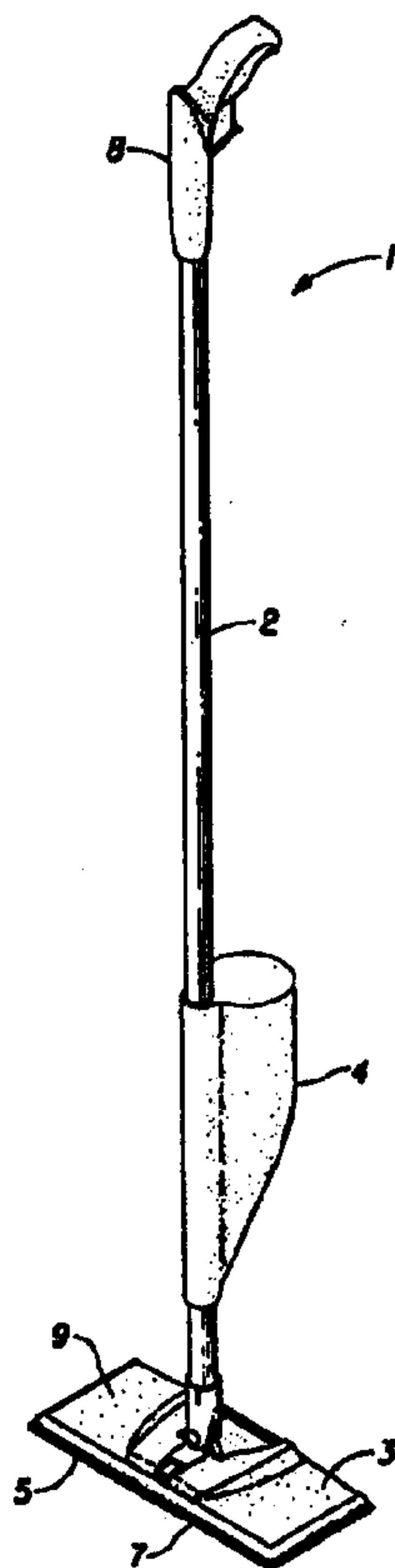


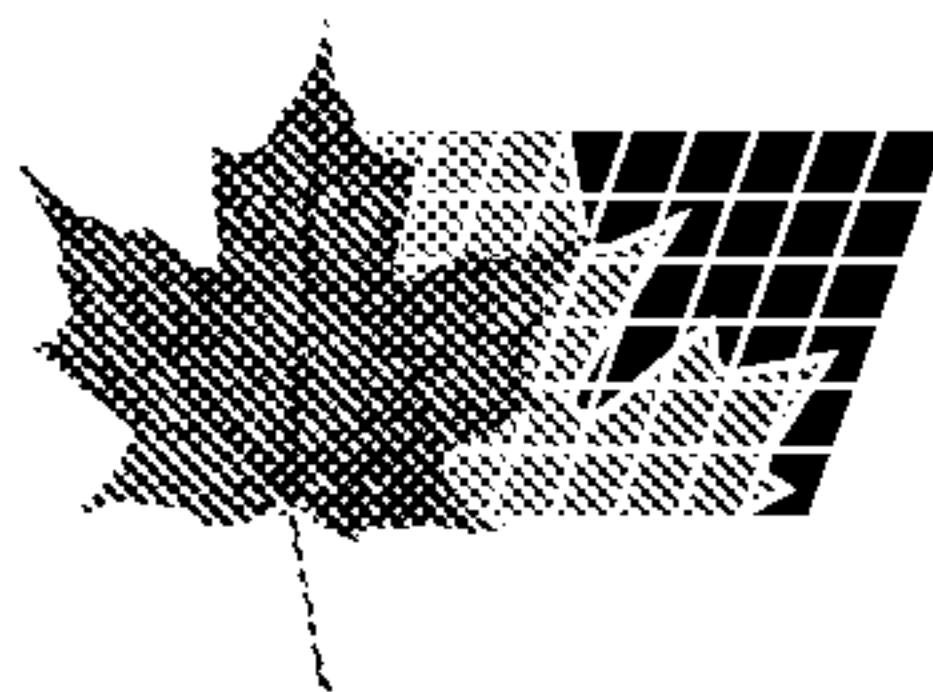


- (72) POLICICCHIO, NICOLA JOHN, US
(72) MASTERS, RONALD ANTHONY, US
(72) SHIERRY, ALAN EDWARD, US
(71) THE PROCTER & GAMBLE COMPANY, US
(51) Int.Cl.⁶ C11D 17/04, A47L 13/16
(30) 1997/03/20 (60/041,273) US
(30) 1997/05/08 (60/045,858) US
(54) **COMPOSITION DETERGENTE A UTILISER AVEC UN
USTENSILE DE NETTOYAGE RENFERMANT UN
MATERIAU SUPERABSORBANT ET KITS CONTENANT CES
DEUX ELEMENTS**
(54) **DETERGENT COMPOSITION FOR USE WITH A CLEANING
IMPLEMENT COMPRISING A SUPERABSORBENT
MATERIAL AND KITS COMPRISING BOTH**



(57) L'invention concerne une composition détergente destinée à être utilisée en association avec un tampon nettoyeur renfermant une quantité efficace d'un matériau superabsorbant, ledit tampon étant, de préférence,

(57) A detergent composition for use with a cleaning pad comprising an effective amount of a superabsorbent material, said pad preferably being part of a cleaning implement comprising a handle and said cleaning pad



amovible et faisant partie d'un ustensile de nettoyage pourvu d'une poignée. La composition détergente comprend une quantité limitée d'un tensioactif détergent, de préférence à structure linéaire et relativement hydrophile, la proportion de matériaux hydrophiles n'excédant pas 0,5 % et le pH étant maintenu au-dessus de 9 environ, de manière à permettre aux fluides d'être rapidement absorbés par le matériau superabsorbant. L'invention concerne également le procédé d'utilisation de la composition détergente en association avec un tel tampon nettoyeur et un kit contenant la composition détergente et le tampon nettoyeur.

preferably being removable. The detergent composition contains a limited amount of a detergent surfactant, preferably linear in structure and relatively hydrophilic, the level of hydrophobic materials being kept below about 0.5 %, and the pH being maintained above about 9, to allow the superabsorbent material to be readily absorbed by the superabsorbent material. The process of using the detergent composition with such a cleaning pad, and the provision of a kit containing both detergent composition and cleaning pad are disclosed.

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C11D 17/04, A47L 13/16	A1	(11) International Publication Number: WO 98/42819 (43) International Publication Date: 1 October 1998 (01.10.98)
(21) International Application Number: PCT/IB98/00356 (22) International Filing Date: 16 March 1998 (16.03.98) (30) Priority Data: 60/041,273 20 March 1997 (20.03.97) US 60/045,858 8 May 1997 (08.05.97) US (71) Applicant (for all designated States except US): THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): POLICICCHIO, Nicola, John [CA/US]; 4976 Laurelwood Court, Mason, OH 45040 (US). MASTERS, Ronald, Anthony [US/US]; 2300 Catalpa Drive, Loveland, OH 45140 (US). SHERRY, Alan, Edward [US/US]; 235 Loraine Avenue #7, Cincinnati, OH 45220 (US). (74) Agents: REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217 (US).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: DETERGENT COMPOSITION FOR USE WITH A CLEANING IMPLEMENT COMPRISING A SUPERABSORBENT MATERIAL AND KITS COMPRISING BOTH (57) Abstract A detergent composition for use with a cleaning pad comprising an effective amount of a superabsorbent material, said pad preferably being part of a cleaning implement comprising a handle and said cleaning pad preferably being removable. The detergent composition contains a limited amount of a detergent surfactant, preferably linear in structure and relatively hydrophilic, the level of hydrophobic materials being kept below about 0.5 %, and the pH being maintained above about 9, to allow the superabsorbent material to be readily absorbed by the superabsorbent material. The process of using the detergent composition with such a cleaning pad, and the provision of a kit containing both detergent composition and cleaning pad are disclosed.		

**DETERGENT COMPOSITION FOR USE WITH A CLEANING
IMPLEMENT COMPRISING A SUPERABSORBENT MATERIAL AND
KITS COMPRISING BOTH**

5

TECHNICAL FIELD

This application relates to detergent compositions for use with a cleaning implement comprising a superabsorbent material useful in removing soils from hard surfaces. The application particularly relates to cleaning implements comprising a removable absorbent cleaning pad, preferably designed so as to provide multiple
10 cleaning surfaces.

BACKGROUND OF THE INVENTION

The literature is replete with products capable of cleaning hard surfaces such as ceramic tile floors, hardwood floors, counter tops and the like. In the context of cleaning floors, numerous devices are described comprising a handle and some
15 means for absorbing a fluid cleaning composition. Such devices include those that are reusable, including mops containing cotton strings, cellulose and/or synthetic strips, sponges, and the like. While these mops are successful in removing many soils from hard surfaces, they typically require the inconvenience of performing one or more rinsing steps during use to avoid saturation of the material with dirt, soil,
20 and other residues. These mops therefore require the use of a separate container to perform the rinsing step(s), and typically these rinsing steps fail to sufficiently remove dirt residues. This may result in redeposition of significant amounts of soil during subsequent passes of the mop. Furthermore, as reusable mops are used over time, they become increasingly soiled and malodorous. This negatively impacts
25 subsequent cleaning performance.

