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(54) Title: ANTIMICROBIAL POLYURETHANE FOAM

(57) Abstract: Flexible cellular polyurethane foam products are described. The foams are primarily comprised of: (a) a polyisocyanate component selected from the group consisting of toluenen diisocyanate (TDI), methylene diisocyanate (MDI), monomeric methylene diisocyanate (MDI), polymeric methylene diisocyanate (MDI), toluene diisocyanate (TDI) prepolymer, methylene diisocyanate (MDI) prepolymer, and combinations thereof; (b) an aqueous component including a polyol or polyol blend, or alternatively, a polyol or polyol blend component; and (c) a controlled release antimicrobial component. The resulting flexible cellular polyurethane foam products, containing the antimicrobial component, are suitable for use as wound dressings, or other skin contact (e.g., medical and/or cosmetic) applications.

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ANTIMICROBIAL POLYURETHANE FOAM

CROSS-REFERENCE TO RELATED APPLICATION

The instant application claims priority to U.S. Provisional Patent Application Serial Nos. 60/395,029 and 60/395,149, both filed on July 11, 2002, the entire specifications of which are expressly incorporated herein by reference.

FIELD OF THE INVENTION

The present invention generally relates to polyurethane foams, and more particularly to antimicrobial cellular polyurethane foam products primarily comprised of an isocyanate component, a polyol component, and a controlled release antimicrobial agent. The present invention also relates to antimicrobial polyurethane cellular hydrophilic foam products primarily comprised of an isocyanate component, an aqueous component with pure or blended polyols or other foaming agents, and a controlled release antimicrobial agent.

BACKGROUND OF THE INVENTION

Flexible cellular polyurethane foams are widely used in a variety of uses, ranging from furniture cushioning, carpet underlayment, and cosmetic and medical pads/applicators. These foams have been traditionally prepared using toluene diisocyanate (TDI) components. Conversely, methylene diisocyanate (MDI) has been used to make flexible high-density, open-cell polyurethane foams. For example, these MDI-based foams can provide high-density foams on the order of greater than 4.5 lbs/ft^3.

Recently, there has been increased interest in the incorporation of antimicrobial agents, such as those used in various household products, into various foam products for cosmetic and/or medical applications. However, conventional attempts to do so have not lead to satisfactory results. Examples of related technology can be found with reference to U.S. Patent Nos. 4,728,323; 5,296,518; 5,662,913, 5,744,151; 6,093,414; 6,288,076; 6,333,093; 6,348,212; 6,355,858; 6,376,565; and 6,455,065; U.S. Patent Application Publication No. 2001/0041188; and International Application Publication Nos. WO 02/062403 and WO 02/078755, the entire specifications of which are expressly incorporated herein by reference.

Therefore, there exists a need for new and improved antimicrobial polyurethane foam products, especially flexible cellular polyurethane foam products and flexible cellular hydrophilic polyurethane foam products, and methods for making the same.

SUMMARY OF THE INVENTION

In accordance with the general teachings of the present invention, new and improved flexible cellular polyurethane foam products, and methods for making the same, are provided. In accordance with another aspect of the present invention, new and improved flexible cellular hydrophilic polyurethane foam products, and methods for making the same, are provided.

In accordance with a first embodiment of the present invention, a flexible cellular polyurethane foam is provided, wherein the flexible cellular polyurethane foam comprises the reaction product of: (a) a polyisocyanate component selected

from the group consisting of toluene diisocyanate, monomeric methylene diisocyanate, polymeric methylene diisocyanate, and combinations thereof; (b) a polyol or polyol blend component reactive with the polyisocyanate component to maintain an isocyanate index between 10 and 120 and a density in the flexible cellular polyurethane foam greater than 4.5 lbs/ft^3; and (c) a controlled release antimicrobial component, wherein the antimicrobial component may be present in an unaltered state or may be incorporated in either component (a) and/or component (b).

In accordance with a second embodiment of the present invention, a method for making a flexible cellular polyurethane foam is provided, comprising: (a) mixing the following components to form a reaction product: (1) a polyisocyanate component selected from the group consisting of toluene diisocyanate, monomeric methylene diisocyanate, polymeric methylene diisocyanate, and combinations thereof; (2) a polyol or polyol blend component reactive with the polyisocyanate component to maintain an isocyanate index between 10 and 120 and a density in the flexible cellular polyurethane foam greater than 4.5 lbs/ft^3; and (3) a controlled release antimicrobial component, wherein the antimicrobial component may be present in an unaltered state or may be incorporated in either component (1) and/or component (2); (b) applying the reaction product onto a moving substrate to form a polyurethane bun; and (c) removing the polyurethane bun from the substrate.

