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(54) **NATURAL OR SYNTHETIC YARNS WITH HIGH ABSORPTION PROPERTY OBTAINED BY INTRODUCTION OF SUPERABSORBENT HYDROGEL**

NATUR- ODER SYNTHESEGARNE MIT HOHER ABSORPTIONSKAPAZITÄT DURCH EINARBEITUNG VON SUPERABSORBIERENDEM HYDROGEL

FILS NATURELS OU SYNTHETIQUES PRESENTANT DES QUALITES D'ABSORPTION ELEVEES OBTENUES PAR INTRODUCTION D'UN HYDROGEL SUPERABSORBANT

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Description

Technical field

[0001] At the present, super absorbent hydrogel are used in bio-medicine as controlled release medicine, artificial muscles and the similar; in cosmetic as absorbents; in agriculture for dry fields cultivation; in advanced technologies as actuators; in building for production of gum - super absorbent compounds, which are used, for example, to prevent water infiltrations between adjacent concrete blocks (as in the Eurotunnel between United Kingdom and Europe); in the production of artificial snow (by using super absorbents, the first indoor track has been open in 1991 near Tokyo).

[0002] A very interesting hydrogel subclass comprises polyelectrolyte hydrogel characterised by the presence of ionic groups (or ionizable, under certain equilibrium conditions) in the macromolecular structure. Actually, the ionic groups are connected to the gel network, forming a real macromolecular poly-ion. In fact, there is no clear distinction between hydrogel and polyelectrolyte hydrogel: due to the presence of fixed charges, the latter are still able to absorb a large quantity of the solvent (water). Often they are called hydrogel with ionizable groups.

[0003] Polyelectrolyte gel can have either anionic or cationic character, according to the presence of carboxylic or tertiary amino groups in the polymeric structure. For this reason, polyelectrolyte gels are very attractive for all the applications requiring a behaviour related with the external conditions under which the gel operates. These conditions (temperature, pH, composition, ionic strength) are the same features of the solution, which the gel is in chemical equilibrium with. In fact, a solvophile gel with pending acid groups has a good polymer-solvent affinity, and shows an absorbent capacity which grows with the increase of the external pH solution. On the contrary, a solvophile gel, having pending basic groups, shows an absorbent capacity which grows with the decrease of the pH. A remarkable attention has been given at the solvophobic reticulated polymeric systems, which have a poor affinity with the solvent. In this case, the polyelectrolyte gel exhibits a discontinuous behaviour of the swelling grade versus pH. In other words, the gel passes from a collapsed state to a swollen state when pH reaches a critical value, which produces a sudden change of the swelling grade.

[0004] This special behaviour encourages the use of polyelectrolyte gel in several applications, like components of chemical separation systems, devices for medicine release, artificial muscles and the similar.

[0005] In textile application hydrogel as super absorbent material has rarely been employed. The best comfort is reached by adding synthetic hollow fibers, like Coolmax®, to the textile which ensures a better transpiration. Document JP000009158049 AA relates to an antielectric, sweat-absorbing and antifouling fabric improved in durability to washing. It discloses how to get a fabric hav-

ing all of antistatic, sweat-absorbing and antifouling properties, good in washing durability and useful as common clothes as well as dust-free clothes. This kind of fabric is obtained by fixing a water-absorbing polymer which is not swollen by water onto the surface of a polyester fiber constituting the fabric. In order to get this, a polyester fiber is covered on the surface by a water-absorbing polymer layer, which is not swollen by water, and by an hydrogel layer. At least a part of the water-absorbing polymer is coated with the hydrogel layer. In this way, the hydrogel gives to the fabric the properties above listed.

Disclosure of the invention

[0006] The invention aims at solving the discomfort deriving from the direct contact between sweat and skin, and the bad smell produced during sport as well as daily like activities. In fact, by using hydrogels, the sweat is absorbed by the gel which releases, in turn, a fragrance, previously added in the fabric washing or to the gel. For this reason, the invention relates to yarns, fabrics or end products, like socks or stockings, **characterized in that** they ensure very high sweat absorption property, given by the addition of super absorbent hydrogel.

[0007] These and other advantages will be pointed out in the detailed description of the invention that will refer to the figures of the tables 1/5, 2/5, 3/5, 4/5 and 5/5. Both are exemplifying and not restrictive.

