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SUPERABSORBENT COMPOSITIONS FOR USE IN SANITARY ARTICLES

The invention relates to superabsorbent compositions for use in the production of sanitary articles intended to
5 absorb and retain body fluids.

When an absorbing article in place is impregnated with such body fluids, in particular urine, powerful and unpleasant smells are produced. Predominant among these are ammoniacal smells resulting from the ammonia
10 originating from the hydrolysis of urea by the ureases of bacteria (*Proteus*, *Acinetobacter*, and the like) present on the skin or in the digestive tract.

In order to suppress these smells, widespread recourse has been had to absorbents of smells or ammonia (US
15 3,340,875, Scott Paper Company), optionally in combination with deodorants, fragrances, and the like. The use of pH buffers (WO-A-94 25077), of oxidants (hydrogen peroxide, chlorine dioxide), of biocides (metals or of metal cations), as well as of bactericides (quaternary ammoniums,
20 in particular), of antibiotics, of complexing agents or of surfactants, both alone and in combination with one another, has also been recommended. Such products have the problem of an irritant effect on the skin and mucosal membranes. Absorbents of smells or of ammonia may be less
25 problematic in this respect but they do not prevent bacterial growth which remains worrying and which it would be advisable to control. For the control of the bacterial

emission of ammonia from urea it was believed necessary to inhibit the enzymes which are responsible for it, that is to say the ureases.

The use of urease inhibitors of low or moderate
5 activity has until now only been envisaged in combination with ammonia scavengers (JP 61-179155). Some powerful urease inhibitors, such as hydroxamic acid derivatives USP 3,920,015, Allied Chem. Corp.), are advantageous but their toxicity excludes them from the proposed use. Others, such
10 as phenyl phosphorodiamidate (PPDA) or dimethyldithiocarbamate (DTC), are compounds which are very effective against the formation of ammonia but give rise, during their use, to other very unpleasant sulfurous or alliaceous smells which are perhaps related, at least in
15 part, to their own decomposition by the bacterial flora present.

The problem is all the more pressing since, nowadays, the absorption capacity of protection articles for body fluids has been very substantially increased by
20 incorporating into them superabsorbent polymers (SAP), in particular hydrophilic polymers and copolymers of acrylic acid. The time during which such materials are maintained in place thus has also been increased, as are the conditions which promote the development of microbial and
25 enzymatic activity and of the smells which result therefrom.

It has now been found that it is possible to formulate

superabsorbent polymers with certain boron derivatives in order to prepare therefrom compositions which, when impregnated with urine or with biological fluids containing it and maintained under conditions of use which are
5 especially propitious for bacterial growth, give rise neither to significant evolution of ammonia nor to repellent or simply unpleasant smells and which communicate this property to sanitary articles which contain them.

According to the present invention there is provided a
10 superabsorbent composition which comprises:

a superabsorbent polymer, and 0.1 to 10%, preferably 0.5 to 5%, based on the composition, of sodium tetraborate or sodium metaborate.

The superabsorbent compositions according to the
15 invention are suitable for the production of sanitary articles of the underwear, diaper or disposable diaper type which do not develop unpleasant smells.

The polymer used is superabsorbent with respect to water, saline solutions and body fluids.

20 Superabsorbent polymers within the meaning of the present invention are polymers obtainable from the polymerization, with partial crosslinking, of water-soluble ethylenically unsaturated monomers, in particular acrylic and methacrylic acids and their alkaline salts. These
25 polymers may be obtained by inverse suspension or solution polymerization. Such polymers possess a very high capacity for absorption and retention of water and aqueous solutions

and are nowadays widely available commercially in the form of powders with particle sizes of between 100 and 800 μ m. The literature relating to them is extensive; reference may be made, for example, to EP-A-0,312,952 (The Dow Chem. Co.)
5 and to EP-A-0,441,507 (Sumitomo Seika Chem.).

Within the meaning of the present invention, sodium tetraborate ($\text{Na}_2\text{B}_4\text{O}_7$) may be the anhydrous, pentahydrate or decahydrate (borax) salt and the metaborate (NaBO_2) may also be regarded independently of its degree of hydration.
10 These boron compounds are suitably mixed with the polymer in powder form in proportions indicated above.