In accordance with a third embodiment of the present invention, a flexible cellular hydrophilic polyurethane foam is provided, wherein the flexible cellular hydrophilic polyurethane foam comprises the reaction product of: (a) a

polyisocyanate component selected from the group consisting of toluene diisocyanate, monomeric methylene diisocyanate, polymeric methylene diisocyanate, toluene diisocyanate prepolymers, methylene diisocyanate prepolymers, and combinations thereof; (b) an aqueous solution component including a polyol or polyol blend and other foaming agents reactive with the polyisocyanate component, wherein the water content of the aqueous solution component is between 5% and 300% by weight; and (c) a controlled release antimicrobial component, wherein the antimicrobial component may be present in an unaltered state or may be incorporated in either component (a) and/or component (b).

In accordance with a fourth embodiment of the present invention, a method for making a flexible cellular hydrophilic polyurethane foam is provided, comprising: (a) mixing the following components to form a reaction product: (1) a polyisocyanate component selected from the group consisting of toluene diisocyanate, monomeric methylene diisocyanate, polymeric methylene diisocyanate, toluene diisocyanate prepolymers, methylene diisocyanate prepolymers, and combinations thereof; (2) an aqueous solution component including a polyol or polyol blend and other foaming agents reactive with the polyisocyanate component, wherein the water content of the aqueous solution component is between 5% and 300% by weight; and (3) a controlled release antimicrobial component, wherein the antimicrobial component may be present in an unaltered state or may be incorporated in either component (a) and/or component (b); (b) applying the reaction product onto a moving substrate to form a polyurethane bun; and (c) removing the polyurethane bun from the substrate.

The resulting above-described cellular polyurethane foams, and products formed therefrom, exhibit antimicrobial properties that are suitable for various cosmetic and/or medical applications.

Further areas of applicability of the present invention will become apparent from the detailed description provided hereinafter. It should be understood that the detailed description and specific examples, while indicating the preferred embodiment of the invention, are intended for purposes of illustration only and are not intended to limit the scope of the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

The present invention will become more fully understood from the detailed description and the accompanying drawings, wherein:

Figure 1 is a photographic illustration of bacterial growth on untreated hydrophilic polyurethane foam, in accordance with the prior art;

Figure 2 is a photographic illustration of the lack of bacterial growth on hydrophilic polyurethane foam treated with a silver-based antimicrobial agent, in accordance with the general teachings of the present invention;

Figure 3 is a graphical illustration of the effectiveness of a silver-based antimicrobial agent over a seven-day period of time, in accordance with the general teachings of the present invention;

Figure 4 is a graphical illustration of effectiveness of a silver-based antimicrobial agent in hydrophilic foam, in accordance with the general teachings of the present invention; and

Figure 5 is a is a graphical illustration of the effectiveness of a silver-based antimicrobial agent

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

While the present disclosure will be described more fully hereinafter, it is to be understood at the outset that persons of skill in the art may modify the invention herein described while still achieving the favorable results of this disclosure. Accordingly, the description that follows is to be understood as being a broad teaching disclosure directed to persons of skill in the appropriate arts, and not as limiting upon the present invention.

The polyisocyanate component is preferably selected from the group consisting of toluene diisocyanate (TDI), monomeric methylene diisocyanate (MDI), polymeric methylene diisocyanate (MDI), toluene diisocyanate (TDI) prepolymers, methylene diisocyanate (MDI) prepolymers, and combinations thereof.

These polyisocyanates are generally well known in the art, and include, without limitation, 4,4'-, 2,4'-, and 2 2'-diphenylmethane diisocyanate, various polyphenylenepolymethylene polyisocyanates (polymeric MDI), and mixtures of some or all of these compounds.

The polyisocyanate component may also include one or more other aliphatic, cycloaliphatic, arylaliphatic, and/or aromatic polyisocyanates. Specific examples of such other polyisocyanates include, without limitation: alkylene diisocyanates with 4 to 12 carbons in the alkylene radical such as, but not limited to 1,12-dodecane diisocyanate, 2-ethyl-1,4,tetramethylene diisocyanate, 2-

methyl-1,5-pentamethylene diisocyanate, 1,4-tetramethylene diisocyanate and 1,6-hexamethylene diisocyanate; cycloaliphatic diisocyanates such as, but not limited to 1,3- and 1,4-cyclohexane diisocyanate as well as any mixtures of these isomers, 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane (isophorone diisocyanate), and 2,4- and 2,6-hexahydrotoluene diisocyanate as well as the corresponding isomeric mixtures; and other aromatic polyisocyanates such as, but not limited to 2,4- and 2,6-toluene diisocyanate (TDI) and the corresponding isomeric mixtures. The polyisocyanate component should preferably contain at least 80% by weight methylene diisocyanate (MDI) or polymeric methylene diisocyanate (MDI).

