The substances currently termed "superabsorbents" are
typically slightly cross-linked hydrophillic polymers. The
10 polymers may differ in their chemical nature but they share
the property of being capable of absorbing and retaining even
under moderate pressure amounts of aqueous fluids equivalent
to many times their own weight. For example superabsorbents
can typically absorb up to 100 times their own weight or even
15 more of distilled water.

Superabsorbents have been suggested for use in many
different industrial applications where advantage can be
taken of their water absorbing and/or retaining properties
20 and examples include agriculture, the building industry, the
production of alkaline batteries and filters. However the
primary field of application for superabsorbents is in the
production of hygienic and/or sanitary products such as
disposable sanitary napkins and disposable diapers either for
25 children or for incontinent adults. In such hygienic and/or
sanitary products, superabsorbents are used, generally in
combination with cellulose fibres, to absorb body fluids such
as menses or urine. However, the absorbent capacity of
superabsorbents for body fluids is dramatically lower than
30 for deionised water. It is generally believed that this
effect results from the electrolyte content of body fluids
and the effect is often referred to as "salt poisoning".

The water absorption and water retention characteristics
35 of superabsorbents are due to the presence in the polymer
structure of ionisable functional groups. These groups are
usually carboxyl groups, a high proportion of which are in

the salt form when the polymer is dry but which undergo dissociation and solvation upon contact with water. In the dissociated state, the polymer chain will have a series of functional groups attached to it which groups have the same electric charge and thus repel one another. This leads to expansion of the polymer structure which, in turn, permits further absorption of water molecules although this expansion is subject to the constraints provided by the cross-links in the polymer structure which must be sufficient to prevent dissolution of the polymer. It is assumed that the presence of a significant concentration of electrolytes in the water interferes with dissociation of the functional groups and leads to the "salt poisoning" effect.

Attempts have been made to counteract the salt poisoning effect and improve the performance of superabsorbents in absorbing electrolyte containing liquids such as menses and urine. Thus Japanese Patent Application OPI No. 57-45,057 discloses an absorbent which comprises a mixture of a superabsorbent such as a cross-linked polyacrylate with an ion exchange resin in powder or granular form. EP-A-0210756 relates to an absorbent structure comprising a superabsorbent and an anion exchanger, optionally together with a cation exchanger, wherein both ion exchangers are in fibrous form. Combining a superabsorbent with an ion exchanger attempts to alleviate the salt poisoning effect by using the ion exchanger, generally as a combination of both an anion exchanger and a cation exchanger, to reduce the salt content of the liquid. The ion exchanger has no direct effect on the performance of the superabsorbent and it may not be possible to reduce the salt content sufficiently to have the desired effect on the overall absorption capacity of the combination. In addition, besides being expensive, the ion exchanger has no absorbing effect itself and thus acts as a diluent to the superabsorbent.

An object of the present invention is to provide a

superabsorbent with improved performance in the presence of electrolyte, for example in the case of menses or urine.

The present invention provides a superabsorbent material
5 which comprises a combination of

(1) an anionic superabsorbent in which from 20 to 100% of the functional groups are in free acid form; and

(2) an anion exchanger in which from 20 to 100% of the
10 functional groups are in basic form.

The anionic superabsorbent preferably has from 50 to 100% and more preferably has substantially 100% of the functional groups in free acid form. The cationic
15 superabsorbent preferably has from 50 to 100% and more preferably has substantially 100% in basic form.

As already noted above, anionic superabsorbents have to have functional groups in salt form before they act as
20 superabsorbents. Commercially available superabsorbents are usually available in salt form. It has now surprisingly been found according to the present invention that a combination of an anionic superabsorbent in free acid form with an anion exchanger in basic form is particularly effective as a
25 superabsorbent in the case of electrolyte containing solutions, for example menses and urine.

Whilst not wishing to be bound by any particular theory, it is believed that there is a two fold effect when the
30 superabsorbent material according to the invention is contacted with an electrolyte containing solution as follows:
(1) the anionic superabsorbent is converted from a non-absorbing form into the salt forms in which it acts as a superabsorbent; and

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(2) conversion of the anionic superabsorbent into the salt form has a de-ionising effect on the solution which is

enhanced by the anion exchanger.

5 In general the anionic superabsorbent does not behave as an ion exchanger in the sense that contacting the material in acid form with an electrolyte containing solution does not result in conversion to the salt form. The functional groups in anionic superabsorbents are typically carboxyl groups which act as a weak acid which does not dissociate when placed, for example, in a sodium chloride solution. However, 10 presence of the anion exchanger has the effect of attaching chloride ions from sodium chloride solution, thereby displacing the equilibrium in favour of conversion of the anionic superabsorbent into the salt form.

