Title: ANTIMICROBIAL HOOK AND LOOP FASTENER

Abstract: Disclosed are antimicrobial fasteners comprising hook and loop means which are formulated with an inorganic antimicrobial agent composition, in an amount effective to impart substantial antimicrobial activity to the fastener.
ANTIMICROBIAL HOOK AND LOOP FASTENER

FIELD OF THE INVENTION

This invention relates to a hook and loop fastener containing an antimicrobial agent.

BACKGROUND OF THE INVENTION

Hook and loop fasteners, of which VELCRO® is one type, are well known and versatile consumer items. Hook and loop fasteners may become contaminated with bacteria, fungi, and other microorganisms directly, for example from exposure during the course of use, and/or indirectly, for example by cross-contamination, whereby attachment or detachment exposes the fastener to microorganisms transferred from contaminated hands. Once contaminated, they become a veritable breeding ground for microorganisms, similar to wall-to-wall carpeting.

Hook and loop fasteners such as VELCRO® have been used in a wide variety of consumer products. Hook and loop fasteners are used in a broad range of medical products, such as in bandages or other wound dressing, hospital gowns, nurses’ uniforms, surgical gowns, and uniforms used in manufacturing facilities requiring highly sanitary conditions.
Attempts have been made to develop hook and loop fasteners which exhibit antimicrobial action at all times. For example, Japanese Abstract No. 06141914 discloses a fastener of a hook and loop configuration containing thiosulfate silver complex which is said to act as an antibacterial agent. The agent is kneaded into the component filaments and spinning yarn prior to assembly of the fastener.

U.S. Patent No. 5,727,677 discloses chemically treated VELCRO® strips said to impart resistance from infection.

U.S. Patent No. 5,180,585 discloses an antimicrobial powder composition containing a metallic coating as the antimicrobial ingredient, which is said to impart biocidal properties when incorporated into polymeric articles such as fibers.

The component added to the hook and loop fastener for imparting antimicrobial action must address certain needs. For example, the component should be convenient to blend into or coat onto the filament of the fastener. In addition, the component should not interfere with engagement of the hook and loop fastener material (e.g., it should not cause fatigue and subsequent cracking of the filament). Since hook and loop fasteners are used extensively in laboratories and in hospitals, the antimicrobial component should not be harmful to the human body and should maintain consistent efficacy over the useful life of the article to which the fastener is affixed. Further, since hook and loop fasteners are
commonly part of disposable consumer items, the antimicrobial component should not generate harmful agents upon disposal.

The component also must not lead to fatiguing of the polymer composition. Generally, particles of greater than 2 microns in diameter will cause fatiguing when added to polymeric compositions.

At first glance, various types of organic antimicrobial compounds would appear to be applicable for achieving the desired goals. However, use of many such compounds is inherently problematic. For example, liquid organic agents are difficult to blend into the filaments of the fastener, do not maintain effectiveness over time, and have been considered to contribute to filament fatigue. Also, microbes have been found to develop resistance to organic antimicrobial agents, and organic agents induce skin irritation in a substantial number of cases. The efficacy of organic antimicrobial agents (e.g., triclosan) declines over time as the active agent leaches out of the substrate. Furthermore, organic antimicrobial agents often have toxic decomposition products (e.g., triclosan is believed to generate dioxin when burned), creating environmental problems on disposal.

The present invention uses antimicrobial agents, such as silver ion-containing zeolite, which provides quick, non-toxic antimicrobial action over a period of time without inducing microbial resistance, or causing toxicity or irritation. The use of a silver-containing composition in particular allows non-toxic and effective hook and loop fasteners to be formulated.
OBJECTS OF THE INVENTION

Accordingly, an object of the present invention is to provide a hook and loop fastener containing an antimicrobial agent.

It is another object of the present invention to provide a hook and loop fastener containing an antimicrobial agent which is nontoxic and safe for human contact.

Yet another object of the present invention is to provide a hook and loop fastener containing an antimicrobial agent that does not generate toxins on disposal.

SUMMARY OF THE INVENTION

The invention is directed to a hook and loop fastener, comprising a hook element and a loop element, which comprises a polymeric composition. At least one of the hook or loop elements of the fastener comprises particles which contain or carry antimicrobial metal cations in an effective amount to impart antimicrobial property to the fastener. In preferred embodiments, the particles are inorganic particles, e.g. inorganic ceramic particles such as zeolite.