Way of carrying out the invention

[0008] With reference to the above mentioned tables:

- Figure 1 represents the spinning cycle
- Figure 2 shows the absorption values in salt solution of the acrylic hydrogel
- Figure 3 shows the absorption tests in salt solution 0.9wg% on a cotton fabric and on a fabric made by 80% cotton and 20%;
- Figure 4 is the chemical structure of the cellulose based macromolecule;
- Figure 5 shows the scheme of the DVS molecule

[0009] Typically, super absorbent hydrogel are prepared by free radical polymerization of the acrylic acid and salts with a cross-linking agent, in water solution or in drops suspension of water solution in hydrocarbons. These two processes, namely "bulk" solution polymerization and suspension polymerization, have several features in common: the monomer and cross-linking agent concentrations, the initiator and its concentration monomers relative reactivity, the polymerization kinetics and reaction temperatures. Monomer concentration in the reactive solution affects the resulting polymer properties, the reaction kinetic and the process economy. High monomer concentrations cause an increase of the polymer gel stiffness during polymerization. Gel stiffness has an effect on the design of the production tools, on the gel

particles size produced during the reacting mass stirring, and the heat removal technique. Moreover, the chain transfer reactions increase with the monomer concentration; and this happens especially at high conversion degrees, causing more "branching" and self-reticulating reactions, which influence the final product properties. Monomer concentration also influences the cross-linking agent efficiency. In fact, said cross-linking agents are water insoluble, but soluble in organic solvents; therefore, by making a more organic solution, the increase of the monomer concentration also improves the cross-linking agent solubility. Moreover, the network cycling reactions decrease by increasing the cross-linking agent concentration, as reported by Flory. Small quantities of cross-linking agent play an important role in altering the super absorbent properties. For these substances/ material, the typically used cross-linking agents are bi- and tri-acrylate esters. The cross-linking agents influence the quantity of soluble polymer formed during polymerization and the mechanic and swelling properties as well.

[0010] There are several techniques for preparing super absorbent. In the graft copolymerization, hydro-soluble polymers (like amid or polyvinyl alcohol), are grafted to the super absorbent to modify its properties. In suspension polymerization, on the contrary, small drops of water-monomer solution are dispersed into another phase, generally aromatic or aliphatic hydrocarbons, before polymerization. Generally, the neutralization degree is higher in the second procedure, because of the acrylic acid solubility in the hydrocarbon phase, which makes the reaction and the manipulation more difficult.

[0011] In textile applications, it can be used either powder hydrogel, dispersed on natural or synthetic fibers, or fiber-shaped hydrogel. In particular, fibers, whose length is suitable for textile applications (40-70mm) are produced by spinning. The spinning technique makes possible the polymerization of a fiber-shaped hydrogel, by acting on both the section and the length of the single fiber.

Description of preferred embodiments

[0012] To manufacture the yarn, cotton has been mixed with acrylic short fiber hydrogel, varying the percentages according to the absorption properties desired.

[0013] The spinning process is schematized in Figure 1. The working flowchart shows 5 basic operations:

- Bale opening, containing a homogeneous mix of the several fibers forming the yarn;
- opening of the tangled tufts to clean the raw material by eliminating impurities;
- creation of a fiber band, without any applied twisting. In this step, the reciprocal adherence between the fibers is enough to provide a uniform cohesion, together with a certain orientation of the fibers towards the band axis (substantially obtained by carding operation);

- band refining and normalization, together with improved fiber parallelism, obtained by following couplings and stretching, until the sliver is reached;
- the spinning itself, consisting of a further stretch and cohesion to the yarn (generally, by twisting), and winding the yarn around a suitable support.

[0014] The spinning has been carried out using a homogeneous mix of fibers in bulk, in other words, the material from each lot is opened into small elements, forming a small cloth; said cloth is made by small tufts comprising two or more components, randomly distributed but in precise ratios. After spinning, weaving follows. The absorption test confirms an absorption of salt solution by a hydrogel-containing fabric higher than a 100% cotton fabric; the washing test confirms a low hydrogel loss during washings.

[0015] Mixed spinning technique can be carried out by using either cellulose hydrogel or acrylic one. An alternative procedure is to use the same hydrogel and bind them to the yarn surface by means of a bonding agent.