Frequently, so-called modified multivalent isocyanates, i.e., products obtained by the partial chemical reaction of organic diisocyanates and/or polyisocyanates may be used. Examples include, without limitation, diisocyanates and/or polyisocyanates containing ester groups, urea groups, biuret groups, allophanate groups, carbodiimide groups, isocyanurate groups, and/or urethane groups. Specific examples include, without limitation, organic, preferably aromatic, polyisocyanates containing urethane groups (also known as isocyanate prepolymers) and having a free NCO content of 20 to 46 weight percent, preferably 25 to 40 weight percent, based on the total weight of the isocyanate component, which may be prepared by reacting polyisocyanate with low molecular weight diols, triols, dialkylene glycols, trialkylene glycols, or polyoxyalkylene glycols with a molecular weight of up to 8000.

Examples of polyols useful for preparing isocyanate prepolymers include, without limitation, diethylene glycol, dipropylene glycol, polyoxyethylene glycol,

polyoxypropylene glycol, and polyoxypropylene polyoxyethylene glycols or triols. Isocyanate prepolymers may optionally be mixed together or mixed with unmodified organic polyisocyanates such as, but not limited to 2,4'- and 4,4'diphenylmethane diisocyanate, polymeric methylene diisocyanate (MDI), 2,4- and/or 2,6-toluene diisocyanate.

Crude polyisocyanates may also be used in the compositions of the present invention, such as, but not limited to crude toluene diisocyanate obtained by the phosgenation of a mixture of toluene diamines or crude diphenylmethane diisocyanate obtained by the phosgenation of crude diphenylmethane diamine.

The polyol component preferably comprises one or more polyol compounds. If a hydrophilic polyurethane foam product is desired, the aqueous solution component preferably comprises water and one or more polyol compounds, such that at least 50% of the hydroxyl (OH) functional groups of the polyol component are secondary OH groups.

Representative polyols, which may be employed in the present invention, are generally well known to those skilled in the art. Representative polyols include, without limitation, polyhydroxy-containing polyesters, polyoxyalkylene polyether polyols, polyhydroxyterminated polyurethane polymers, polyhydroxyl-containing phosphorus compounds, and alkylene oxide adducts of polyhydric polythioesters, polyacetals, aliphatic polyols and thiols, ammonia, and amines including aromatic, aliphatic and heterocyclic amines, as well as mixtures thereof. Alkylene oxide adducts of compounds, which contain two, or more different groups (e.g., amino alcohols) within the above-defined classes may also be used. Also, alkylene oxide adducts of compounds which contain one SH group and one

OH group, as well as those which contain an amino group and an SH group, may be used. Generally, the equivalent weight of the polyols will preferably vary from 500 to 10,000, and still more preferably from 750 to 3000.

Any suitable hydroxy-terminated polyester may be used such as can be prepared, for example, from polycarboxylic acids and polyhydric alcohols. Any suitable polycarboxylic acid may be used such as, but not limited to oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, maleic acid, fumaric acid, glutaconic acid, terephthalic acid, and the like.

Any suitable polyhydric alcohol, including both aliphatic and aromatic may be used such as, but not limited to ethylene glycol, propylene glycol, trimethylene glycol, 1,2-butanediol, 1,3-butanediol, 1,4-butanediol, 1,2-pentanediol, 1,4-pentanediol, 1,5-pentanediol, 1,6-hexanediol, 1,7-heptanediol, glycerol, 1,1,1-trimethyolpropane, 1,1,1-trimethylolethane, 1,2,6-hexantriol, alpha-methyl glucoside, pentaerythritol, and sorbitol.

Also included within the term "polyhydric alcohol" are compounds derived from phenol such as 2,2-bis(4-hydroxyphenyl)propane, commonly known as bisphenol A. In order to obtain secondary hydroxyl functional groups, the polyester should preferably be capped with a secondary hydroxyl-containing polyol, such as, but not limited to 1,2-propanediol, 1,3-butanediol, 1,2-butanediol, or similar materials.

Also polyols containing ester groups can also be employed in the present invention. These polyols are prepared by the reaction of an alkylene oxide with an organic dicarboxylic acid anhydride and a compound containing reactive

hydrogen atoms. A more comprehensive discussion of these polyols and their preparation can be found in U.S. Patent Nos. 3,585,185; 3,639,541, and 3,639,542, the entire specifications of which are expressly incorporated herein by reference.

Although a variety of polyol compounds may be utilized to incorporate secondary hydroxyl groups, such as the above-described polyester polyols, the polyol component is preferably principally composed of polyether polyol(s).