In one embodiment, the polymeric composition of the fastener may be coated with a composition comprising the inorganic antimicrobial agent. In
other embodiments, the inorganic antimicrobial composition may be blended in the masterbatch of the polymer composition which forms the hook and loop fastener.

The antimicrobial ceramic particles are preferably approximately 1-2 microns in diameter.

**DETAILED DESCRIPTION OF THE INVENTION**

1. **Antibacterial hook and loop fastener:**

   The present invention is directed to a hook and loop fastener containing an inorganic antimicrobial agent composition.

   As used herein, the term “hook and loop” is given its ordinary meaning, and includes hook and loop fasteners made from polymeric compositions, fibers or filaments. The filament comprising the hook and loop material may comprise nylon, polyester or other polymeric substances. Polymeric compositions used to form the hook and loop fasteners may contain, for example, plasticizers, colorants, fillers, anti-oxidants and UV-stabilizers. Suitable hook and loop fasteners are those sold under the name VELCRO®, manufactured by the Velcro Company.

   The hook and loop may but need not be of the same composition.

   Typically, smaller fibers are used to form loops, and larger fibers are used to form hooks. The hooks and fibers may then be woven or stitched into backings, which may also be formed from a polymeric composition.

   As used herein, the term “effective amount” is used synonymously with “sufficient amount”, both terms referring to the amount of active ingredient in the hook
and loop fastener of the invention required to achieve the antimicrobial properties thereof.

This amount is at least equal to MBC (minimum biocidal content, i.e., the content necessary to kill 99.9% of an inoculum of microbes within 24 hours of inoculation) when a biocidal effect is desired (or MIC (minimum inhibitory content) when an effect that is merely inhibitory of microbial growth is desired). The MBC or MIC of an antimicrobial agent is used to evaluate the efficacy of the agent in vitro. The MIC is defined as the minimum concentration in micrograms/ml of antimicrobial agent required for inhibiting the growth of each type of microorganism. The smaller the MIC value, the greater the efficacy of the antimicrobial agent. The assay for determining MIC is known, and can be carried out by smearing a solution containing a particular microorganism for inoculation onto a plate culture medium to which a test sample of antimicrobial compound of the invention is added in a particular concentration, followed by incubation and culturing of the plate. In such a test, the following microorganisms, for example, may be employed:

*S. mutans, porphyromonas gingivalis, Bacillus cereus var mycoides, E. coli, Pseudomonas aeruginosa, Staphylococcus aureus, Streptococcus faecalis, Aspergillus niger, Aureobasidium pullulans, Chaetomium globosum, Gliocladium virens, Penicillum funiculosum, Candida albicans, and Saccharomyces cerevisiae.*

As used herein, the term "biocompatible" means compatible with and non-toxic to the human body, in the context of a use being contemplated. In other words, the
degree of required biocompatibility for an ingestible use is greater than for something that
merely touches the skin.

The method used to impart bactericidal activity to the hook and loop fastener may be done by introducing the antimicrobial agent into the master batch formulation of the filament. Alternatively, it can be applied post-formulation. The antimicrobial agent may be uniformly distributed throughout the hook and loop filaments, as well as throughout the base material on which the filaments are attached. It is understood that the agent must be present in an effective amount, i.e., in sufficient concentration to kill microbes that may come in contact with the fastener, or to resist the growth of microbes in, or between the fibers of the fastener.

In a preferred embodiment, the antimicrobial agent may be kneaded into the polymeric composition used to form the fastener. A binder may also be present to aid in the incorporation of the antimicrobial agent. The agent may be incorporated into the polymeric composition before spinning into the fiber.