To alleviate some of the negative attributes associated with reusable mops, attempts have been made to provide mops having disposable cleaning pads. For example, U.S. Patent No. 5,094,559, issued March 10, 1992 to Rivera et al., describes a mop that includes a disposable cleaning pad comprising a scrubber layer
30 for removing soil from a soiled surface, a blotter layer to absorb fluid after the cleaning process, and a liquid impervious layer positioned between the scrubber and blotter layer. The pad further contains a rupturable packet means positioned between the scrubber layer and the liquid impervious layer. The rupturable packets are so located such that upon rupture, fluid is directed onto the surface to be cleaned.
35 During the cleaning action with the scrubber layer, the impervious sheet prevents

fluid from moving to the absorbent blotter layer. After the cleaning action is completed, the pad is removed from the mop handle and reattached such that the blotter layer contacts the floor. While this device may alleviate the need to use multiple rinsing steps, it does require that the user physically handle the pad and
5 reattach a soiled, damp pad in order to complete the cleaning process.

Similarly, U.S. Patent 5,419,015, issued May 30, 1995 to Garcia, describes a mop having removable, washable work pads. The pad is described as comprising an upper layer which is capable of attaching to hooks on a mop head, a central layer of synthetic plastic microporous foam, and a lower layer for contacting a surface during
10 the cleaning operation. The lower layer's composition is stated to depend on the end-use of the device, i.e., washing, polishing or scrubbing. While the reference addresses the problems associated with mops that require rinsing during use, the patent fails to provide a cleaning implement that sufficiently removes the soil deposited on typical household hard surfaces, in particular floors, such that the
15 surface is perceived as essentially free of soil. In particular, the synthetic foam described by Garcia for absorbing the cleaning solution has a relatively low absorbent capacity for water and water-based solutions. As such, the user must either use small amounts of cleaning solution to remain within the absorbent capacity of the pad, or the user must leave a significant amount of cleaning solution
20 on the surface being cleaned. In either situation, the overall performance of the cleaning pad is not optimal.

While many known devices for cleaning hard surfaces are successful at removing a vast majority of the soil encountered by the typical consumer during the cleaning process, they are inconvenient in that they require one or more cleaning
25 steps. The prior art devices that have addressed the issue of convenience typically do so at the cost of cleaning performance. As such, there remains a need for a device that offers both convenience and beneficial soil removal.

Therefore, the present invention preferably provides a cleaning implement that comprises a removable cleaning pad, which alleviates the need to rinse the pad
30 during use. This requires an implement that comprises a removable cleaning pad with sufficient absorbent capacity, on a gram of absorbed fluid per gram of cleaning pad basis, that allows the cleaning of a large area, such as that of the typical hard surface floor (e.g., 80-100 ft²), without the need to change the pad. This, in turn, requires the use of a superabsorbent material, preferably of the type disclosed
35 hereinafter. It has now been found that the detergent composition that is used with such superabsorbent materials must be carefully formulated to avoid defeating the goal of using such superabsorbent material.

The preferred cleaning implements have a pad which offers beneficial soil removal properties due to continuously providing a fresh surface, and/or edge to contact the soiled surface, e.g., by providing a plurality of surfaces that contact the soiled surface during the cleaning operation.

5

SUMMARY OF THE INVENTION

Detergent compositions which are to be used with an implement containing a superabsorbent material require sufficient detergent to enable the solution to provide cleaning without overloading the superabsorbent material with solution, but cannot have more than about 0.5% detergent surfactant without the performance suffering. Therefore, the level of detergent surfactant should be from about 0.01% to about 0.5%, preferably from about 0.1% to about 0.9%, more preferably from about 0.2% to about 0.8%; the level of hydrophobic materials, including solvent, should be less than about 0.5%, preferably less than about 0.2%, more preferably less than about 0.1%; and the pH should be more than about 9, preferably more than about 9.5, more preferably more than about 10, to avoid hindering absorption, and the alkalinity should preferably be provided, at least in part, by volatile materials, to avoid streaking/filming problems. The detergent surfactant is preferably predominantly linear, e.g., aromatic groups should not be present, and the detergent surfactant is preferably relatively water soluble, e.g., having a hydrophobic chain containing from about 8 to about 12, preferably from about 8 to about 11, carbon atoms, and, for nonionic detergent surfactants, having an HLB of from about 9 to about 14, preferably from about 10 to about 13, more preferably from about 10 to about 12.

The invention also comprises a detergent composition as disclosed herein in a container in association with instructions to use it with an absorbent structure comprising an effective amount of a superabsorbent material, and, optionally, in a container in a kit comprising the implement, or, at least, a disposable cleaning pad comprising a superabsorbent material.

The invention also relates to the use of the composition and a cleaning pad comprising a superabsorbent material to effect cleaning of soiled surfaces, i.e., the process of cleaning a surface comprising applying an effective amount of a detergent composition containing no more than about 1% detergent surfactant; a level of hydrophobic materials, including solvent, that is less than about 0.5%; and a pH of more than about 9 and absorbing the composition in an absorbent structure comprising a superabsorbent material.

In one preferred aspect, the present invention relates to the use of the described detergent composition with an implement for cleaning a surface, the implement comprising:

- a. a handle; and
- 5 b. a removable cleaning pad comprising a suberabsorbent material and having a plurality of substantially planar surfaces, wherein each of the substantially planar surfaces contacts the surface being cleaned, and preferably a pad structure which has both a first layer and a second layer, wherein the first layer is located between the scrubbing layer and the second
10 layer and has a smaller width than the second layer.

Depending on the means used for attaching the cleaning pad to the cleaning implement's handle, it may be preferable for the cleaning pad to further comprise a distinct attachment layer. In these embodiments, the absorbent layer would be positioned between the scrubbing layer and the attachment layer.

- 15 The detergent composition and, preferably, the implement of the present invention are compatible with all hard surface substrates, including wood, vinyl, linoleum, no wax floors, ceramic, Formica®, porcelain, glass, wall board, and the like.

BRIEF DESCRIPTION OF THE DRAWING

- 20 Figure 1 is a perspective view of a cleaning implement of the present invention which has an on-board fluid dispensing device which will dispense the detergent composition.

Figure 1a is a perspective view of a cleaning implement of the present invention which does not have an on-board fluid dispensing device, so that the
25 composition is supplied separately.

Figure 1b is a side view of the handle grip of the implement shown in Figure 1a.

Figure 2 is a perspective view of a removable cleaning pad of the implement.

- 30 Figure 3 is a perspective view of an absorbent layer of a disposable cleaning pad of the present invention.

Figure 4 is a blown perspective view of the absorbent layer of a removable cleaning pad of the present invention.

Figure 5 is a cross sectional view of a cleaning pad of the present invention, taken along the y-z plane.

DETAILED DESCRIPTIONI. The Cleaning Pad

The present invention is based on providing the convenience of a cleaning pad, preferably removable and/or disposable, that contains a superabsorbent material and which preferably also provides significant cleaning benefits. The preferred cleaning performance benefits are related to the preferred structural characteristics described below, combined with the ability of the pad to remove solubilized soils. The cleaning pad, as described herein requires the use of the detergent composition, as described hereinafter, to provide optimum performance.

The cleaning pads will preferably have an absorbent capacity when measured under a confining pressure of 0.09 psi after 20 minutes (1200 seconds) (hereafter referred to as "t₁₂₀₀ absorbent capacity") of at least about 10 g deionized water per g of the cleaning pad. The absorbent capacity of the pad is measured at 20 minutes (1200 seconds) after exposure to deionized water, as this represents a typical time for the consumer to clean a hard surface such as a floor. The confining pressure represents typical pressures exerted on the pad during the cleaning process. As such, the cleaning pad should be capable of absorbing significant amounts of the cleaning solution within this 1200 second period under 0.09 psi. The cleaning pad will preferably have a t₁₂₀₀ absorbent capacity of at least about 15 g/g, more preferably at least about 20 g/g, still more preferably at least about 25 g/g and most preferably at least about 30 g/g. The cleaning pad will preferably have a t₉₀₀ absorbent capacity of at least about 10 g/g, more preferably a t₉₀₀ absorbent capacity of at least about 20 g/g.

Values for t₁₂₀₀ and t₉₀₀ absorbent capacity are measured by the performance under pressure (referred to herein as "PUP") method, which is described in detail in the Test Methods section below.

The cleaning pads will also preferably, but not necessarily, have a total fluid capacity (of deionized water) of at least about 100 g, more preferably at least about 200 g, still more preferably at least about 300 g and most preferably at least about 400 g. While pads having a total fluid capacity less than 100 g are within the scope of the invention, they are not as well suited for cleaning large areas, such as seen in a typical household, as are higher capacity pads.

Each of the components of the absorbent pad are described in detail. However, the skilled artisan will recognize that various materials known to serve similar purposes may substituted with similar results.

A. Absorbent Layer

The absorbent layer is the essential component which serves to retain any fluid and soil absorbed by the cleaning pad during use. While the preferred scrubbing layer, described hereinafter, has some affect on the pad's ability to absorb fluid, the absorbent layer plays the major role in achieving the desired overall absorbency. Furthermore, the absorbent layer preferably comprises multiple layers which are designed to provide the cleaning pad with multiple planar surfaces.

From the essential fluid absorbency perspective, the absorbent layer will be capable of removing fluid and soil from any "scrubbing layer" so that the scrubbing layer will have capacity to continually remove soil from the surface. The absorbent layer also should be capable of retaining absorbed material under typical in-use pressures to avoid "squeeze-out" of absorbed soil, cleaning solution, etc.

The absorbent layer will comprise any material that is capable of absorbing and retaining fluid during use. To achieve desired total fluid capacities, it will be preferred to include in the absorbent layer a material having a relatively high capacity (in terms of grams of fluid per gram of absorbent material). As used herein, the term "superabsorbent material" means any absorbent material having a g/g capacity for water of at least about 15 g/g, when measured under a confining pressure of 0.3 psi. Because a majority of the cleaning fluids useful with the present invention are aqueous based, it is preferred that the superabsorbent materials have a relatively high g/g capacity for water or water-based fluids.