The composition according to the invention may readily be prepared, since it is sufficient to incorporate the boron derivative in powder form, preferably also with a
15 particle size of between 100 and 800 μ m, in the superabsorbent polymer powder by simple mixing. However, it has been observed that, if the boron derivative is introduced within the superabsorbent polymer particles, an odor-preventing efficiency was obtained, at equivalent
20 concentration, which is greater than that obtained by simple mixing of the powders. This results in an alternative form of the process, which also forms part of the invention, whereby the polymer powder is swollen using an aqueous solution of boron derivative and then any excess
25 water thus introduced is removed by evaporation.

The superabsorbent compositions of the invention become gelled on contact with water, aqueous saline

solutions or body fluids, like the superabsorbents of the prior art, and the gels thus formed behave in a substantially identical way. The boron derivatives used may be regarded as inoffensive and are widely used in various mild antiseptic compositions at contents of the order of 1% by weight. The compositions according to the invention may be used in place of conventional superabsorbents in the manufacture of sanitary articles such as disposable diapers for babies, for young children, for adults or for elderly people of both sexes. This use is a further aspect of the present invention.

Assessment of the true effectiveness of odor-preventing products is not straightforward. Since the invention comes within the context of urease inhibitors, the candidate compounds which can be envisaged to compare their anti-urease activity are therefore generally classified by an IC_{50} value according to the results of an enzymatic test which will be described later. On the other hand, the process which generates smells is a biological process and thus it is necessary to be able to estimate the effectiveness of various urease inhibitors for their ability to limit the biological emission, by urea-fermenting microorganisms, of at least the most common odorous compound, in this case ammonia, this effectiveness being for the inhibitor as is or in the presence of various substances with which it may be combined in the production of diapers and other sanitary articles, in particular

superabsorbent polymers. The results of this test correlate fairly well with the IC_{50} values. Finally and particularly, it is necessary to be able to decide on the satisfactory overall result by olfactive tests under
5 conditions which give acceptable simulation of the conditions of use of the products which the superabsorbent composition which is believed to inhibit smells is incorporated. They are carried out by impregnating a disposable diaper with urine under standardized conditions,
10 by heating the combination in an oven at a low temperature and by subjecting the object to a nose panel for overall assessment of its possible unpleasant smells.

Such tests are described in the Examples given below, which illustrate the unexpected effectiveness of the
15 compositions according to the invention. In these tests, the superabsorbent polymer (SAP) used is a partially neutralized polyacrylic acid marketed under the name of Aqua-Keep®D (Elf Atochem S.A.).

The accompanying drawing illustrates an apparatus for
20 use in tests described in the Examples.

The invention is further illustrated in the following Examples.

Example 1: IC_{50} values of several molecules believed to operate as urease inhibitors.

25 The test comprises the decomposition of a neutral solution of urea at 1g/l (0.016 M) in a 0.1M triethanolamine buffer, to which solution has or has not

been added the compound whose anti-urease activity it is desired to estimate, by a solution of soybean urease (1500 U from Sigma) at 1 mg/ml in the buffer + 10 mM of glutathion under the following conditions. 400 μ l of
5 urease solution and 10 ml of urea solution are mixed. The mixture is maintained at 37°C. 1 ml samples are taken with time and assayed for NH_3 by the Nessler method: each 1 ml sample is added to 24.5 ml of dilute Nessler reagent (0.5 for 24) and, after incubating for 10 minutes, the
10 absorbance at 425 nm is measured. An IC_{50} value is determined, which value is the concentration of inhibitor in the mixture, expressed as μM , capable of reducing the urease activity by 50% under the conditions of the test.

The IC_{50} values for several urease inhibitors known in
15 the literature are reported in Table I below.