In another embodiment, the inorganic antimicrobial agent is sprayed onto the surface of the hook and loop fastener of the invention. The inorganic antimicrobial agent is preferably formed with a binder to create a dispersion which is sprayed or coated on the fastener. Examples of binders that can be used include methyl cellulose, methyl methacrylate, and cellulose acetate phthalate. The particular binder is selected so that it is compatible with the polymeric composition of the hook and loop fastener. The dispersion is then sprayed or coated onto the binder.
The content of antimicrobial zeolite is incorporated into the filament batch during formulation is 0.1 to 20% by weight, preferably 0.5 to 10% by weight, and most preferably 0.5 to 5% by weight, e.g. about 3%. The concentration of antimicrobial zeolite for spray coating onto an already formed filament is 0.1 to 100% by weight, preferably 0.5 to 75% by weight, and most preferably 0.5 to 50% by weight. Weight % as used herein is determined for materials dried in the conventional manufacturing drying process.

Care must be taken so that the incorporation of the particles into the resin does not damage the mechanical properties of the polymeric composition, i.e. cause fatigue or elongation to failure, or weaken the impact properties. Particles of 10 microns or greater may cause mechanical failure. Thus, it is preferred that the antimicrobial particles do not exceed 10 microns in size. Preferred particles are those of 5 microns or less, and most preferred are those of about 1-2 microns.

It is also important that a high degree of dispersion be obtained, so that the antimicrobial particles are well-dispersed in the polymeric composition. Suitable dispersion may be obtained by using any of the instruments typically used to obtain a high degree of dispersion, such as a twin screw extruder.

Once the inorganic antimicrobial particles are compounded into the polymeric composition in a suitable amount, the composition may be formed into a hook and loop fastener by any of the methods commonly used in the art. Typically, the polymeric composition is spun into fibers of varying size. Smaller fibers may be used to
form hooks, whereas the longer fibers are woven to form loops. The backing is also generally formed from the polymeric fibers. The fibers may then be formed into hook and loop fasteners by any of the methods commonly done in the art, such as by the methods described in U.S. Patents Nos. 3,943,981 to De Brabander; 4,271,566, to Perina; 4,794,028, to Fischer; 5,436,051, to Donaruma et al.; 5,457,855 to Kenney et al., and 5,755,016 to Provost, all of which are hereby incorporated by reference.

B. Antimicrobial agent:

The preferred antimicrobial agent is an inorganic antimicrobial metal-containing composition. A number of metal ions have been shown to possess antimicrobial activity, including silver, copper, zinc, mercury, tin, lead, bismuth, cadmium, chromium and thallium ions. These antimicrobial metal ions are believed to exert their effects by disrupting respiration and electron transport systems upon absorption into bacterial or fungal cells. Antimicrobial metal ions of silver, gold, copper and zinc, in particular, are considered safe for in vivo use. Antimicrobial silver ions are particularly useful for in vivo use due to the fact that they are not substantially absorbed into the body.

One type of inorganic antimicrobial metal containing composition contemplated by the invention is an antimicrobial metal salt. Such salts include silver
iodate, silver iodide, silver nitrate, and silver oxide. Silver nitrate is preferred. These salts are particularly quick acting, as release from ceramic particles is necessary for the fastener to have an effective amount of antimicrobial activity.

The ceramics employed in the antimicrobial ceramic particles of the present invention include zeolites, hydroxyapatite, zirconium phosphates, or other ion-exchange ceramics. Zeolites are preferred, and are described in the preferred embodiments referred to below. Hydroxyapatite particles containing antimicrobial metals are described, e.g., in U.S. Patent No. 5,009,898. Zirconium phosphates containing antimicrobial metals are described, e.g., in U.S. Patent Nos. 5,296,238; 5,441,717; and 5,405,644.

Inorganic particles, such as the oxides of titanium, aluminum, zinc and copper, may be coated with a composition which confers antimicrobial properties, for example, by releasing antimicrobial metal ions such as silver ions, which are described, e.g., in U.S. Patent No. 5,1890,585. Inorganic soluble glass particles containing antimicrobial metal ions, such as silver, are described, e.g. in U.S. Patent Nos., 5,766,611 and 5,290,544.