Representative superabsorbent materials include water insoluble, water-swellingable superabsorbent gelling polymers (referred to herein as "superabsorbent gelling polymers") which are well known in the literature. These materials demonstrate very high absorbent capacities for water. The superabsorbent gelling polymers useful in the present invention can have a size, shape and/or morphology varying over a wide range. These polymers can be in the form of particles that do not have a large ratio of greatest dimension to smallest dimension (e.g., granules, flakes, pulverulents, interparticle aggregates, interparticle crosslinked aggregates, and the like) or they can be in the form of fibers, sheets, films, foams, laminates, and the like. The use of superabsorbent gelling polymers in fibrous form provides the benefit of providing enhanced retention of the superabsorbent material, relative to particles, during the cleaning process. While their capacity is generally lower for aqueous-based mixtures, these materials still demonstrate significant absorbent capacity for such mixtures. The patent literature is replete with disclosures of water-swellingable materials. See, for example, U.S. Patent 3,699,103 (Harper et al.), issued June 13, 1972; U.S. Patent 3,770,731 (Harmon), issued June 20, 1972; U.S.

Reissue Patent 32,649 (Brandt et al.), reissued April 19, 1989; U.S. Patent 4,834,735 (Alemany et al.), issued May 30, 1989.

Superabsorbent gelling polymers useful in the present invention include a variety of water-insoluble, but water-swellaable polymers capable of absorbing large quantities of fluids. Such polymeric materials are also commonly referred to as "hydrocolloids", and can include polysaccharides such as carboxymethyl starch, carboxymethyl cellulose, and hydroxypropyl cellulose; nonionic types such as polyvinyl alcohol, and polyvinyl ethers; cationic types such as polyvinyl pyridine, polyvinyl morpholinone, and N,N-dimethylaminoethyl or N,N-diethylaminopropyl acrylates and methacrylates, and the respective quaternary salts thereof. Typically, superabsorbent gelling polymers useful in the present invention have a multiplicity of anionic functional groups, such as sulfonic acid, and more typically carboxy, groups. Examples of polymers suitable for use herein include those which are prepared from polymerizable, unsaturated, acid-containing monomers. Thus, such monomers include the olefinically unsaturated acids and anhydrides that contain at least one carbon to carbon olefinic double bond. More specifically, these monomers can be selected from olefinically unsaturated carboxylic acids and acid anhydrides, olefinically unsaturated sulfonic acids, and mixtures thereof.

Some non-acid monomers can also be included, usually in minor amounts, in preparing the superabsorbent gelling polymers useful herein. Such non-acid monomers can include, for example, the water-soluble or water-dispersible esters of the acid-containing monomers, as well as monomers that contain no carboxylic or sulfonic acid groups at all. Optional non-acid monomers can thus include monomers containing the following types of functional groups: carboxylic acid or sulfonic acid esters, hydroxyl groups, amide-groups, amino groups, nitrile groups, quaternary ammonium salt groups, aryl groups (e.g., phenyl groups, such as those derived from styrene monomer). These non-acid monomers are well-known materials and are described in greater detail, for example, in U.S. Patent 4,076,663 (Masuda et al), issued February 28, 1978, and in U.S. Patent 4,062,817 (Westerman), issued December 13, 1977, both of which are incorporated by reference.

Olefinically unsaturated carboxylic acid and carboxylic acid anhydride monomers include the acrylic acids typified by acrylic acid itself, methacrylic acid, ethacrylic acid, α -chloroacrylic acid, α -cyanoacrylic acid, β -methylacrylic acid (crotonic acid), α -phenylacrylic acid, β -acryloxypropionic acid, sorbic acid, α -chlorosorbic acid, angelic acid, cinnamic acid, p-chlorocinnamic acid, β -sterylacrylic acid, itaconic acid, citraconic acid, mesaconic acid, glutaconic acid,

aconitic acid, maleic acid, fumaric acid, tricarboxyethylene and maleic acid anhydride.

Olefinically unsaturated sulfonic acid monomers include aliphatic or aromatic vinyl sulfonic acids such as vinylsulfonic acid, allyl sulfonic acid, vinyl toluene sulfonic acid and styrene sulfonic acid; acrylic and methacrylic sulfonic acid such as sulfoethyl acrylate, sulfoethyl methacrylate, sulfopropyl acrylate, sulfopropyl methacrylate, 2-hydroxy-3-methacryloxypropyl sulfonic acid and 2-acrylamide-2-methylpropane sulfonic acid.

Preferred superabsorbent gelling polymers for use in the present invention contain carboxy groups. These polymers include hydrolyzed starch-acrylonitrile graft copolymers, partially neutralized hydrolyzed starch-acrylonitrile graft copolymers, starch-acrylic acid graft copolymers, partially neutralized starch-acrylic acid graft copolymers, saponified vinyl acetate-acrylic ester copolymers, hydrolyzed acrylonitrile or acrylamide copolymers, slightly network crosslinked polymers of any of the foregoing copolymers, partially neutralized polyacrylic acid, and slightly network crosslinked polymers of partially neutralized polyacrylic acid. These polymers can be used either solely or in the form of a mixture of two or more different polymers. Examples of these polymer materials are disclosed in U.S. Patent 3,661,875, U.S. Patent 4,076,663, U.S. Patent 4,093,776, U.S. Patent 4,666,983, and U.S. Patent 4,734,478.

Most preferred polymer materials for use in making the superabsorbent gelling polymers are slightly network crosslinked polymers of partially neutralized polyacrylic acids and starch derivatives thereof. Most preferably, the hydrogel-forming absorbent polymers comprise from about 50 to about 95%, preferably about 75%, neutralized, slightly network crosslinked, polyacrylic acid (i.e. poly (sodium acrylate/acrylic acid)). Network crosslinking renders the polymer substantially water-insoluble and, in part, determines the absorptive capacity and extractable polymer content characteristics of the superabsorbent gelling polymers. Processes for network crosslinking these polymers and typical network crosslinking agents are described in greater detail in U.S. Patent 4,076,663.

While the superabsorbent gelling polymers is preferably of one type (i.e., homogeneous), mixtures of polymers can also be used in the implements of the present invention. For example, mixtures of starch-acrylic acid graft copolymers and slightly network crosslinked polymers of partially neutralized polyacrylic acid can be used in the present invention.

While any of the superabsorbent gelling polymers described in the prior art may be useful in the present invention, it has recently been recognized that where

significant levels (e.g., more than about 50% by weight of the absorbent structure) of superabsorbent gelling polymers are to be included in an absorbent structure, and in particular where one or more regions of the absorbent layer will comprise more than about 50%, by weight of the region, the problem of gel blocking by the swollen particles may impede fluid flow and thereby adversely affect the ability of the gelling polymers to absorb to their full capacity in the desired period of time. U.S. Patent 5,147,343 (Kellenberger et al.), issued September 15, 1992 and U.S. Patent 5,149,335 (Kellenberger et al.), issued September 22, 1992, describe superabsorbent gelling polymers in terms of their Absorbency Under Load (AUL), where gelling polymers absorb fluid (0.9% saline) under a confining pressure of 0.3 psi. (The disclosure of each of these patents is incorporated herein.) The methods for determining AUL are described in these patents. Polymers described therein may be particularly useful in embodiments of the present invention that contain regions of relatively high levels of superabsorbent gelling polymers. In particular, where high concentrations of superabsorbent gelling polymer are incorporated in the cleaning pad, those polymers will preferably have an AUL, measured according to the methods described in U.S. Patent 5,147,343, of at least about 24 ml/g, more preferably at least about 27 ml/g after 1 hour; or an AUL, measured according to the methods described in U.S. Patent 5,149,335, of at least about 15 ml/g, more preferably at least about 18 ml/g after 15 minutes. Commonly assigned copending U.S. application Serial Numbers 08/219,547 (Goldman et al.), filed March 29, 1994 and 08/416,396 (Goldman et al.), filed April 6, 1995 (both of which are incorporated by reference herein), also address the problem of gel blocking and describe superabsorbent gelling polymers useful in overcoming this phenomena. These applications specifically describe superabsorbent gelling polymers which avoid gel blocking at even higher confining pressures, specifically 0.7 psi. In the embodiments of the present invention where the absorbent layer will contain regions comprising high levels (e.g., more than about 50% by weight of the region) of superabsorbent gelling polymer, it may be preferred that the superabsorbent gelling polymer be as described in the aforementioned applications by Goldman et al.

Other useful superabsorbent materials include hydrophilic polymeric foams, such as those described in commonly assigned copending U.S. patent application Serial No. 08/563,866 (DesMarais et al.), filed November 29, 1995 and U.S. Patent No. 5,387,207 (Dyer et al.), issued February 7, 1995. These references describe polymeric, hydrophilic absorbent foams that are obtained by polymerizing a high internal phase water-in-oil emulsion (commonly referred to as HIPEs). These foams are readily tailored to provide varying physical properties (pore size, capillary

suction, density, etc.) that affect fluid handling ability. As such, these materials are particularly useful, either alone or in combination with other such foams or with fibrous structures, in providing the overall capacity required by the present invention.

5 Where superabsorbent material is included in the absorbent layer, the absorbent layer will preferably comprise at least about 15%, by weight of the absorbent layer, more preferably at least about 20%, still more preferably at least about 25%, of the superabsorbent material.