15 This conversion of the anionic superabsorbent into the salt form on contact with an electrolyte containing solution and the effect of the anion exchanger in attaching chloride ions has a significant desalting effect on the solution thereby improving the performance of the superabsorbent by 20 alleviating the salt-poisoning effect. In contrast with the use of an ion-exchange resin to desalt the solution in combination with a superabsorbent which is already in salt form (see Japanese Patent Application OPI No. 57-45057 and EP-A-0210756 referred to above), the superabsorbent in acid 25 form also has a de-salting effect on the solution. This allows a much greater de-salting effect to be achieved than by use of ion exchanger and superabsorbent in salt form. It should be noted that the effect of the electrolyte in solution on the absorption capacity of a superabsorbent for 30 that solution is not linear in that absorption capacity does not decrease regularly with increasing salt content. Accordingly over certain concentration ranges it is possible to bring about a relatively large increase in absorption capacity by effecting a relatively small reduction in salt 35 content of the solution.

The anionic superabsorbent can be any material having

superabsorbent properties in which the functional groups are anionic, namely sulphonic groups, sulphate groups, phosphate groups or carboxyl groups. Preferably the functional groups are carboxyl groups. Generally the functional groups are attached to a slightly cross-linked acrylic base polymer. For example, the base polymer may be a polyacrylamide, polyvinyl alcohol, ethylene maleic anhydride copolymer, polyvinylether, polyvinyl sulphonic acid, polyacrylic acid, polyvinylpyrrolidone and polyvinylmorpholine. Copolymers of these monomers can also be used. Starch and cellulose based polymers can also be used including hydroxypropyl cellulose, carboxymethyl cellulose and acrylic grafted starches. Particular base polymers include cross-linked polyacrylates, hydrolysed acrylonitrile grafted starch, starch polyacrylates, and isobutylene maleic anhydride copolymers. Particularly preferred base polymers are starch polyacrylates and cross-linked polyacrylates.

The functional groups will generally be carboxyl groups.

For cellulose derivatives the degree of substitution (DS) of the derivative with the functional group is defined as the number of functional groups (generally carboxyl groups) per anhydroglucose units of cellulose. The DS is generally from 0.1 to 1.5. In an analogous manner the DS for synthetic polymers may be defined as the number of functional groups per monomer or comonomer unit. The DS is generally 1, for example 1 carboxyl group per monomer unit of polyacrylate.

Many anionic superabsorbents are available commercially, for example Favor 922 (Stockhausen), Sanwet IM 1500 (Sanyo), AQU D3236 (Aqualon Company (Hercules)) or DOW 2090. (DOW). A particularly preferred anionic superabsorbent is FAVOR 922 (Stockhausen). Commercially available anionic superabsorbents are generally sold in salt form and need to be converted to the free acid form for use according to the

invention, for example by the following method:

Preparation of Favor H

10g of Favor 922 were placed in a 1 litre beaker, and
5 swelled with 500ml of distilled water, under continuous
stirring with a magnetic stirrer and a magnetic bar. 250ml
of HCl 0.01 M were added under continuous stirring, and after
30 minutes the gel was filtered with a nonwoven fabric
filter. The acidification and filtration steps were repeated
10 until there were no further sodium ions in the washing waters
(the sodium ion content may be determined by a potentiometric
method using a selective sodium sensitive electrode).
Finally the gel was washed with distilled water to remove the
excess acid and the gel was dried in an air ventilated oven
15 at 60°C for 10 hours. The dried polymer obtained was called
Favor H.

Ion exchange is the reversible interchange of ions
between a solid and liquid in which there is no permanent
20 change in the structure of the solid, which is the ion-
exchange material.

Ion exchange occurs in a variety of substances - e.g.
silicates, phosphates, fluorides, humus, cellulose, wool,
25 proteins, alumina, resins, lignin, cells, glass, barium
sulphate, and silver chloride.

However, they are used for ion exchange materials that
depend on properties other than the interchange of ions
30 between liquid and solid phases. Ion exchange has been used
on an industrial basis since 1910 with the introduction of
water softening using natural and, later, synthetic zeolites.

The introduction of synthetic organic ion exchange
35 resins in 1935 resulted from the synthesis of phenolic
condensation products containing either sulfonic or amine
groups which could be used for the reversible exchange of

cations or anions.