C. Zeolites:

Antimicrobial zeolites have been prepared by replacing all or part of the ion-exchangeable ions in zeolite with ammonium ions and antimicrobial metal ions, as described in U.S. Patent Nos. 4,938,958 and 4,911,898. Such zeolites have been
incorporated in antimicrobial resins (as shown in U.S. Patent Nos. 4,938,955 and 4,906,464) and polymer articles (U.S. Patent No. 4,775,585). Polymers including the antimicrobial zeolites have been used to make refrigerators, dish washers, rice cookers, plastic film, plastic cutting boards, vacuum bottles, plastic pails and garbage containers. Other materials in which antimicrobial zeolites have been incorporated include flooring, wall paper, cloth, paint, napkins, plastic automobile parts, catheters, bicycles, pens, toys, sand, and concrete. Examples of such uses are described in U.S. Patents 5,714,445; 5,697,203; 5,562,872; 5,180,585; 5,714,430; and 5,102,401.

Either natural zeolites or synthetic zeolites can be used to make the antimicrobial zeolites used in the present invention. “Zeolite” is an aluminosilicate having a three dimensional skeletal structure that is represented by the formula: XM_{2n-O-Al_{2}O_{3}}-YSiO_{2}-ZH_{2}O. M represents an ion-exchangeable ion, generally a monovalent or divalent metal ion, n represents the atomic valency of the (metal) ion, X and Y represent coefficients of metal oxide and silica respectively, and Z represents the number of water of crystallization. Examples of such zeolites include A-type zeolites, X-type zeolites, Y-type zeolites, T-type zeolites, high-silica zeolites, sodalite, mordenite, analcite, clinoptilolite, chabazite and erionite. The present invention is not restricted to use of these specific zeolites.

The ion-exchange capacities of these zeolites are as follows: A-type zeolite = 7 meq/g; X-type zeolite = 6.4 meq/g; Y-type zeolite = 5 meq/g; T-type zeolite = 3.4 meq/g; sodalite = 11.5 meq/g; mordenite = 2.6 meq/g; analcite = 5 meq/g;
clinoptilolite = 2.6 meq/g; chabazite = 5 meq/g; and erionite = 3.8 meq/g. These ion-exchange capacities are sufficient for the zeolites to undergo ion-exchange with ammonium and antimicrobial metal ions.

The specific surface area of preferred zeolite particles is preferably at least 150 m$^2$/g (anhydrous zeolite as standard) and the SiO$_2$/A1$_2$O$_3$ mol ratio in the zeolite composition is preferably less than 14, more preferably less than 11. The antimicrobial metal ions used in the antimicrobial zeolites should be retained on the zeolite particles through an ion-exchange reaction. Antimicrobial metal ions which are adsorbed or attached without an ion-exchange reaction exhibit a decreased bactericidal effect and their antimicrobial effects are not long-lasting. Nevertheless, it is advantageous for imparting quick antimicrobial action to maintain a sufficient amount of metal ions absorbed by the surface of zeolite.

In the ion-exchange process, the antimicrobial metal ions (cations) tend to be converted into their oxides, hydroxides, basic salts etc. either in the micropores or on the surfaces of the zeolite and also tend to deposit there, particularly when the concentration of metal ions in the vicinity of the zeolite surface is high. Such deposition tends to adversely affect the bactericidal properties of ion-exchanged zeolite. This undesirable deposition could be limited to acceptable levels or prevented by adjusting the pH value of the solution to the range of 3 to 10.

In an embodiment of the antimicrobial zeolites, a relatively low degree of ion exchange is employed to obtain superior bactericidal properties. At least a portion of
the zeolite particles should retain metal ions (cations) having bactericidal properties at
ion-exchangeable sites of the zeolite in an amount less than the ion-exchange saturation
capacity of the zeolite. In one embodiment, the zeolite employed in the present invention
retains antimicrobial metal ions in an amount up to 41% of the theoretical ion-exchange
capacity of the zeolite. Such ion-exchanged zeolite with a relatively low degree of
ion-exchange may be prepared by performing ion-exchange using a metal ion solution
having a low concentration, for example 0.3 wt%, as compared with solutions
conventionally used for ion exchange.

In antimicrobial zeolite particles used in the present invention,
ion-exchangeable ions present in zeolite, such as sodium ions, calcium ions, potassium
ions and iron ions are preferably partially replaced with ammonium and antimicrobial
metal ions. Such ions may co-exist in the antimicrobial zeolite particle since they do not
prevent the bactericidal effect. While antimicrobial metal ions include ions of silver,
copper, zinc, mercury, tin, lead, bismuth, cadmium, chromium and thallium, edible
antimicrobial zeolites to be formulated into compositions to be used in the fastener of the
invention include silver, gold, copper and zinc ions. These antimicrobial metal ions can
be used by themselves or in a mixture.