10 The absorbent layer may also consist of or comprise fibrous material. Fibers useful in the present invention include those that are naturally occurring (modified or unmodified), as well as synthetically made fibers. Examples of suitable unmodified/modified naturally occurring fibers include cotton, Esparto grass, bagasse, kemp, flax, silk, wool, wood pulp, chemically modified wood pulp, jute, ethyl cellulose, and cellulose acetate. Suitable synthetic fibers can be made from
15 polyvinyl chloride, polyvinyl fluoride, polytetrafluoroethylene, polyvinylidene chloride, polyacrylics such as ORLON®, polyvinyl acetate, Rayon®, polyethylvinyl acetate, non-soluble or soluble polyvinyl alcohol, polyolefins such as polyethylene (e.g., PULPEX®) and polypropylene, polyamides such as nylon, polyesters such as DACRON® or KODEL®, polyurethanes, polystyrenes, and the like. The absorbent
20 layer can comprise solely naturally occurring fibers, solely synthetic fibers, or any compatible combination of naturally occurring and synthetic fibers.

 The fibers useful herein can be hydrophilic, hydrophobic or can be a combination of both hydrophilic and hydrophobic fibers. As indicated above, the particular selection of hydrophilic or hydrophobic fibers will depend upon the other
25 materials included in the absorbent (and to some degree the scrubbing) layer. That is, the nature of the fibers will be such that the cleaning pad exhibits the necessary fluid delay and overall fluid absorbency. Suitable hydrophilic fibers for use in the present invention include cellulosic fibers, modified cellulosic fibers, rayon, polyester fibers such as hydrophilic nylon (HYDROFIL®). Suitable hydrophilic
30 fibers can also be obtained by hydrophilizing hydrophobic fibers, such as surfactant-treated or silica-treated thermoplastic fibers derived from, for example, polyolefins such as polyethylene or polypropylene, polyacrylics, polyamides, polystyrenes, polyurethanes and the like.

 Suitable wood pulp fibers can be obtained from well-known chemical
35 processes such as the Kraft and sulfite processes. It is especially preferred to derive these wood pulp fibers from southern soft woods due to their premium absorbency characteristics. These wood pulp fibers can also be obtained from mechanical

processes, such as ground wood, refiner mechanical, thermomechanical, chemimechanical, and chemi-thermomechanical pulp processes. Recycled or secondary wood pulp fibers, as well as bleached and unbleached wood pulp fibers, can be used.

5 Another type of hydrophilic fiber for use in the present invention is chemically stiffened cellulosic fibers. As used herein, the term "chemically stiffened cellulosic fibers" means cellulosic fibers that have been stiffened by chemical means to increase the stiffness of the fibers under both dry and aqueous conditions. Such means can include the addition of a chemical stiffening agent that, for example, coats and/or impregnates the fibers. Such means can also include the stiffening of
10 the fibers by altering the chemical structure, e.g., by crosslinking polymer chains.

Where fibers are used as the absorbent layer (or a constituent component thereof), the fibers may optionally be combined with a thermoplastic material. Upon melting, at least a portion of this thermoplastic material migrates to the intersections
15 of the fibers, typically due to interfiber capillary gradients. These intersections become bond sites for the thermoplastic material. When cooled, the thermoplastic materials at these intersections solidify to form the bond sites that hold the matrix or web of fibers together in each of the respective layers. This may be beneficial in providing additional overall integrity to the cleaning pad.

20 Amongst its various effects, bonding at the fiber intersections increases the overall compressive modulus and strength of the resulting thermally bonded member. In the case of the chemically stiffened cellulosic fibers, the melting and migration of the thermoplastic material also has the effect of increasing the average pore size of the resultant web, while maintaining the density and basis weight of the
25 web as originally formed. This can improve the fluid acquisition properties of the thermally bonded web upon initial exposure to fluid, due to improved fluid permeability, and upon subsequent exposure, due to the combined ability of the stiffened fibers to retain their stiffness upon wetting and the ability of the thermoplastic material to remain bonded at the fiber intersections upon wetting and
30 upon wet compression. In net, thermally bonded webs of stiffened fibers retain their original overall volume, but with the volumetric regions previously occupied by the thermoplastic material becoming open to thus increase the average interfiber capillary pore size.

Thermoplastic materials useful in the present invention can be in any of a
35 variety of forms including particulates, fibers, or combinations of particulates and fibers. Thermoplastic fibers are a particularly preferred form because of their ability to form numerous interfiber bond sites. Suitable thermoplastic materials can be

made from any thermoplastic polymer that can be melted at temperatures that will not extensively damage the fibers that comprise the primary web or matrix of each layer. Preferably, the melting point of this thermoplastic material will be less than about 190°C, and preferably between about 75°C and about 175°C. In any event, the melting point of this thermoplastic material should be no lower than the temperature at which the thermally bonded absorbent structures, when used in the cleaning pads, are likely to be stored. The melting point of the thermoplastic material is typically no lower than about 50°C.

The thermoplastic materials, and in particular the thermoplastic fibers, can be made from a variety of thermoplastic polymers, including polyolefins such as polyethylene (e.g., PULPEX®) and polypropylene, polyesters, copolyesters, polyvinyl acetate, polyethylvinyl acetate, polyvinyl chloride, polyvinylidene chloride, polyacrylics, polyamides, copolyamides, polystyrenes, polyurethanes and copolymers of any of the foregoing such as vinyl chloride/vinyl acetate, and the like. Depending upon the desired characteristics for the resulting thermally bonded absorbent member, suitable thermoplastic materials include hydrophobic fibers that have been made hydrophilic, such as surfactant-treated or silica-treated thermoplastic fibers derived from, for example, polyolefins such as polyethylene or polypropylene, polyacrylics, polyamides, polystyrenes, polyurethanes and the like. The surface of the hydrophobic thermoplastic fiber can be rendered hydrophilic by treatment with a surfactant, such as a nonionic or anionic surfactant, e.g., by spraying the fiber with a surfactant, by dipping the fiber into a surfactant or by including the surfactant as part of the polymer melt in producing the thermoplastic fiber. Upon melting and resolidification, the surfactant will tend to remain at the surfaces of the thermoplastic fiber. Suitable surfactants include nonionic surfactants such as Brij® 76 manufactured by ICI Americas, Inc. of Wilmington, Delaware, and various surfactants sold under the Pegosperse® trademark by Glyco Chemical, Inc. of Greenwich, Connecticut. Besides nonionic surfactants, anionic surfactants can also be used. These surfactants can be applied to the thermoplastic fibers at levels of, for example, from about 0.2 to about 1 g. per sq. of centimeter of thermoplastic fiber.

Suitable thermoplastic fibers can be made from a single polymer (monocomponent fibers), or can be made from more than one polymer (e.g., bicomponent fibers). As used herein, "bicomponent fibers" refers to thermoplastic fibers that comprise a core fiber made from one polymer that is encased within a thermoplastic sheath made from a different polymer. The polymer comprising the sheath often melts at a different, typically lower, temperature than the polymer

comprising the core. As a result, these bicomponent fibers provide thermal bonding due to melting of the sheath polymer, while retaining the desirable strength characteristics of the core polymer.

Suitable bicomponent fibers for use in the present invention can include sheath/core fibers having the following polymer combinations: polyethylene/polypropylene, polyethylvinyl acetate/polypropylene, polyethylene/polyester, polypropylene/polyester, copolyester/polyester, and the like. Particularly suitable bicomponent thermoplastic fibers for use herein are those having a polypropylene or polyester core, and a lower melting copolyester, polyethylvinyl acetate or polyethylene sheath (e.g., those available from Danaklon a/s, Chisso Corp., and CELBOND®, available from Hercules). These bicomponent fibers can be concentric or eccentric. As used herein, the terms "concentric" and "eccentric" refer to whether the sheath has a thickness that is even, or uneven, through the cross-sectional area of the bicomponent fiber. Eccentric bicomponent fibers can be desirable in providing more compressive strength at lower fiber thicknesses.

Methods for preparing thermally bonded fibrous materials are described in co-pending U.S. application Serial No. 08/479,096 (Richards et al.), filed July 3, 1995 (see especially pages 16-20) and U.S. Patent 5,549,589 (Horney et al.), issued August 27, 1996 (see especially Columns 9 to 10). The disclosure of both of these references are incorporated by reference herein.

The absorbent layer may also comprise a HIPE-derived hydrophilic, polymeric foam that does not have the high absorbency of those described above as "superabsorbent materials". Such foams and methods for their preparation are described in U.S. Patent 5,550,167 (DesMarais), issued August 27, 1996; and commonly assigned copending U.S. patent application Serial No. 08/370,695 (Stone et al.), filed January 10, 1995 (both of which are incorporated by reference herein).

The absorbent layer of the cleaning pad may be comprised of a homogeneous material, such as a blend of cellulosic fibers (optionably thermally bonded) and swellable superabsorbent gelling polymer. Alternatively, the absorbent layer may be comprised of discrete layers of material, such as a layer of thermally bonded airlaid material and a discrete layer of a superabsorbent material. For example, a thermally bonded layer of cellulosic fibers can be located lower than (i.e., beneath) the superabsorbent material (i.e., between the superabsorbent material and the scrubbing layer). In order to achieve high absorptive capacity and retention of fluids under pressure, while at the same time providing initial delay in fluid uptake, it may be preferable to utilize such discrete layers when forming the absorbent layer. In this regard, the superabsorbent material can be located remote from the scrubbing layer

by including a less absorbent layer as the lower-most aspect of the absorbent layer. For example, a layer of cellulosic fibers can be located lower (i.e., beneath) than the superabsorbent material (i.e., between the superabsorbent material and the scrubbing layer).

5 In a preferred embodiment, the absorbent layer will comprise a thermally bonded airlaid web of cellulose fibers (Flint River, available from Weyerhaeuser, Wa) and AL Thermal C (thermoplastic available from Danaklon a/s, Varde, Denmark), and a swellable hydrogel-forming superabsorbent polymer. The superabsorbent polymer is preferably incorporated such that a discrete layer is
10 located near the surface of the absorbent layer which is remote from the scrubbing layer. Preferably, a thin layer of, e.g., cellulose fibers (optionally thermally bonded) are positioned above the superabsorbent gelling polymer to enhance containment.