The polyether polyol composition useful in the present invention preferably contains a predominant amount of secondary hydroxyl groups, with a composition consisting of all secondary hydroxyl groups being preferred. By a predominant amount of secondary hydroxyl group containing polyether polyol composition, it is meant that at least 50 weight percent of the hydroxyl groups should be secondary hydroxyl groups such as those derived from propylene oxide. It may be preferable to add ethylene oxide during chain extension of the polyether polyol to prepare a heteric or internal block polyether polyol so long as less than 50 weight percent of the polyol is terminated with primary hydroxyl groups such as those derived from ethylene oxide. Although it is within the scope of the invention to add the above minor amounts of ethylene oxide to an initiator molecule as a cap, it is preferable to prepare a polyoxyalkylene polyether polyol exclusively containing secondary hydroxyl groups.

Methods of making polyether polyols are well known and include those polyethers prepared from the base catalyzed addition of an alkylene oxide such as, but not limited to ethylene oxide, propylene oxide or butylenes oxide, preferably ethylene oxide, to an initiator molecule containing, on the average, two

or more active hydrogens. The polyalkylene polyether polyols are well known in the art and may be prepared by any known process.

Examples of initiator molecules include, without limitation, diethylene glycol, ethylene glycol, dipropylene glycol, propylene glycol, trimethylene glycol, 1,2-butanediol, 1,3-butanediol, 1,4-butanediol, 1,4-pentanediol, 1,5-pentanediol, 1,6-hexanediol, 1,7-heptanediol, glycerine, 1,1,1-trimethyolpropane, 1,1,1-trimethylolethane, 1,2,6-hexantriol, or triethylolpropane.

Particularly preferred initiators include, without limitation, trimethylolpropane, glycerine, propylene glycol, and blends of polyoxyalkylene polyether polyols initiated thereby, with glycerine and trimethylolpropane being most preferred. Suitable alkylene oxides include, without limitation, ethylene oxide, propylene oxide, butylenes oxide, amylene oxide, and mixtures of these oxides. Particularly preferred is the reaction product of ethylene oxide or a mixture of ethylene oxide and propylene oxide with one of the aforementioned initiators, followed by capping of the polyether with propylene oxide, to yield a polyether polyol having only predominantly secondary hydroxyl groups.

The polyol component may also contain solid polymer particles. Preferred polymer particle-containing polyols are the so-called graft polyols comprising a carrier polyol containing predominantly secondary hydroxyl groups along with polymer particles. Graft polyols are well known to the art and are typically prepared by the *in situ* polymerization of one or more vinyl monomers, preferably acrylonitrile and styrene, in the presence of a polyether or polyester polyol, particularly polyols containing minor a minor amount of natural or induced unsaturation, followed by optional blending with additional liquefied polyol.

The polyurethane foams employed in the present invention are generally prepared by the reaction of a polyoxyalkylene polyether polyol with an organic polyisocyanate in the presence of a blowing agent and optionally in the presence of additional polyhydroxyl-containing components, chain-extending agents, catalysts, surfactants, stabilizers, dyes, fillers and pigments.

Chain extending agents may also be used in the preparation of the polyurethane foams according to the present invention. These include compounds having at least two functional groups bearing active hydrogen atoms such as, but not limited to water, hydrazine, primary and secondary diamines, amino alcohols, amino acids, hydroxy acids, glycols, or mixtures thereof. A preferred group of chain-extending agents includes, without limitation, water, ethylene glycol, 1,4-butanediol and primary and secondary diamines which react more readily with the prepolymer than does water such as, but not limited to phenylene diamine, 1,4-cyclohexane-bis-(methylamine), ethylenediamine, diethylenetriamine, N-(2-hydroxylpropyl)ethylenediamine, N,N'-di(2-hydroxypropyl)ethylenediamine, piperazine, and 2-methylpiperazine.

Any suitable catalysts or surfactants may be used, along with suitable processes for the preparation of cellular polyurethane foams as disclosed in U.S. Patent No. Re. 24,514, the entire specification of which is expressly incorporated herein by reference, together with suitable machinery to be used in conjunction therewith. When water is added to generate CO_2 as blowing agent, corresponding quantities of excess isocyanate to react with water may be used. It is possible to proceed with the preparation of the polyurethane foams by a prepolymer technique wherein an excess of organic polyisocyanate is reacted in

a first step with the polyol of the present invention to prepare a prepolymer having free isocyanate groups which is then reacted in a second step with water and/or additional polyol to prepare a foam. Alternatively, the components may be reacted in a single working step commonly known as the "one-shot" technique of preparing polyurethanes.

The foam of the present invention preferably incorporates a controlled release antimicrobial agent or component. The controlled release antimicrobial can be any form. This antimicrobial can either be substantially unaltered (i.e., unreacted) or alternatively, can be incorporated in either the isocyanate or aqueous/polyol components.