The zeolite preferably comprises an integral discoloration agent such as
ion-exchanged ammonium. Although ammonium ions may be contained in the zeolite at a
concentration as high as about 20% by weight of the zeolite, it is desirable to limit the
content of ammonium ions to about 0.5 to about 2.5%, more preferably from about 0.5 to about 2.0%, and most preferably, from about 0.5 to about 1.5% by weight of the zeolite.

A preferred antimicrobial zeolite for use in the hook and loop fastener of the invention is type A zeolite containing either a combination of ion-exchanged silver, zinc, and ammonium or silver and ammonium. One such zeolite is manufactured by Shinagawa Fuel Co. Ltd. (a/k/a Shinanen, Tokyo, Japan) under the product number AW-10N and consists of 0.6% by weight of silver ion-exchanged in Type A zeolite particles having a diameter of about 2.5µ. Another formulation, AJ-10N, consists of about 2% by weight silver ion-exchanged in Type A zeolite particles having a diameter of about 2.5µ. Another formulation, AW-80, contains 0.6% by weight of silver ion-exchanged in Type A zeolite particles having a diameter of about 1.0µ. These zeolites preferably contain about between 0.5% and 2.5% by weight of ion-exchanged ammonium. The zeolites are often obtained in master batches of low density polyethylene, polypropylene, or polystyrene, containing 20 wt.% of the zeolite.

D. **Examples:**

The present invention is explained in more detail with reference to the following non-limiting examples.

**Example 1**
A nylon polymeric composition is compounded with a Shinagawa AW-80 particles. The AW-80 zeolite particles (in the form of a powder) have been subject to ion-exchange with antimicrobial silver ions. A concentrate of 20% of AW-80 particles is prepared in the nylon and compounding is begun by any of the methods commonly used in the art, such as with any of the types of compounders commonly used in the prior art to achieve a high degree of dispersion, i.e. a twin screw extruder. Thereafter, the polymeric composition is diluted with additional amounts of nylon, to result in a composition having about 3% by weight antimicrobial zeolite particles.

The resulting polymeric composition is then spun into both large and small fibers. The large fibers are used to form hooks, and the small fibers are used to form loops, of the hook and loop fastener. The fibers are then weaved to form the antimicrobial hook and loop fastener of the invention.

**Example 2**

Antimicrobial zeolite particles (Shinagawa AW-80) are mixed with a solvent (water or acetone) in a concentration of 30%. The concentrate is then added to a binder, which may comprise commonly used binders such as acrylic polymers, silicone, urethane, or mixtures thereof to form a mixture. The mixture is adjusted to achieve final load levels after evaporation of the solvent of from 0.1-10% by weight of the antimicrobial zeolite particles. The mixture is then used to coat a previously formed hook
and loop fastener. The coating may be achieved by dipping, spraying or rolling the fastener into the mixture.

E. **Safety and Biocompatibility Data**

The antimicrobial properties of the antimicrobial zeolite particles of the invention may be assayed while in aqueous formulations using conventional assay techniques, including for example determining the minimum growth inhibitory concentration (MIC) with respect to a variety of bacteria, eumycetes and yeast. In such a test, the bacteria listed may be employed:

- *Bacillus cereus varmycoides;*
- *Escherichia coli;*
- *Pseudomonas aeruginosa;*
- *Staphylococcus aureus;*
- *Streptococcus faecalis;*
- *Streptococcus mutans;*
- *Aspergillus niger;*
- *Aureobasidium pullulans;*
- *Chaetomium globosum;*
- *Gliocladium virens;*
- *Penicillium funiculosum;*
- *Candida albicans;* and
- *Saccharomyces cerevisiae.*

The assay for determining MIC can be carried out by smearing a solution containing bacteria for inoculation onto a plate culture medium to which a test sample of the encapsulated antibiotic zeolite particles is added in a particular concentration, followed by incubation and culturing of the plate. The MIC is defined as a minimum concentration thereof required for inhibiting the growth of each bacteria.
Safety and Biocompatibility tests were conducted on the antimicrobial zeolites employed in the invention. ISO 10993-1 procedures were employed. The following results were obtained:

<table>
<thead>
<tr>
<th>Test Type</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cytotoxicity</td>
<td>Non-Toxic</td>
</tr>
<tr>
<td>Acute Systemic Toxicity</td>
<td>Non-Toxic</td>
</tr>
<tr>
<td>Intracutaneous Toxicity</td>
<td>Passed</td>
</tr>
<tr>
<td>Skin Irritation Test</td>
<td>Non-Irritant</td>
</tr>
<tr>
<td>Chronic Toxicity</td>
<td>No Observable Effect</td>
</tr>
<tr>
<td>In-vitro Hemolysis</td>
<td>Non-Hemolytic</td>
</tr>
<tr>
<td>30-day Muscle Implant Test</td>
<td>Passed</td>
</tr>
<tr>
<td>60-day Muscle Implant Test</td>
<td>Passed</td>
</tr>
<tr>
<td>90-day Muscle Implant Test</td>
<td>Passed</td>
</tr>
<tr>
<td>Ames Mutagenicity Test</td>
<td>Passed</td>
</tr>
<tr>
<td>Pyrogenicity</td>
<td>Non-Pyrogenic</td>
</tr>
</tbody>
</table>

Thus, the antimicrobial zeolites are exceptionally suitable under relevant toxicity and biocompatibility standards for use in a fastener.

While preferred embodiments of the invention have been described in the foregoing examples, it will be understood by one skilled in the art that various changes and modifications may be made therein without departing from the spirit and the scope of the invention. All patent applications, patents, patent publications, and literature references cited in this specification are hereby incorporated by reference in their entirety. In the case of inconsistencies, the present description, including definitions, is intended to control. Accordingly, the above description should be construed as
illustrating and not limiting the scope of the invention. All such obvious changes and modifications are within the patented scope of the appended claims.
WHAT IS Claimed IS:

1. A fastener comprising a hook element and a loop element, each of said hook and loop comprising a polymeric composition, said polymeric composition in at least one of said hook and loop element comprising zeolite particles carrying anti-microbial metal cations in an effective amount to impart antimicrobial activity to said fastener.

2. The fastener of claim 1 wherein said zeolite particles have a particle diameter size of between about 0.5 and 500μm.

3. The fastener of claim 1 wherein said zeolite particles are A-type zeolites.

4. The fastener of claim 1 wherein both said hook element and loop element comprise zeolite particles carrying antimicrobial metal cations in an effective amount to impart antimicrobial activity to said fastener.

5. The fastener of claim 1 wherein said antimicrobial metal cations are silver ions.
6. The fastener of claim 1 wherein said zeolite particles are prepared by replacing all or part of the ion-exchangeable ions in said zeolite with antimicrobial metal cations.

7. The fastener of claim 1, wherein said polymeric composition comprises nylon.

8. The fastener of claim 1 wherein the antimicrobial zeolite is present in at least one of said hook and loop element in the amount between about 0.5 and about 20 wt. %

9. The fastener of claim 8 wherein the antimicrobial zeolite is present in at least one of said hook and loop element in the amount between about 0.5 and about 10.0 wt. %

10. The fastener of claim 9 wherein the antimicrobial zeolite is present in at least one of said hook and loop element in an amount of between about 0.5 and about 5.0 wt %

11. A fastener comprising a hook element and a loop element, each of said hook and loop comprising a polymeric composition, said polymeric composition in at
least one of said hook and loop element coated with a composition comprising an inorganic
antimicrobial agent in an effective amount to impart antimicrobial property to said fastener.

12. The fastener of claim 11 wherein said inorganic agent comprises
antimicrobial ceramic particles.

13. The fastener of claim 12 wherein said antimicrobial ceramic particles are
zeolites.

14. A fastener comprising a hook element and loop element, each of said
hook and loop comprising a polymeric composition, said polymeric composition in at least
one of said hook and loop element comprising inorganic particles containing antimicrobial
metal cations in an effective amount to impart substantial antimicrobial action to said
fastener.

15. The fastener of claim 14 wherein said inorganic particles contain silver
cations as an active agent.

16. The fastener of claim 14 wherein said inorganic particles are ceramic.