B. Optional, but Preferred, Scrubbing Layer

The scrubbing layer is the portion of the cleaning pad that contacts the soiled
15 surface during cleaning. As such, materials useful as the scrubbing layer must be sufficiently durable that the layer will retain its integrity during the cleaning process. In addition, when the cleaning pad is used in combination with a solution, the scrubbing layer must be capable of absorbing liquids and soils, and relinquishing those liquids and soils to the absorbent layer. This will ensure that the scrubbing
20 layer will continually be able to remove additional material from the surface being cleaned. Whether the implement is used with a cleaning solution (i.e., in the wet state) or without cleaning solution (i.e., in the dry state), the scrubbing layer will, in addition to removing particulate matter, facilitate other functions, such as polishing, dusting, and buffing the surface being cleaned.

25 The scrubbing layer can be a monolayer, or a multi-layer structure one or more of whose layers may be slitted to facilitate the scrubbing of the soiled surface and the uptake of particulate matter. This scrubbing layer, as it passes over the soiled surface, interacts with the soil (and cleaning solution when used), loosening and emulsifying tough soils and permitting them to pass freely into the absorbent
30 layer of the pad. The scrubbing layer preferably contains openings (e.g., slits) that provide an easy avenue for larger particulate soil to move freely in and become entrapped within the absorbent layer of the pad. Low density structures are preferred for use as the scrubbing layer, to facilitate transport of particulate matter to the pad's absorbent layer.

35 In order to provide desired integrity, materials particularly suitable for the scrubbing layer include synthetics such as polyolefins (e.g., polyethylene and polypropylene), polyesters, polyamides, synthetic cellulose (e.g., Rayon®), and

blends thereof. Such synthetic materials may be manufactured using known process such as carded, spunbond, meltblown, airlaid, needlepunched and the like.

C. Optional Attachment Layer

The cleaning pads of the present invention can optionally have an attachment layer that allows the pad to be connected to an implement's handle or the support head in preferred implements. The attachment layer will be necessary in those embodiments where the absorbent layer is not suitable for attaching the pad to the support head of the handle. The attachment layer may also function as a means to prevent fluid flow through the top surface (i.e., the handle-contacting surface) of the cleaning pad, and may further provide enhanced integrity of the pad. As with the scrubbing and absorbent layers, the attachment layer may consist of a mono-layer or a multi-layer structure, so long as it meets the above requirements.

In a preferred embodiment of the present invention, the attachment layer will comprise a surface which is capable of being mechanically attached to the handle's support head by use of known hook and loop technology. In such an embodiment, the attachment layer will comprise at least one surface which is mechanically attachable to hooks that are permanently affixed to the bottom surface of the handle's support head.

To achieve the desired fluid imperviousness and attachability, it is preferred that a laminated structure comprising, e.g., a meltblown film and fibrous, nonwoven structure be utilized. In a preferred embodiment, the attachment layer is a tri-layered material having a layer of meltblown polypropylene film located between two layers of spun-bonded polypropylene.

D. Optional, but Preferred, Multiple Planar Surfaces

While the ability of the cleaning pad to absorb and retain fluids has been determined to be important to hard surface cleaning performance (see, e.g., copending U.S. Patent Application Serial No. 08/756,507 (Holt et al.), copending U.S. Patent Application Serial No. 08/756,864 (Sherry et al.), and copending U.S. Patent Application Serial No. 08/756,999 (Holt et al.), all filed November 26, 1996 and incorporated by reference herein.), preferred performance can be achieved by properly defining the overall structure of the cleaning pad. In particular, pads having an essentially flat floor contacting surface (i.e., essentially one planar surface for contacting the soiled surface during cleaning) do not provide the best performance because soil tends to build up on the leading edge, which also is the main point where the cleaning solution is transferred to the absorbent layer.

The preferred pads provide multiple planar surfaces during cleaning and provide enhanced performance. Referring to Figure 2 in the drawings, cleaning pad

100 is depicted as having an upper surface 103 that allows the pad to be releasably attached to a handle. Cleaning pad 100 also has a lower surface depicted generally as 110 which contacts the floor or other hard surface during cleaning. This lower surface 110 actually consists of 3 substantially planar surfaces 112, 114 and 116. As depicted, the planes corresponding to surfaces 112 and 116 intersect the plane corresponding to surface 114. Thus, when an implement to which pad 100 is attached is moved from rest in the direction indicated by Y_f , friction causes pad 100 to "rock" such that lower surface 112 contacts the surface being cleaned. As the movement in the Y_f direction diminishes, lower surface 114 will then contact the surface being cleaned. As the implement and pad are moved from rest in the Y_b direction, friction causes pad 100 to rock such that lower surface 116 then contacts the surface being cleaned. As this cleaning motion is repeated, the portion of the pad contacting the soiled surface are constantly changing.

Applicants believe that the enhanced cleaning of the preferred pads is in-part due to the "lifting" action that results from the back and forth motion during cleaning. In particular, when the cleaning motion in one direction is stopped and the forces exerted on the implement allow pad 100 to "rock" such that the surface-contacting planar surface moves from surface 112 (or 116) to surface 114, soil is moved in an upward direction.

The cleaning pad of the present invention should be capable of retaining absorbed fluid, even during the pressures exerted during the cleaning process. This is referred to herein as the cleaning pad's ability to avoid "squeeze-out" of absorbed fluid, or conversely its ability to retain absorbed fluid under pressure. The method for measuring squeeze-out is described in the Test Methods section. Briefly, the test measures the ability of a saturated cleaning pad to retain fluid when subjected to a pressure of 0.25 psi. Preferably, the cleaning pads of the present invention will have a squeeze-out value of not more than about 40%, more preferably not more than about 25%, still more preferably not more than about 15%, and most preferably not more than about 10%.

II. Detergent Composition

The cleaning implement of the present invention is used in combination with a detergent composition which acts as a cleaning solution. Detergent compositions which are to be used with an implement containing a superabsorbent material require sufficient detergent to enable the solution to provide cleaning without overloading the superabsorbent material with solution, but cannot have more than about 0.5% detergent surfactant without the performance suffering. Therefore, the level of detergent surfactant should be from about 0.01% to about 0.5%, preferably

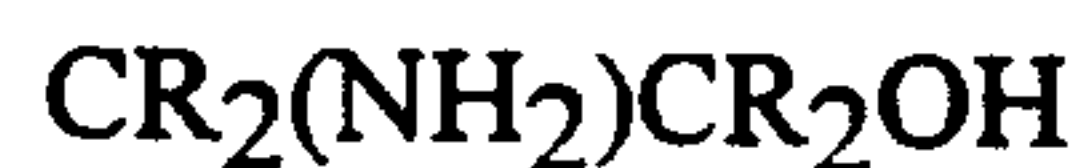
from about 0.1% to about 0.45%, more preferably from about 0.2% to about 0.45%; the level of hydrophobic materials, including solvent, should be less than about 0.5%, preferably less than about 0.2%, more preferably less than about 0.1%; and the pH should be more than about 9.3, preferably more than about 10, more preferably more than about 10.3, to avoid hindering absorption, and the alkalinity should preferably be provided, at least in part, by volatile materials, to avoid streaking/filming problems. The detergent surfactant is preferably linear, e.g., branching and aromatic groups should not be present, and the detergent surfactant is preferably relatively water soluble, e.g., having a hydrophobic chain containing from about 8 to about 12, preferably from about 8 to about 11, carbon atoms, and, for nonionic detergent surfactants, having an HLB of from about 9 to about 14, preferably from about 10 to about 13, more preferably from about 10 to about 12. The invention also comprises a detergent composition as disclosed herein in a container in association with instructions to use it with an implement comprising an effective amount of a superabsorbent material, and, optionally, in a container in a kit comprising the implement, or, at least, a disposable cleaning pad comprising a superabsorbent material. The invention also relates to the use of the composition and a cleaning pad comprising a superabsorbent material to effect cleaning of soiled surfaces.

The detergent composition, (cleaning solution) is an aqueous-based solution comprising one or more detergent surfactants, alkaline materials to provide the desired alkaline pH, and optional solvents, builders, chelants, suds suppressors, enzymes, etc. Suitable surfactants include anionic, nonionic, zwitterionic, and amphoteric surfactants, preferably anionic and nonionic detergent surfactants having hydrophobic chains containing from about 8 to about 12, preferably from about 8 to about 11, carbon atoms. Examples of anionic surfactants include, but are not limited to, linear alkyl sulfates, alkyl sulfonates, and the like. Examples of nonionic surfactants include alkylethoxylates and the like. Examples of zwitterionic surfactants include betaines and sulfobetaines. Examples of amphoteric surfactants include alkylampho glycines, and alkyl imino propionate. All of the above materials are available commercially, and are described in McCutcheon's Vol. 1: Emulsifiers and Detergents, North American Ed., McCutcheon Division, MC Publishing Co., 1995.

Suitable solvents include short chain (e.g., C₁-C₆) derivatives of oxyethylene glycol and oxypropylene glycol, such as mono- and di-ethylene glycol n-hexyl ether, mono-, di- and tri-propylene glycol n-butyl ether, and the like. The

level of hydrophobic solvents, e.g., those having solubilities in water of less than about 3%, more preferably less than about 2%.