[0016] Tests on hydrogel fibers give the following results:

Absorption (g/g): 0.9 wg% salt solution

[0017] In Figure 2, the absorption values in salt solution of the acrylic hydrogel under different measurement conditions have been reported.

[0018] The tests have been carried out with a salt solution, to best simulate the typical conditions of sweat absorption. As shown in Figure 2, absorption properties are also exceptional under load, typical operating condition for some cloths, socks or stockings for example. Retention property is also excellent, meaning that the sweat, once absorbed by the hydrogel-containing fabric is not released, until the fabric itself dries.

[0019] Absorption tests in salt solution 0.9wg% have been carried out on a cotton fabric and on a fabric made by 80% cotton and 20% hydrogel; the results are summarized in Figure 3.

[0020] As shown in Table 2, the fabric containing 20% hydrogel effectively absorbs much more than a 100% cotton fabric.

[0021] Adding hydrogel to the yarn allows producing ideal fabrics for all applications in which sweat and bad smells can cause discomfort; hydrogel-yarn absorbs sweat and in turn releases fragrance previously added to the hydrogel. Once washed and dried, this fabric is ready for reuse, keeping the same absorption properties.

[0022] According to the described processes, it is also possible to add natural hydrogel to the yarn. Natural cross-linkable polymers are derived by cellulose, like carboxyl-methyl-cellulose (CMC) hydroxyl-ethyl-cellulose (HEC) sodium salt. Once reticulated, CMC has all the features to be used as super absorbent material. First of all, such polymer is biodegradable and available on the market at reasonable price. Furthermore, thanks to the

ionic group, the carboxyl-methyl group, bounded by an ether bond with the cellulose structure, CMC has all the polyelectrolyte characteristics, which are needed to develop a Donnan equilibrium with the external solution. Moreover, CMC is watersoluble, therefore has great affinity with the external solution. HEC is also derived from cellulose and is highly hydrophilic, but, unlike CMC, has not any charge group connected to the polymeric network, therefore, does not provide support the "Donnan effect", which improves the absorption. HEC is employed in many applications, even industrial ones, as for example detergent agent for hair shampoo.

[0023] The root structure of CMC and HEC is shown in Figure 4. As cross-linking agent agent to produce the polymeric network, bi-vinyl- sulphonal (DVS) has been used. DVS molecular scheme is represented in Figure 5. Double bonds $\text{CH}_2=\text{CH}$ are very reactive: once opened, they can bind both sides of the molecule to other reactive groups, like the cellulose ones, creating the polymeric network. In this case too, natural hydrogel is polymerized as short fiber, by spinning technique.

Claims

1. Yam having high sweat absorption, obtained by super absorbent hydrogel integration **characterized in that** hydrogel fibre is integrated by spinning.
2. Yam according to claim 1 containing natural (cotton or wool) or polymeric fibre.
3. Yarn according to claim 1 wherein the super absorbent hydrogel is acrylic.
4. Yarn according to claim 1 wherein the super absorbent hydrogel is cellulose.
5. Yam according to one of the claim from 1 to 4 wherein said hydrogel comprises perfumed substances, which can be released during absorption with a controlled kinetic.
6. Yam as in claim 5, wherein the perfume absorption and release is a reversible and repeatable process.
7. Sock or stocking **characterized in that** it contains the yam of claims from 1 to 6.

Patentansprüche

1. Garn mit hoher Schweißaufnahme, die durch Einbindung eines superabsorbierenden Hydrogels erhalten wird, **dadurch gekennzeichnet, dass** Hydrogelfasern durch Spinnen eingebunden sind.
2. Garn nach Anspruch 1, das natürliche (Baumwolle

oder Wolle) oder Polymerfasern enthält.

3. Garn nach Anspruch 1, worin das superabsorbierende Hydrogel Acrylstoff ist.
4. Garn nach Anspruch 1, worin das superabsorbierende Hydrogel Zellulose ist.
5. Garn nach einem der Ansprüche 1 bis 4, worin das Hydrogel Duftstoffsubstanzen umfasst, die während der Aufnahme mit einer gesteuerten Kinetik freigesetzt werden können.
6. Garn nach Anspruch 5, bei dem es sich bei der Duftstoffaufnahme und -freisetzung um einen umkehrbaren und wiederholbaren Prozess handelt.
7. Socke bzw Strumpf, **dadurch gekennzeichnet, dass** sie bzw. er das Garn nach den Ansprüchen 1 bis 6 enthält.