In accordance with a preferred embodiment of the present invention, the antimicrobial is comprised of a controlled release silver-based compound. By way of a non-limiting example, one such suitable material is ALPHA SAN RC5000, which is readily commercially available from Milliken Corporation (Spartanburg, North Carolina). The ALPHA SAN antimicrobial effectively uses a molecular "cage" which allows for a controlled release of ion through an ion exchange mechanism.

Referring to Figs. 1 and 2, Fig. 1 shows untreated hydrophilic polyurethane foam, while Fig. 2 shows hydrophilic polyurethane foam treated with 0.12% by weight silver-based antimicrobial agent. As shown in Fig. 2, there is no bacterial growth. Both samples shown in Figs. 1 and 2 were incubated after contact with a bacterial medium.

The effectiveness over time of the antimicrobial agent is illustrated in Fig. 3. Displayed are several concentration levels of silver elution during exposure

over a 7-day period of time. Specifically, the concentrations, by weight, of ALPHA SAN forming the test samples were 0.12 percent, 0.50 percent, 1.00 percent and 2.00 percent. The test of Figure 3 was conducted in a lactated ringers solution. In this test the chloride level was kept at about .85 percent by weight. The results are shown in parts per billion silver/cm^2. In order to convert from parts per billion silver/cm^2 to micrograms of silver/cm^2 a conversion factor is applied. The parts per billion/cm^2 are multiplied by .0157 to convert to micrograms/cm^2.

Fig.4 shows that bacterial counts are severely reduced using foams prepared in accordance with the present invention. Various ALPHA SAN antimicrobial concentrations are shown as noted in the log reduction scale. The foams shown in Fig. 4 include a polyisocyanate component of toluene diisocyanate (TDI) prepolymer, and a polyol reacted to maintain an isocyanate index of 15. The density of the foams was 5.2 pounds per cubic foot. ALPHA SAN RC5000 was added in 0.5% and 1.0% concentrations (by weight) shown in Fig. 4. An additional control sample of PET fabric was used in conjunction with untreated polyurethane foam.

Figure 5 shows the results of a silver elution test. The test was conducted in a sodium-potassium-phosphate buffer solution. Additionally, the samples were diluted with 5 percent nitric acid after 24 hours. The test samples included 1 and 2 percent ALPHA SAN. Again, the test results are shown in parts per million silver/cm^2. The same correction factor is used as above to convert to micrograms Ag/cm^2.

Each of the elution tests resulted in the releasing of antimicrobial silver in the range of about 0.157 micrograms Ag/cm^2 to about 1.45 micrograms Ag/ cm^2.

The composition of the present invention is particularly useful for producing slab or bun foams, or continuous rolls or sheets, particularly as it relates to medical sponge foam products as used in wound dressings. By way of a non-limiting example, flexible cellular polyurethane foams, in accordance with the general teachings of the present invention, can be prepared by:

(a) mixing:

(1) a polyisocyanate component selected from the group consisting of toluene diisocyanate (TDI), monomeric methylene diisocyanate (MDI), polymeric methylene diisocyanate (MDI), toluene diisocyanate (TDI) prepolymer, methylene diisocyanate (MDI) prepolymer, and combinations thereof;

(2) a polyol or polyol blend component, reacted to maintain an isocyanate index between 10 and 120 and densities in the flexible cellular polyurethane foam greater than 4.5 lbs/ft3; and

(3) a controlled release antimicrobial agent, preferably containing a silver-based compound, either mixed in separately, or blended in one or both of the above two components;

(b) applying the polyurethane reaction mixture onto a moving substrate to form a polyurethane bun; and

(c) removing the polyurethane bun from the substrate.

By way of another non-limiting example, flexible cellular hydrophilic polyurethane foams, in accordance with the general teachings of the present invention, can be prepared by:

(a) mixing:

(1) a polyisocyanate component selected from the group consisting of toluene diisocyanate (TDI), monomeric methylene diisocyanate (MDI), polymeric methylene diisocyanate (MDI), toluene diisocyanate (TDI) prepolymer, methylene diisocyanate (MDI) prepolymer, and combinations thereof;

(2) an aqueous solution component containing a polyol or polyol blend reacted to maintain an isocyanate index between 10 and 90 and densities in the flexible cellular polyurethane foam greater than 4.5 lbs/ft3; and (3) a controlled release antimicrobial agent, preferably containing a silver-based compound, either mixed in separately, or blended in one or both of the above two components;

(b) applying the polyurethane reaction mixture onto a moving substrate to form a polyurethane bun; and

(c) removing the polyurethane bun from the substrate.

The silver concentrations in the resultant foam are preferably in the range of about 0.00375 mg Ag/cm^3 to about .0632 mg Ag/cm^3. More specifically, foams made for the test samples above incorporating .12 percent by weight ALPHA SAN have a silver concentration of about 0.00375 mg Ag/cm^3. Similarly foams made for the test samples above incorporating 0.5, 1 and 2 percent by weight ALPHA SAN have a silver concentration of about .01565, .0313 and .0632 mg Ag/cm^3, respectively.