Suitable builders include those derived from phosphorous sources, such as orthophosphate and pyrophosphate, and non-phosphorous sources, such as nitrilotriacetic acid, S,S-ethylene diamine disuccinic acid, and the like. Suitable chelants include ethylenediaminetetraacetic acid and citric acid, and the like. Suitable suds suppressors include silicone polymers and linear or branched C₁₀-C₁₈ fatty acids or alcohols. Suitable enzymes include lipases, proteases, amylases and other enzymes known to be useful for catalysis of soil degradation. The total level of such ingredients is low, preferably less than about 0.1%, more preferably less than about 0.05%, to avoid causing filming streaking problems. Preferably, the compositions should be essentially free of materials that cause filming streaking problems. Accordingly, it is desirable to use alkaline materials that do not cause filming and/or streaking for the majority of the buffering. Suitable alkaline buffers are carbonate, bicarbonate, citrate, etc. The preferred alkaline buffers are alkanol amines having the formula:



wherein each R is selected from the group consisting of hydrogen and alkyl groups containing from one to four carbon atoms and the total of carbon atoms in the compound is from three to six, preferably, 2-amino,2-methylpropanol.

A suitable cleaning solution for use with the present implement comprises from about 0.1% to about 0.5% of detergent surfactant, preferably comprising a linear alcohol ethoxylate detergent surfactant (e.g., Neodol 1-5®, available from Shell Chemical Co.) and an alkylsulfonate (e.g., Bioterge PAS-8s, a linear C₈ sulfonate available from Stepan Co.); from about 0 to about 0.2%, preferably from about 0.05% to about 0.01, potassium hydroxide, potassium carbonate, and/or bicarbonate; from about 0.01% to about 1%, preferably from about 0.1% to about 0.6%, of volatile alkaline material, e.g., 2-amino,2-methylpropanol; optional adjuvants such dyes and/or perfumes; and from about 99.9% to about 90% deionized or softened water.

II. Cleaning Implements

The detergent compositions described above can be desirably used with an implement for cleaning a surface, the implement comprising:

- a. a handle; and
- b. a removable cleaning pad containing an effective amount of a superabsorbent material, and having a plurality of substantially planar surfaces, wherein each of the substantially planar surfaces

contacts the surface being cleaned, more preferably said pad is a removable cleaning pad having a length and a width, the pad comprising

- i. a scrubbing layer; and
- 5 ii. an absorbent layer comprising a first layer and a second layer, where the first layer is located between the scrubbing layer and the second layer (i.e., the first layer is below the second layer) and has a smaller width than the second layer.

An important aspect of the cleaning performance provided by the preferred
10 pad is related to the ability to provide multiple planar surfaces that contact the soiled surface during the cleaning operation. In the context of a cleaning implement such as a mop, these planar surfaces are provided such that during the typical cleaning operation (i.e., where the implement is moved back and forth in a direction substantially parallel to the pad's Y-dimension or width), each of the planar surfaces
15 contact the surface being cleaned as a result of "rocking" of the cleaning pad. This aspect of the invention, and the benefits provided, are discussed in detail with reference to the drawings.

The skilled artisan will recognize that various materials may be utilized to carry out the claimed invention. Thus, while preferred materials are described
20 below for the various implement and cleaning pad components, it is recognized that the scope of the invention is not limited to such disclosures.

a. The Handle

The handle of the above cleaning implement can be any material that will facilitate gripping of the cleaning implement. The handle of the cleaning implement
25 will preferably comprise any elongated, durable material that will provide practical cleaning. The length of the handle will be dictated by the end-use of the implement.

The handle will preferably comprise at one end a support head to which the cleaning pad can be releasably attached. To facilitate ease of use, the support head can be pivotably attached to the handle using known joint assemblies. Any suitable
30 means for attaching the cleaning pad to the support head may be utilized, so long as the cleaning pad remains afixed during the cleaning process. Examples of suitable fastening means include clamps, hooks & loops (e.g., Velcro®), and the like. In a preferred embodiment, the support head will comprise hooks on its lower surface that will mechanically attach to the upper layer (preferably a distinct attachment
35 layer) of the absorbent cleaning pad.

A preferred handle, comprising a fluid dispensing means, is depicted in Figure 1 and is fully described in co-pending U.S. Patent Application Serial No.

_____, filed November 15, 1996 by V. S. Ping, et al. (Case 6383), which is incorporated by reference herein. Another preferred handle, which does not contain a fluid dispensing means, is depicted in Figs. 1a and 1b, and is fully described in co-pending U.S. Patent Application Ser. No. _____, filed September 23, 1996 by A. J. Irwin (P&G Case 6262), which is incorporated by reference herein.

b. The Cleaning Pad

The cleaning pads described hereinbefore can be used without attachment to a handle, or as part of the above cleaning implement. They may therefore be constructed without the need to be attachable to a handle, i.e., such that they may be used either in combination with the handle or as a stand-alone product. As such, it may be preferred to prepare the pads with an optional attachment layer as described hereinbefore. With the exception of an attachment layer, the pads themselves are as described above.

As used herein, the term "direct fluid communication" means that fluid can transfer readily between two cleaning pad components or layers (e.g., the scrubbing layer and the absorbent layer) without substantial accumulation, transport, or restriction by an interposed layer. For example, tissues, nonwoven webs, construction adhesives, and the like may be present between the two distinct components while maintaining "direct fluid communication", as long as they do not substantially impede or restrict fluid as it passes from one component or layer to another.

As used herein, the term "Z-dimension" refers to the dimension orthogonal to the length and width of the cleaning pad of the present invention, or a component thereof. The Z-dimension usually corresponds to the thickness of the cleaning pad or a pad component.

As used herein, the term "X-Y dimension" refers to the plane orthogonal to the thickness of the cleaning pad, or a component thereof. The X and Y dimensions usually correspond to the length and width, respectively, of the cleaning pad or a pad component. In general, when the cleaning pad is used in conjunction with a handle, the implement will be moved in a direction parallel to Y-dimension of the pad. (See Figure __, and the discussion below.)

As used herein, the term "layer" refers to a member or component of a cleaning pad whose primary dimension is X-Y, i.e., along its length and width. It should be understood that the term layer is not necessarily limited to single layers or sheets of material. Thus the layer can comprise laminates or combinations of several sheets or webs of the requisite type of materials. Accordingly, the term "layer" includes the terms "layers" and "layered."

As used herein, the term "hydrophilic" is used to refer to surfaces that are wettable by aqueous fluids deposited thereon. Hydrophilicity and wettability are typically defined in terms of contact angle and the surface tension of the fluids and solid surfaces involved. This is discussed in detail in the American Chemical Society publication entitled Contact Angle, Wettability and Adhesion, edited by Robert F. Gould (Copyright 1964), which is hereby incorporated herein by reference. A surface is said to be wetted by a fluid (i.e., hydrophilic) when either the contact angle between the fluid and the surface is less than 90°, or when the fluid tends to spread spontaneously across the surface, both conditions normally co-existing. Conversely, a surface is considered to be "hydrophobic" if the contact angle is greater than 90° and the fluid does not spread spontaneously across the surface.

As used herein, the term "scrim" means any durable material that provides texture to the surface-contacting side of the cleaning pad's scrubbing layer, and also has a sufficient degree of openness to allow the requisite movement of fluid to the absorbent layer of the cleaning pad. Suitable materials include materials that have a continuous, open structure, such as synthetic and wire mesh screens. The open areas of these materials may be readily controlled by varying the number of interconnected strands that comprise the mesh, by controlling the thickness of those interconnected strands, etc. Other suitable materials include those where texture is provided by a discontinuous pattern printed on a substrate. In this aspect, a durable material (e.g., a synthetic) may be printed on a substrate in a continuous or discontinuous pattern, such as individual dots and/or lines, to provide the requisite texture. Similarly, the continuous or discontinuous pattern may be printed onto a release material that will then act as the scrim. These patterns may be repeating or they may be random. It will be understood that one or more of the approaches described for providing the desired texture may be combined to form the optional scrim material. The Z direction height and open area of the scrim and or scrubbing substrate layer help to control and or retard the flow of liquid into the absorbent core material. The Z height of the scrim and or scrubbing substrate help provide a means of controlling the volume of liquid in contact with the cleaning surface while at the same time controlling the rate of liquid absorption, fluid communication into the absorption core material.

For purposes of the present invention, an "upper" layer of a cleaning pad is a layer that is relatively further away from the surface that is to be cleaned (i.e., in the implement context, relatively closer to the implement handle during use). The term "lower" layer conversely means a layer of a cleaning pad that is relatively closer to

the surface that is to be cleaned (i.e., in the implement context, relatively further away from the implement handle during use). As such, the scrubbing layer is the lower-most layer and the absorbent layer is an upper layer relative to the scrubber layer. The terms "upper" and "lower" are similarly used when referring to layers that are multi-ply (e.g., when the scrubbing layer is a two-ply material). The terms "above" and "below" are used to describe relative locations of two or more materials in a cleaning pad's thickness. By way of illustration, a material A is "above" material B if material B is positioned closer to the scrubbing layer than material A. Similarly, material B is "below" material A in this illustration.

10 All percentages, ratios and proportions used herein are by weight unless otherwise specified.

III. Other Embodiments of the Cleaning Pad

To enhance the pad's ability to remove tough soil residues and increase the amount of cleaning fluid in contact with the cleaning surface, it may be desirable to incorporate a scrim material into the cleaning pad. The scrim will be comprised of a durable, tough material that will provide texture to the pad's scrubbing layer, particularly when in-use pressures are applied to the pad. Preferably, the scrim will be located such that it is in close proximity to the surface being cleaned. Thus, the scrim may be incorporated as part of the scrubbing layer or the absorbent layer; or it may be included as a distinct layer, preferably positioned between the scrubbing and absorbent layers. In one preferred embodiment, where the scrim material is of the same X-Y dimension as the overall cleaning pad, it is preferred that the scrim material be incorporated such that it does not directly contact, to a significant degree, the surface being cleaned. This will maintain the ability of the pad to move readily across the hard surface and will aid in preventing non-uniform removal of the cleaning solution employed. As such, if the scrim is part of the scrubbing layer, it will be an upper layer of this component. Of course, the scrim must at the same time be positioned sufficiently low in the pad to provide its scrubbing function. Thus, if the scrim is incorporated as part of the absorbent layer, it will be a lower layer thereof. In a separate embodiment, it may be desirable to place the scrim such that it will be in direct contact with the surface to be cleaned.