Inorganic ion exchange materials include both the naturally occurring materials such as the mineral zeolites (e.g. cliptonite) the green sands and clay (e.g. the montmorillonite group), and synthetic products such as the gel zeolites, the hydrous oxides of polyvalent metals and the insoluble salts of polybaric acids with polyvalent metals.

Synthetic organic products include cation and anion ion exchange resins both of strong and weak type.

The ability of the weak base resins to sorb acids depends on their own basicity and the pH of the acid involved.

A variety of base strengths are obtained depending on the nature of the amine functionality. Primary, secondary and tertiary amine functionality, or mixtures of them, can be put into various structures ranging from epichlorohydrin amine condensates and acrylic polymers, to styrene-devinyl benzene (DVB) copolymers.

These resins are capable of sorbing strong acids in good capacity but are limited by kinetics.

Strong base, anion exchange resins especially those based on styrene-DVB copolymer are classed as type I and II. Type I is a quaternarized amine product made by the reaction of trimethylamine with the copolymer after chloromethylation with chloromethyl methyl ether (CMME).

The type I functional group is the most strongly basic functional group available and has the greatest affinity for the weak acids that commonly are removing during a water demineralization process (e.g. silic acid and carbonic acid).

Type II functionality is obtained by the reaction of the styrene-DVB copolymer with dimethylethanolamine. This quaternary amine has lower basicity than that of the type I resin, yet it is enough to remove the weak acid anions for most applications.

Quaternary amine functionality has been introduced into pyridinic and acrylate polymers with limited commercial application.

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The anion exchanger is preferably an anion exchange resin containing functional groups in basic form. Suitable functional groups include amine groups, i.e. primary, secondary and tertiary amine groups and quaternary ammonium groups.

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Anion exchange resins which are commercially available and may be used in the present invention are:

Amberlite IRA 400 - This is a strong anion exchanger having quaternary ammonium functionality which is available in the chloride form. For use in the present invention it is necessary to convert it to OH^- form, for example by NaOH treatment in a chromatographic column and washing with distilled water. The total exchange capacity is 3.8 meq/g of dry resin.

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Amberlite IRA 68 - This a weak basic anion exchanger having tertiary amine functionality which is available in the free base form. The total exchange capacity is 5.6 meq (milliequivalents/g of dry resin). Amberlite ion exchangers are a trade mark of Rohn.

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ION exchanger type III from Merck - This is a strong anion exchanger resin, the exchange capacity is about 5 meq/g.

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ION exchanger type II from Merck - This is a weak anion exchange resin, the exchange capacity is about 5 meq/g.

Preferred anion exchange resins include Duolite A-102-OH, (Dia-prosim, France) which is a strong anionic exchange resin having quaternary ammonium functionality. The ion exchange capacity is 1.3 meq/ml. Other suitable anion
5 exchange resins can be found in the product ranges of manufacturers such as Rohn and Merck.

In general the weight ratio of anionic superabsorbent to anionic exchanger is in the range 1:20 to 1:1 depending on
10 molecular weight and ion exchange capacity, preferably the weight ratio is 1:2 to 1:4

The absorbent material according to the invention is particularly suitable for use in applications where it is
15 desired to absorb electrolyte containing aqueous liquids. Examples of such liquids include in particular menses and urine and the absorbent material can be used as the filling in catamenials and diapers generally in admixture with a fibrous absorbent such as cellulose fluff. For this purpose
20 the absorbent according to the invention can be present as granules or fibres.

The absorbent materials according to the invention show particularly good absorption of electrolyte containing
25 aqueous liquids as is demonstrated below in the following examples by tests carried out using saline solution (1% NaCl) and synthetic urine.

Examples1. Preparation of Favor H⁺:

5 10g of Favor 922 were placed in a 1 litre beaker, and swelled
with 500ml of distilled water, under continuous stirring with
a magnetic stirrer and a magnetic bar. 250ml of HCl 0.01 M
were added under continuous stirring, and after 30 minutes
the gel was filtered with a nonwoven fabric filter. The
10 acidification and filtration steps were repeated until there
were no further sodium ions in the washing waters (the sodium
ion content may be determined by a potentiometric method using
a selective sodium sensitive electrode). Finally the gel was
washed with distilled water to remove the excess acid and the
15 gel was dried in an air ventilated oven at 60°C for 10 hours.
The dried polymer obtained was called Favor H.

2. Comparative tests of Liquid Absorption

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The test was performed to show that, when in contact with an
aqueous saline solution, an anion exchange resin in basic
form together with an anionic superabsorbent in acid form act
as an anion and cationic exchange mixture and thus
25 deionization of the saline solution occurs. The anionic
superabsorbent is then converted to the salt form and thus
has improved absorbency due to the low salt content of the
solution.