Revendications

1. Fil comportant une haute absorption de la sueur, obtenu par intégration d'hydrogel super-absorbant, **caractérisé en ce que** la fibre d'hydrogel est intégrée par filature.
2. Fil selon la revendication 1 contenant des fibres naturelles (coton ou laine) ou polymères.
3. Fil selon la revendication 1, dans lequel l'hydrogel super-absorbant est de l'acrylique.
4. Fil selon la revendication 1, dans lequel l'hydrogel super-absorbant est de la cellulose.
5. Fil selon l'une des revendications 1 à 4, dans lequel ledit hydrogel comprend des substances parfumées, lesquelles peuvent être libérées durant l'absorption avec une cinétique contrôlée.
6. Fil selon la revendication 5, dans lequel l'absorption et la libération de parfum est un processus réversible et répétable.
7. Chaussette ou bas **caractérisé en ce qu'il** comprend le fil selon les revendications 1 à 6.

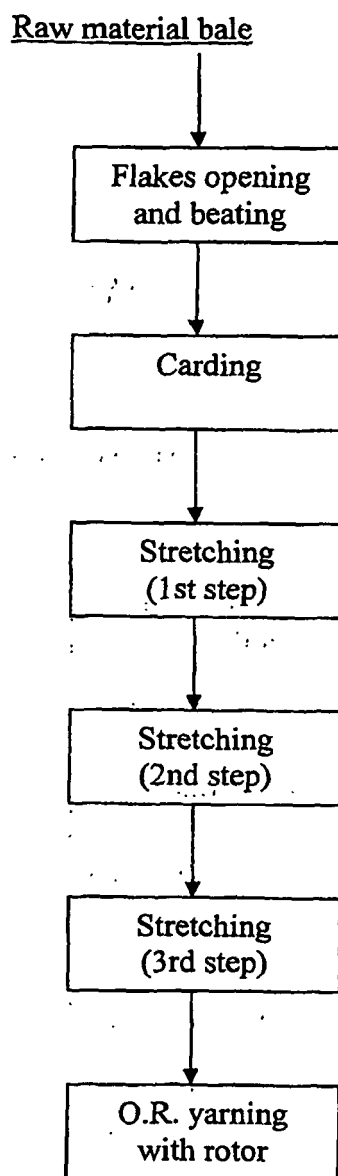


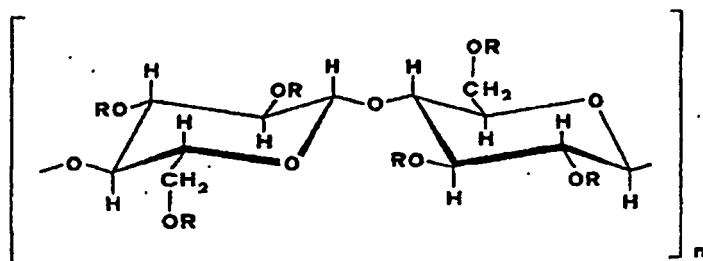
Fig. 1

	Min.	Ave.	Max.
15 minutes Free-swelling capability	43	45	48
Retention capability at 0.5 psi	33	35	38
Absorption under load at 0.3 psi	17	-	24

Fig. 2

	Absorption [%]
80% Cotton -20%hydrogel fabric	413
100% Cotton fabric	291

Fig. 3



NaCMC

-H, -CH₂COONa

HEC

-H, -CH₂CH₂OH, -CH₂CH₂OCH₂CH₂OH,

-CH₂CH₂OCH₂CH₂OCH₂CH₂OH

Fig. 4

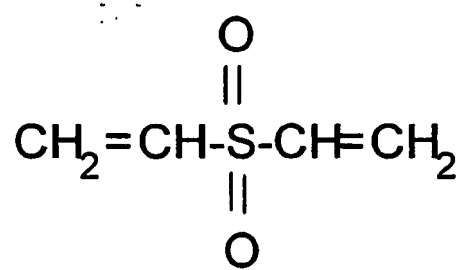


Fig. 5

REFERENCES CITED IN THE DESCRIPTION

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