In addition to the importance of properly positioning the scrim is that the scrim not significantly impede fluid flow through the pad. The scrim therefore is a relatively open web.

35 The scrim material will be any material that can be processed to provide a tough, open-textured web. Such materials include polyolefins (e.g., polyethylene, polypropylene), polyesters, polyamides, and the like. The skilled artisan will

recognize that these different materials exhibit a different degree of hardness. Thus, the hardness of the scrim material can be controlled, depending on the end-use of the pad/implement. Where the scrim is incorporated as a discrete layer, many commercial sources of such materials are available (e.g., design number VO1230,
5 available from Conwed Plastics, Minneapolis, MN). Alternatively, the scrim may be incorporated by printing a resin or other synthetic material (e.g. latex) onto a substrate, such as is disclosed in U.S. Patent No. 4,745,021, issued May 17, 1988 to Ping, III et al., and U.S. Patent No. 4,733,774, issued March 29, 1988 to Ping, III et al., both of which are incorporated by reference herein.

10 The various layers that comprise the cleaning pad may be bonded together utilizing any means that provides the pad with sufficient integrity during the cleaning process. The scrubbing and attachment layers may be bonded to the absorbent layer or to each other by any of a variety of bonding means, including the use of a uniform continuous layer of adhesive, a patterned layer of adhesive or any
15 array of separate lines, spirals or spots of adhesive. Alternatively, the bonding means may comprise heat bonds, pressure bonds, ultrasonic bonds, dynamic mechanical bonds or any other suitable bonding means or combinations of these bonding means as are known in the art. Bonding may be around the perimeter of the cleaning pad (e.g., heat sealing the scrubbing layer and optional attachment layer
20 and/or scrim material), and/or across the area (i.e., the X-Y plane) of the cleaning pad so as to form a pattern on the surface of the cleaning pad. Bonding the layers of the cleaning pad with ultrasonic bonds across the area of the pad will provide integrity to avoid shearing of the discrete pad layers during use.

Referring to the figures which depict the cleaning pad of the present
25 invention, Figure 3 is a perspective view of a removable cleaning pad 200 comprising a scrubbing layer 201, an attachment layer 203 and an absorbent layer 205 positioned between the scrubbing layer and the attachment layer. Cleaning pad 200 is not depicted as having multiple substantially planar surfaces. As indicated above, while Figure 3 depicts each of layers 201, 203 and 205 as a single layer of
30 material, one or more of these layers may consist of a laminate of two or more plies. For example, in a preferred embodiment, scrubbing layer 201 is a two-ply laminate of carded polypropylene, where the lower layer is slitted. Also, though not depicted in Figure 3, materials that do not inhibit fluid flow may be positioned between scrubbing layer 201 and absorbent layer 203 and/or between absorbent layer 203 and
35 attachment layer 205. However, it is important that the scrubbing and absorbent layers be in substantial fluid communication, to provide the requisite absorbency of the cleaning pad. While Figure 3 depicts pad 200 as having all of the pad's layers of

equal size in the X and Y dimensions, it is preferred that the scrubbing layer 201 and attachment layer 205 be larger than the absorbent layer, such that layers 201 and 205 can be bonded together around the periphery of the pad to provide integrity. The scrubbing and attachment layers may be bonded to the absorbent layer or to each other by any of a variety of bonding means, including the use of a uniform continuous layer of adhesive, a patterned layer of adhesive or any array of separate lines, spirals or spots of adhesive. Alternatively, the bonding means may comprise heat bonds, pressure bonds, ultrasonic bonds, dynamic mechanical bonds or any other suitable bonding means or combinations of these bonding means as are known in the art. Bonding may be around the perimeter of the cleaning pad, and/or across the surface of the cleaning pad so as to form a pattern on the surface of the scrubbing layer 201.

Figure 4 is a blown perspective view of the absorbent layer 305 of an embodiment of a cleaning pad of the present invention. The cleaning pad's scrubbing layer and optional attachment layer are not shown in Figure 4. Absorbent layer 305 is depicted in this embodiment as consisting of a tri-laminate structure. Specifically absorbent layer 305 is shown to consist of a discrete layer of particulate superabsorbent gelling material, shown as 307, positioned between two discrete layers 306 and 308 of fibrous material. In this embodiment, because of the region 307 of high concentration of superabsorbent gelling material, it is preferred that the superabsorbent material not exhibit gel blocking discussed above. In a particularly preferred embodiment, fibrous layers 306 and 308 will each be a thermally bonded fibrous substrate of cellulosic fibers, and lower fibrous layer 308 will be in direct fluid communication with the scrubbing layer (not shown). (Layer 307 may alternatively be a mixture of fibrous material and superabsorbent material, where the superabsorbent material is preferably present in a relatively high percentage by weight of the layer.) Also, while depicted as having equal widths, in a preferred embodiment layer 306 will be wider than layer 307 and layer 307 will be wider than layer 308. When a scrubbing and attachment layer are included, such a combination will provide a pad having the multiple substantially planar surfaces of the present invention.

Figure 5 is a cross-sectional view (taken along the y-z plane) of cleaning pad 400 having a scrubbing layer 401, an attachment layer 403, and an absorbent layer indicated generally as 404 positioned between the scrubbing and attachment layers. Absorbent layer 404 consists of three separate layers 405, 407 and 409. Layer 409 is wider than layer 407 which is wider than layer 405. Again, this tapering of absorbent layer materials provides multiple planar surfaces indicated generally as

411, 413 and 415. (For purposes of discussion, surface 411 is referred to as the front edge of the cleaning pad 400 when the pad is attached to an implement; surface 413 is referred to as the back edge of pad 400.) In one embodiment, layers 405 and 407 comprise a high concentration of superabsorbent material, while layer 409 contains
5 little or no superabsorbent material. In such embodiments, one or both of layers 405 and 407 may be comprised of a homogenous blend of superabsorbent material and fibrous material. Alternatively, one or both layers may be comprised of discrete layers, e.g., two fibrous layers surrounding an essentially continuous layer of superabsorbent particles.

10 Though not a requirement, Applicants have found that it may be desirable to reduce the level of or eliminate superabsorbent particles at the extreme front and rear edges. This is accomplished in pad 400 by constructing absorbent layer 409 without superabsorbent material.

IV. Test Methods

15 A. Performance Under Pressure

 This test determines the gram/gram absorption of deionized water for a cleaning pad that is laterally confined in a piston/cylinder assembly under an initial confining pressure of 0.09 psi (about 0.6 kPa). (Depending on the composition of the cleaning pad sample, the confining pressure may decrease slightly as the sample
20 absorbs water and swells during the time of the test.) The objective of the test is to assess the ability of a cleaning pad to absorb fluid, over a practical period of time, when the pad is exposed to usage conditions (horizontal wicking and pressures).

 The test fluid for the PUP capacity test is deionized water. This fluid is absorbed by the cleaning pad under demand absorption conditions at near-zero
25 hydrostatic pressure.

 A suitable apparatus 510 for this test is shown in Figure 6. At one end of this apparatus is a fluid reservoir 512 (such as a petri dish) having a cover 514. Reservoir 512 rests on an analytical balance indicated generally as 516. The other end of apparatus 510 is a fritted funnel indicated generally as 518, a piston/cylinder
30 assembly indicated generally as 520 that fits inside funnel 518, and cylindrical plastic fritted funnel cover indicated generally as 522 that fits over funnel 518 and is open at the bottom and closed at the top, the top having a pinhole. Apparatus 510 has a system for conveying fluid in either direction that consists of sections glass capillary tubing indicated as 524 and 531a, flexible plastic tubing (e.g., 1/4 inch i.d.
35 and 3/8 inch o.d. Tygon tubing) indicated as 531b, stopcock assemblies 526 and 538 and Teflon connectors 548, 550 and 552 to connect glass tubing 524 and 531a and stopcock assemblies 526 and 538. Stopcock assembly 526 consists of a 3-way valve

528, glass capillary tubing 530 and 534 in the main fluid system, and a section of glass capillary tubing 532 for replenishing reservoir 512 and forward flushing the fritted disc in fritted funnel 518. Stopcock assembly 538 similarly consists of a 3-way valve 540, glass capillary tubing 542 and 546 in the main fluid line, and a
5 section of glass capillary tubing 544 that acts as a drain for the system.

Referring to Figure 7, assembly 520 consists of a cylinder 554, a cup-like piston indicated by 556 and a weight 558 that fits inside piston 556. Attached to bottom end of cylinder 554 is a No. 400 mesh stainless steel cloth screen 559 that is biaxially stretched to tautness prior to attachment. The cleaning pad sample
10 indicated generally as 560 rests on screen 559 with the surface-contacting (or scrubbing) layer in contact with screen 559. The cleaning pad sample is a circular sample having a diameter of 5.4 cm. (While sample 560 is depicted as a single layer, the sample will actually consist of a circular sample having all layers contained by the pad from which the sample is cut.) Cylinder 554 is bored from a
15 transparent LEXAN[®] rod (or equivalent) and has an inner diameter of 6.00 cm (area = 28.25 cm^2), with a wall thickness of approximately 5 mm and a height of approximately 5 cm. The piston 556 is in the form of a Teflon cup and is machined to fit into cylinder 554 within tight tolerances. Cylindrical stainless steel weight 558 is machined to fit snugly within piston 556 and is fitted with a handle on the top (not
20 shown) for ease in removing. The combined weight of piston 556 and weight 558 is 145.3 g, which corresponds to a pressure of 0.09 psi for an area of 22.9 cm^2 .