The resulting cellular polyurethane foam products are then suitable for uses wherever cosmetic and/or medical applications are required. By way of a non-limiting example, these products may include cosmetic pads, puffs,

applicators, foam gauzes, bandages, wound dressings, wipes or any other application requiring the use of cosmetic and/or medical foam products.

The foregoing embodiments and examples are to be considered illustrative, rather than restrictive of the invention, and those modifications, which come within the meaning and range of equivalence of the claims, are to be included therein.

What is claimed is:

1. A flexible cellular polyurethane foam, comprising:

a reaction product of:

(a) a polyisocyanate component selected from the group consisting of toluene diisocyanate, monomeric methylene diisocyanate, polymeric methylene diisocyanate, and combinations thereof;

(b) a polyol or polyol blend component reactive with the polyisocyanate component to maintain an isocyanate index between 10 and 120 and a density in the flexible cellular polyurethane foam greater than 4.5 lbs/ft^3; and

(c) a controlled release antimicrobial component, wherein the antimicrobial component may be present in an unaltered state or may be incorporated in either component (a) and/or component (b).

2. The invention according to claim 1, wherein the polyisocyanate component comprises at least 80% by weight methylene diisocyanate or polymeric methylene diisocyanate.

3. The invention according to claim 1, wherein the polyol component is comprised of a polyether polyol.

4. The invention according to claim 1, wherein the antimicrobial component is comprised of a silver-based compound.

5. The invention according to claim 1, wherein the antimicrobial component is present in an amount of about .12 to about 2 weight percent based on the total weight of the foam.

6. A method for making a flexible cellular polyurethane foam, comprising:

(a) mixing the following components to form a reaction product:

(1) a polyisocyanate component selected from the group consisting of toluene diisocyanate, monomeric methylene diisocyanate, polymeric methylene diisocyanate, and combinations thereof;

(2) a polyol or polyol blend component reactive with the polyisocyanate component to maintain an isocyanate index between 10 and 120 and a density in the flexible cellular polyurethane foam greater than 4.5 lbs/ft^3; and

(3) a controlled release antimicrobial component, wherein the antimicrobial component may be present in an unaltered state or may be incorporated in either component (1) and/or component (2);

(b) applying the reaction product onto a moving substrate to form a polyurethane bun; and

(c) removing the polyurethane bun from the substrate.

7. The invention according to claim 6, wherein the polyisocyanate component comprises at least 80% by weight methylene diisocyanate or polymeric methylene diisocyanate.

8. The invention according to claim 6, wherein the polyol component is comprised of a polyether polyol.

9. The invention according to claim 6, wherein the antimicrobial component is comprised of a silver-based compound.

10. The invention according to claim 6, wherein the antimicrobial component is present in an amount of about .12 to about 2 weight percent based on the total weight of the foam.

11. A flexible cellular hydrophilic polyurethane foam, comprising:

a reaction product of:

(a) a polyisocyanate component selected from the group consisting of toluene diisocyanate, monomeric methylene diisocyanate, polymeric methylene diisocyanate, toluene diisocyanate prepolymers, methylene diisocyanate prepolymers, and combinations thereof;

(b) an aqueous solution component including a polyol or polyol blend and other foaming agents reactive with the polyisocyanate component, wherein the water content of the aqueous solution component is between 5% and 300% by weight of the aqueous solution component; and

(c) a controlled release antimicrobial component, wherein the antimicrobial component may be present in an unaltered state or may be incorporated in either component (a) and/or component (b).

12. The invention according to claim 11, wherein the polyisocyanate component comprises at least 80% by weight methylene diisocyanate or polymeric methylene diisocyanate.

13. The invention according to claim 11, wherein the polyol component is comprised of a polyether polyol.

14. The invention according to claim 11, wherein the antimicrobial component is comprised of a silver-based compound.

15. The invention according to claim 11, wherein the antimicrobial component is present in an amount of about .12 to about 2 weight percent based on the total weight of the foam.

16. A method for making a flexible cellular hydrophilic polyurethane foam, comprising:

(a) mixing the following components to form a reaction product:

(1) a polyisocyanate component selected from the group consisting of toluene diisocyanate, monomeric methylene diisocyanate, polymeric methylene diisocyanate, toluene diisocyanate prepolymers, methylene diisocyanate prepolymers, and combinations thereof;

(2) an aqueous solution component including a polyol or polyol blend and other foaming agents reactive with the polyisocyanate component,

wherein the water content of the aqueous solution component is between 5% and 300% by weight of the aqueous solution component; and

(3) a controlled release antimicrobial component, wherein the antimicrobial component may be present in an unaltered state or may be incorporated in either component (a) and/or component (b);

(b) applying the reaction product onto a moving substrate to form a polyurethane bun; and

(c) removing the polyurethane bun from the substrate.