TABLE I

Compound	IC ₅₀ (μM)
Phenyl phosphorodiamidate (PPDA)	0.05
Boric acid	450
5 Sodium metaborate	260
Sodium tetraborate 5H ₂ O	160
Sodium pyrophosphate	8000
Hydroquinone	500
Dimethyldithiocarbamate (DTC)	10
10 Salicylhydroxamic acid	310
Glycolic acid	450
Acetohydroxamic acid	600
Nitrilotriacetic acid	5000

15 **Example 2: SAP/sodium tetraborate pentahydrate synergy.**

The IC₅₀ value is determined as described above. These tests are carried out to compare residual urease activity for a control medium and media containing respectively solely SAP, sodium tetraborate pentahydrate (Na₂B₄O₇·5H₂O),

20 and SAP to which has been added 3.9% by weight of sodium tetraborate pentahydrate, which was obtained by mixing 29 kg of Na₂B₄O₇·5H₂O with 718.5 kg of superabsorbent polymer, so as finally to obtain 750 kg of borate-containing composition. The results are reported in Table II below.

TABLE II

	Composition	Residual urease activity %
	Control (without SAP and without inhibitor)	100
5	SAP alone (10 mg/15 ml of medium)	100
	SAP alone (100 mg/15 ml of medium)	100
10	Borate-containing SAP (10 mg/15 ml of medium)	50
	Borate-containing SAP (100 mg/15 ml of medium)	0

The effectiveness of the borate-containing SAP is
15 clearly demonstrated by the test.

It was noted that the curve of the urease activity as
a function of the additive-containing SAP content in the
medium was a smooth curve. Under these conditions, the
point of 50% residual urease activity for this SAP
20 containing 3.9% of tetraborate pentahydrate can be
interpreted in terms of IC_{50} with respect to the tetraborate
and is calculated at 90 μM . This figure will be compared
with the value of 160 μM for the tetraborate pentahydrate
alone in Table I in Example 1 in order to observe that the
25 IC_{50} which can be attributed to sodium tetraborate
pentahydrate in the presence of SAP is superior to that
which is calculated with the tetraborate alone. This

synergic effect between the SAP and the tetraborate with respect to its anti-urease activity is most unexpected and remains unexplained.

5 **Example 3:** Inhibiting effect on formation of ammonia.

There were introduced into a 100 ml Erlenmeyer flask equipped (see Figure 1 of the accompanying drawing) with a Prolabo No. 02.436.112 measuring tube (1) (such measuring tubes are graduated glass tubes containing a reagent for ammonia which changes from violet to yellow, the position of the demarcation between the two colorings giving an indication of the amount of ammonia evolved), urine (2) and a mixture of defibrated cellulose pulp and of SAP (3) in the following proportions:

15	fresh urine	50 ml
	fermented urine (inoculum)	2 ml
	superabsorbent	0.5 g
	defibrated cellulose pulp (fluff)	0.5 g

The inoculum is necessary because fresh urine is sterile. This inoculum is prepared in the following way: 0.25 g of urea and 1 g of soiled fluff originating from a used baby disposable diaper are added to 100 ml of fresh urine (for greater convenience, the medium could be inoculated with, in place of the used fluff, a strain of *Bacillus*, *Proteus* or *Acinetobacter*). This solution, withdrawn after 24 hours at room temperature, constitutes the inoculum.

In this test, the odor inhibitor is not introduced separately, but with the superabsorbent formulated as indicated above and at a content in the superabsorbent such that its dose in the medium to be fermented is 10 times its IC_{50} .

The system is left for 18 hours at 40°C, after which the position of the region of transition of violet/yellow coloring in the measuring tube is noted.

This provides a comparative estimation of the evolution of ammonia and thus of the influence on this evolution of the products which have been subjected to the test. After this, the Erlenmeyer flask is carefully opened and the experimenter gives his assessment of the smell of the contents. The results are recorded in Table III below.

TABLE III

Substrate/inhibitor	Reading on the measuring tube	Smell
Control (neither SAP nor inhibitor)	>500	Strong ammoniacal
SAP alone	>500	Strong ammoniacal
SAP + $\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$	90	No perceptible ammonia smell. Neutral smell of fresh urine
SAP + PPDA	120	Unpleasant smell of rotten cabbage
SAP + DTC	1070	Unpleasant smell of rotten cabbage
SAP + hydroquinone	120	Slight nauseating

Example 4: Comparative test of odor-prevention by mixing powders or by impregnation.