30 1% NaCl solution (150ml) was placed in contact with the anion
exchange resin A102 OH (3.9g), in a 250ml beaker for 2 hours
under continuous stirring. This step allows the chloride
ions from the solution to be replaced by the hydroxide ions
from the resin. The solution was then drawn up by a Pasteur
35 pipette and transferred into another 250l beaker containing
0.25g of Favor H being stirred. The addition of solution was
stopped when the gel did not swell any further. Thereafter

the gel was placed into a nonwoven tissue tea bag type envelope, which had one edge which was not sealed, and the absorbency after centrifugation at 60 x g for 10 minutes was measured as follows:

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$$A = (W_{\text{wet}} - W_{\text{dry}}) / G$$

where:

- A = absorbency after centrifugation in g/g
 10 W_{wet} = weight of envelope containing the wet AGM after centrifugation in g
 W_{dry} = weight of the envelope containing the dry AGM in g
 G = weight of the AGM used in the test in g.

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Results are as follows:

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	Amount (g)	Water Retention g/g	
		Deionised Water	1% NaCl Solution
(A) FAVOR (H ⁺)	0.25	30	3
(B) FAVOR (Na ⁺)	0.25	400	40
25 (C) ANION EXCHANGE RESIN (A-102-OH)	3.9	-	0.29
(D) FAVOR (H ⁺) + A-102-OH	0.25 + 3.9	-	100

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NOTE: Results relate to 25 ml of 1% NaCl solution.

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The above results show that the anionic superabsorbent in acid form (FAVOR H⁺) shows very little absorption by itself in 1% NaCl solution. FAVOR Na⁺ shows some absorption but much less than for deionised water. The anion exchange resin has essentially no absorption. However, in combination

with the anion exchanger in base form (A-102-OH), FAVOR (H⁺) shows significantly increased absorption over FAVOR Na⁺.

5 It should be noted that 1% NaCl represents a stringent test of the superabsorbent. Studies in the literature show that the salt content of urine varies depending on a number of factors but 1% by weight represents the maximum likely to be encountered in practice.

Claims

1. A superabsorbent material which comprises a combination of
 - i) an anionic superabsorbent in which from 20 to 100% of the functional groups are in free acid form; and
 - ii) an anion exchanger in which from 20 to 100% of the functional groups are in basic form.
2. A superabsorbent material as claimed in claim 1 wherein the anionic superabsorbent has from 50 to 100% and, preferably has substantially 100% of the functional groups in free acid form and the anion exchanger has from 50 to 100% and preferably has substantially 100% of the functional groups in basic form.
3. A superabsorbent material as claimed in claim 1 or 2 wherein the functional groups in the anionic superabsorbent are sulphonic, sulphate, phosphate or carboxyl groups.
4. A superabsorbent material as claimed in claim 3 wherein the functional groups are carboxyl groups.
5. A superabsorbent material as claimed in any of claims 1 to 4 wherein the functional groups are attached to a polyacrylamide, polyvinyl alcohol, ethylene maleic anhydride copolymer, polyvinylether, polyvinyl sulphonic acid, polyacrylic acid, polyvinylpyrrolidone or polyvinylmorpholine base polymer or copolymer thereof of a starch or cellulose based polymer.
6. A superabsorbent material as claimed in claim 5 wherein the starch or cellulose based polymer is hydroxypropyl cellulose, carboxymethyl cellulose or acrylic grafted starch.
7. A superabsorbent material as claimed in claim 5 or 6 wherein the base polymer is a crosslinked polyacrylate, hydrolysed acrylonitrile grafted starch, a starch



polyacrylate or a isobutylene maleic anhydride copolymer.

8. A superabsorbent material as claimed in claim 7 wherein
the base polymer is a starch polyacrylate or a crosslinked
5 polyacrylate.

9. A superabsorbent as claimed in claims 1 or 2 wherein the
functional groups in the anion exchange resin are primary,
secondary and tertiary amine groups or quaternary ammonium
10 groups.

10. A superabsorbent as claimed in any of claims 1 to 9
wherein the weight ratio of anionic superabsorbent to anionic
exchanger is in the range 1:20 to 1:1.

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11. Use of a superabsorbent as claimed in any of claims 1
to 10 for the absorption of electrolyte containing aqueous
liquids.

20 12. Use as claimed in claim 11 wherein the liquids are
menses or urine.