17. The invention according to claim 16, wherein the polyisocyanate component comprises at least 80% by weight methylene diisocyanate or polymeric methylene diisocyanate.

18. The invention according to claim 16, wherein the polyol component is comprised of a polyether polyol.

19. The invention according to claim 16, wherein the antimicrobial component is comprised of a silver-based compound.

20. The invention according to claim 16, wherein the antimicrobial component is present in an amount of about .12 to about 2 weight percent based on the total weight of the foam.

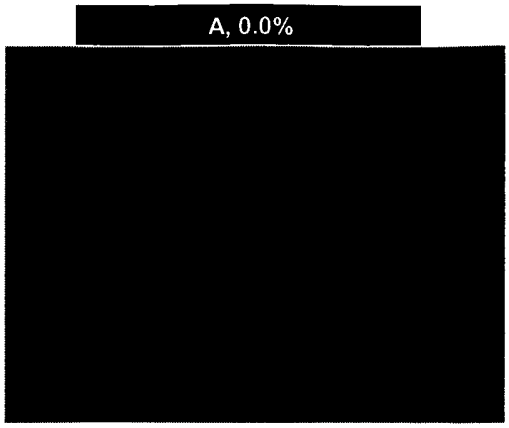

Figure 1

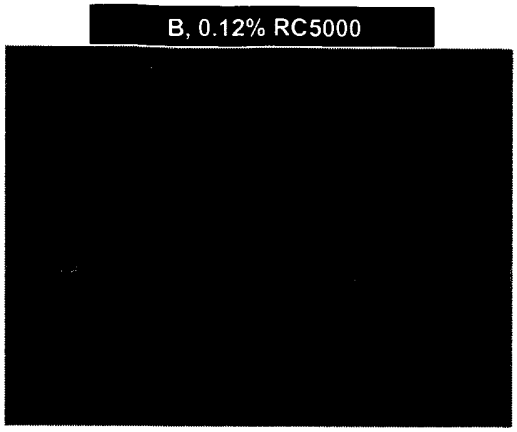

Figure 2

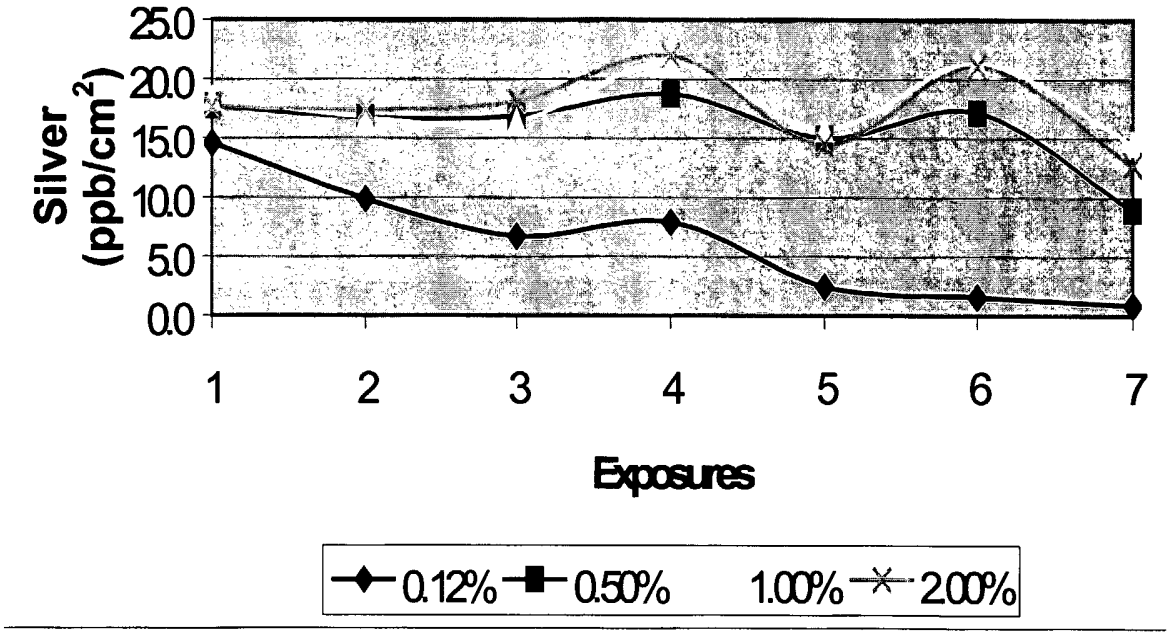

Figure 3

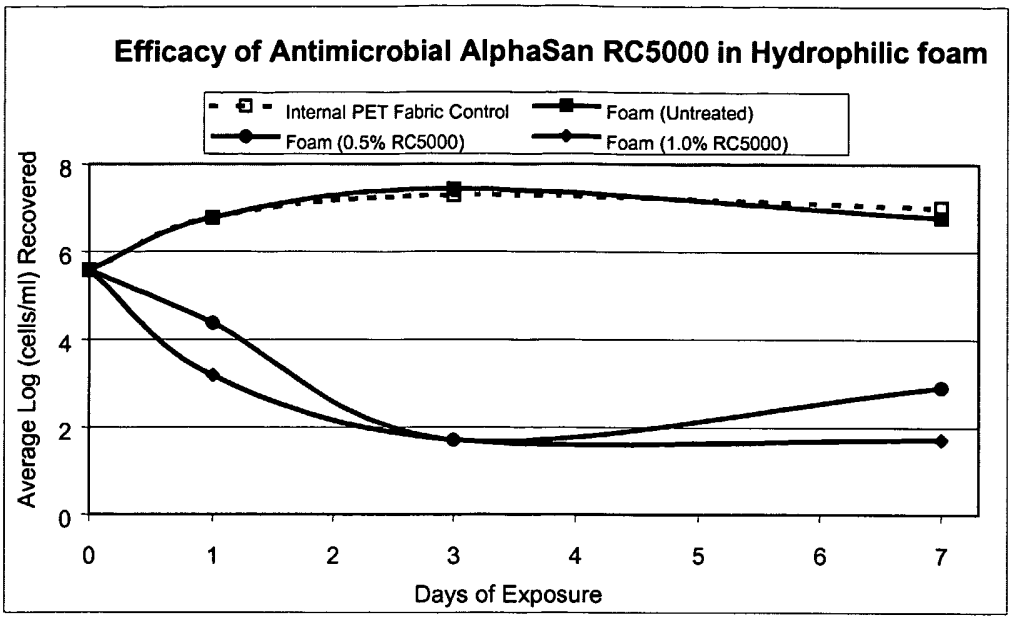

Figure 4

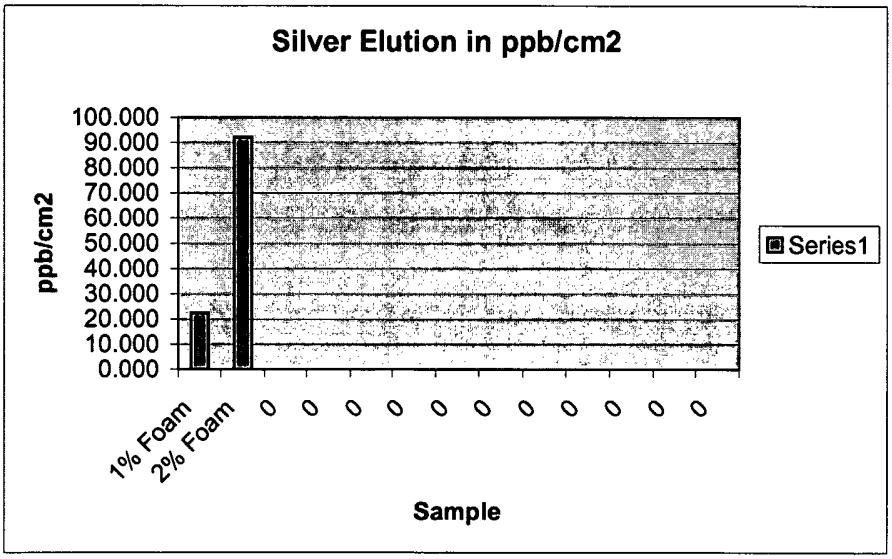

Figure 5

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US03/21771

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : C08J 9/08; C08G 18/48
US CL : 521/123, 124, 130, 170, 174

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
U.S. : 521/123, 124, 130, 170, 174

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,194, 453 A (JOURQUIN et al.) 16 March 1993 (16.03.1993), see the entire document.	1-20
Y	US 6,093,414 A (CAPELLI) 25 July 2000 (25.07.2000), column 19 line 26 - column 20 line 67, as well as, the entire document.	1-20
Y	US 6,238,691 B1 (HUANG) 29 May 2001 (29.05.2001), see the entire document.	1-20
Y	US 6,287,584 B1 (FEUER et al.) 11 September 2001 (11.09.2001), column 1 lines 51-64, column 3 lines 61-63.	1-20

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent published on or after the international filing date

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
09 November 2003 (09.11.2003)	01 DEC 2003
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US Commissioner for Patents P.O. Box 1450 Alexandria, Virginia 22313-1450 Facsimile No. (703)305-3230	Authorized officer John m Cooney Telephone No. 703-306-5665

Form PCT/ISA/210 (second sheet) (July 1998)