There were introduced, into the device used in Example 3, a synthetic urine inoculated by *B. pasteurii* (ATCC 11859) and a mixture of defibrated cellulose pulp and of SAP containing 4% borax, one being produced by mixing SAP and borax powders and the other by impregnation of SAP by the necessary amount of aqueous borax solution at 80°C (22% by weight solution). The comparative amounts of NH_3 evolved (in ppm) at different times are reported in Table IV below.

TABLE IV

t (hours)	SAP alone	SAP + 4% borax powder	SAP + 4% borax solution
0	0	0	0
6	7	7	7
8	20	18	10
10	off the scale	24	12
30	off the scale	off the scale	13

These results show the advantage, particularly with respect to relatively long time periods, of tetraborate impregnation compared with simple mixing.

Example 5

The test is carried out by using, as substrates, disposable diaper material not containing SAP. Such a blank disposable diaper, with a size of 31 x 11 cm, is taken and opened and 4 grams of SAP are spread over it over a surface area of approximately 15 x 9 cm. The centre of the disposable diaper is moistened with a mixture of 50 ml of fresh urine and 2 ml of inoculum. The disposable diaper is enclosed in a plastic bag which is welded. The whole assembly is placed in a ventilated oven at 37°C for 12 hours. At the end of this period, the bag is opened and an estimation of the smell is made by a nose panel (8 people). In a system of notation which confers the grade 0 for the complete absence of smell to 5 for a very strong

smell of ammonia, the following are obtained:

Control disposable diaper	4.6
Disposable diaper with ordinary SAP	4.6
4% of "powder" borax	3.3
5 4% of "liquid" borax	2.8

There has thus been found:

a strong smell of ammonia with the control disposable diaper,

a strong smell of ammonia with the disposable diaper
10 carrying an ordinary polyacrylic superabsorbent,

no smell of ammonia with the disposable diaper with a
polyacrylic superabsorbent containing 3.9% of sodium
tetraborate pentahydrate.

A test of the same type, carried out with a synthetic
15 urine, confirms the above results:

Control disposable diaper	5
Disposable diaper with ordinary SAP	5
4% of "powder" borax	4
4% of "liquid" borax	3



THIS SHEET HAS BEEN
REPLACED

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CLAIMS

1. A superabsorbent composition which comprises:
a superabsorbent polymer obtainable from the
polymerization, with partial crosslinking, of a water-
5 soluble ethylenically unsaturated monomer, and 0.1 to 10%,
based on the superabsorbent composition, of sodium
tetraborate or sodium metaborate.
2. A composition according to claim 1 wherein the
water-soluble ethylenically unsaturated monomer is acrylic
10 or methacrylic acid or an alkaline salt thereof.
3. A composition according to claim 1 or 2 which
contains 0.5 to 5%, based on the superabsorbent
composition, of sodium tetraborate or sodium metaborate.
4. A composition according to any preceding claim,
15 wherein the sodium tetraborate is in anhydrous,
pentahydrate or decahydrate form.
5. A composition according to claim 5, which
contains sodium tetraborate pentahydrate.
6. A composition according to any preceding claim
20 having a particle size of between 100 and 800 μ m.
7. A process for the production of a superabsorbent
composition which process comprises mixing a superabsorbent
polymer, obtainable from the polymerization, with partial
crosslinking, of a water soluble ethylenically unsaturated
25 monomer in powder form, with sodium tetraborate or sodium
metaborate, in the powder form.
8. A process for the production of a superabsorbent

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composition which process comprises swelling a
superabsorbent polymer, obtainable from the polymerization,
with partial crosslinking, of a water-soluble ethylenically
unsaturated monomer, in powder form with an aqueous
5 solution of sodium tetraborate or sodium metaborate, and
removing any excess water by evaporation.

9. A process according to claim 7 or 8 wherein the
water-soluble ethylenically unsaturated monomer is acrylic
or methacrylic acid or an alkaline salt thereof.

10 10. A superabsorbent composition prepared by the
process claimed in any of claims 7 to 9.

11. Use of a composition as claimed in any one of
claims 1 to 5 and 10 in the preparation of sanitary
articles such as underwear, diapers and disposable diapers
15 for babies, for young children, for adults or for elderly
people of both sexes.