The components of apparatus 510 are sized such that the flow rate of deionized water therethrough, under a 10 cm hydrostatic head, is at least $0.01 \text{ g/cm}^2/\text{sec}$, where the flow rate is normalized by the area of fritted funnel 518.
25 Factors particularly impactful on flow rate are the permeability of the fritted disc in fritted funnel 518 and the inner diameters of glass tubing 524, 530, 534, 542, 546 and 531a, and stopcock valves 528 and 540.

Reservoir 512 is positioned on an analytical balance 516 that is accurate to at least 0.01g with a drift of less than 0.1g/hr. The balance is preferably interfaced to a
30 computer with software that can (i) monitor balance weight change at pre-set time intervals from the initiation of the PUP test and (ii) be set to auto initiate on a weight change of 0.01-0.05 g, depending on balance sensitivity. Capillary tubing 524 entering the reservoir 512 should not contact either the bottom thereof or cover 514. The volume of fluid (not shown) in reservoir 512 should be sufficient such that air is
35 not drawn into capillary tubing 524 during the measurement. The fluid level in reservoir 512, at the initiation of the measurement, should be approximately 2 mm below the top surface of fritted disc in fritted funnel 518. This can be confirmed by

placing a small drop of fluid on the fritted disc and gravimetrically monitoring its slow flow back into reservoir 512. This level should not change significantly when piston/cylinder assembly 520 is positioned within funnel 518. The reservoir should have a sufficiently large diameter (e.g., ~14 cm) so that withdrawal of ~40 ml portions results in a change in the fluid height of less than 3 mm.

Prior to measurement, the assembly is filled with deionized water. The fritted disc in fritted funnel 518 is forward flushed so that it is filled with fresh deionized water. To the extent possible, air bubbles are removed from the bottom surface of the fritted disc and the system that connects the funnel to the reservoir. The following procedures are carried out by sequential operation of the 3-way stopcocks:

1. Excess fluid on the upper surface of the fritted disc is removed (e.g. poured) from fritted funnel 518.
2. The solution height/weight of reservoir 512 is adjusted to the proper level/value.
3. Fritted funnel 518 is positioned at the correct height relative to reservoir 512.
4. Fritted funnel 518 is then covered with fritted funnel cover 522.
5. The reservoir 512 and fritted funnel 518 are equilibrated with valves 528 and 540 of stopcock assemblies 526 and 538 in the open connecting position.
6. Valves 528 and 540 are then closed.
7. Valve 540 is then turned so that the funnel is open to the drain tube 544.
8. The system is allowed to equilibrate in this position for 5 minutes.
9. Valve 540 is then returned to its closed position.

Steps Nos. 7-9 temporarily "dry" the surface of fritted funnel 518 by exposing it to a small hydrostatic suction of ~5 cm. This suction is applied if the open end of tube 544 extends ~5 cm below the level of the fritted disc in fritted funnel 518 and is filled with deionized water. Typically ~0.04 g of fluid is drained from the system during this procedure. This procedure prevents premature absorption of deionized water when piston/cylinder assembly 520 is positioned within fritted funnel 518. The quantity of fluid that drains from the fritted funnel in this procedure (referred to as the fritted funnel correction weight, or "Wffc")) is measured by conducting the PUP test (see below) for a time period of 20 minutes without piston/cylinder assembly 520. Essentially all of the fluid drained from the fritted funnel by this procedure is very quickly reabsorbed by the funnel when the

test is initiated. Thus, it is necessary to subtract this correction weight from weights of fluid removed from the reservoir during the PUP test (see below).

A round die-cut sample 560 is placed in cylinder 554. The piston 556 is slid into cylinder 554 and positioned on top of the cleaning pad sample 560. The piston/cylinder assembly 520 is placed on top of the frit portion of funnel 518, the weight 558 is slipped into piston 556, and the top of funnel 518 is then covered with fritted funnel cover 522. After the balance reading is checked for stability, the test is initiated by opening valves 528 and 540 so as to connect funnel 518 and reservoir 512. With auto initiation, data collection commences immediately, as funnel 518 begins to reabsorb fluid.

Data is recorded at intervals over a total time period of 1200 seconds (20 minutes). PUP absorbent capacity is determined as follows:

$$t_{1200} \text{ absorbent capacity (g/g)} = [W_{r(t=0)} - W_{r(t=1200)} - W_{ffc}] / W_{ds}$$

where t_{1200} absorbent capacity is the g/g capacity of the pad after 1200 seconds, $W_{r(t=0)}$ is the weight in grams of reservoir 512 prior to initiation, $W_{r(t=1200)}$ is the weight in grams of reservoir 512 at 1200 seconds after initiation, W_{ffc} is the fritted funnel correction weight and W_{ds} is the dry weight of the cleaning pad sample. It follows that the sample's t_{30} and t_{900} absorbent capacities are measured similarly, except $W_{r(t=30)}$ and $W_{r(t=900)}$ (i.e., the weight of the reservoir at 30 seconds and 900 seconds after initiation, respectively) are used in the above formula. The t_{30} percent absorbency of the sample is calculated as $[t_{30} \text{ absorbent capacity}] / [t_{1200} \text{ absorbent capacity}] \times 100\%$.

B. Squeeze-out

The ability of the cleaning pad to retain fluid when exposed to in-use pressures, and therefor to avoid fluid "squeeze-out", is another important parameter to the present invention. "Squeeze-out" is measured on an entire cleaning pad by determining the amount of fluid that can be blotted from the sample with Whatman filter paper under pressures of 0.25 psi (1.5 kPa). Squeeze-out is performed on a sample that has been saturated to capacity with deionized water via horizontal wicking (specifically, via wicking from the surface of the pad consisting of the scrubbing or surface-contacting layer). (One means for obtaining a saturated sample is described as the Horizontal Gravimetric Wicking method of U.S. application Serial No. 08/542,497 (Dyer et al.), filed October 13, 1995, which is incorporated by reference herein.) The fluid-containing sample is placed horizontally in an apparatus capable of supplying the respective pressures, preferably by using an air-filled bag

that will provide evenly distributed pressure across the surface of the sample. The squeeze-out value is reported as the weight of test fluid lost per weight of the wet sample.

EXAMPLE I

5 A detergent composition/solution containing about 0.5% of detergent surfactant, comprising a linear alcohol ethoxylate detergent surfactant (Neodol 1-5®, available from Shell Chemical Co.) and an alkylsulfonate (Bioterge PAS-8s, a linear C₈ sulfonate available from Stepan Co.); about 0.1%, potassium carbonate; and about 0.5% 2-amino,2-methylpropanol; adjuvants including dyes and perfumes;
10 and the balance deionized water, was applied to a floor surface and removed by an implement as disclosed above (containing an effective amount of sodium polyacrylate, preferably cross-linked sodium polyacrylate, a superabsorbent material) and as exemplified in the drawings. The result is a clean floor.

15

EXAMPLE II

Ingredient	Tradename	% Concentration	CAS#
C11 alkyl E05	Neodol 1 - 5	0.35	34398-01-1
C8 alkyl sodium sulfonate	Witconate NAS-8	0.1	5324-84-5
Perfume		0.015	
K ₂ CO ₃		0.01	
2-amino-2-methyl-1-propanol	AMP-95	0.5	124-68-5
Suds suppressor	Dow Corning Suds suppressor *	0.0025	*
Deionized Water		99.023	7732-18-5

pH = 10.75

* The suds suppressor contains: Polyethylene glycol stearate (4% Wt, CAS # 9004993); Methylated silica (2% Wt, CAS # 67762907); Octamethyl cyclotetrasiloxane (2% Wt, CAS # 556672).
20

The suds suppressor at an effective level, typically from about 0.0005 to about 0.02, preferably from about 0.001 to about 0.01, more preferably from about 0.002 to about 0.003, provides a technical improvement in spotting and filming,
25 particularly on ceramic surfaces. The reason for this is the grout lines on ceramic create low spots as the mop moves across, generating suds. If too high a level of suds is generated, it can dry down into streaks. Furthermore, consumer research shows that suds seen on floor during mopping is perceived by some consumers as leading to film/streaking.

WO 98/42819

PCT/IB98/00356

30

Lowering suds on floor during mopping can provide varying degrees of technical and perceptual benefits for not leaving film/streaks. The degree of benefit depends on the level of suds created and to what degree the level of suds is controlled, particularly during mopping.

- 5 Known suds suppressors can be used, but it is highly desirable to use a silicone suds suppressor since they are effective at very low levels and therefore can minimize the total water insoluble material needed while having at least an effective amount of suds suppressor present.

WHAT IS CLAIMED IS:

1. Detergent composition to be used with an implement containing a pad containing superabsorbent material containing no more than about 10% of one or more detergent surfactants; a level of hydrophobic materials, including solvent, that is less than about 0.5%; and a pH of more than about 9.

2. The detergent composition of Claim 1 wherein the level of detergent surfactant is from about 0.01% to about 0.5%, preferably from about 0.1% to about 0.45%; the level of hydrophobic materials, including solvent, is less than about 0.2%, preferably less than about 0.1%; and the pH is greater than about 10, preferably greater than about 10.3.

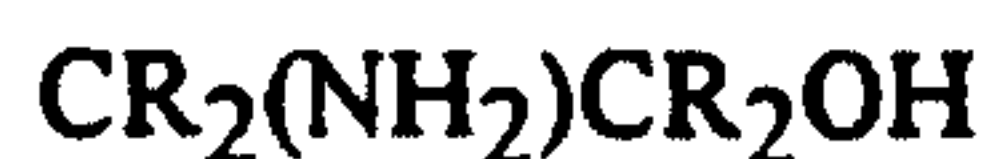
3. The detergent composition of Claim 1 or Claim 2 containing an effective amount of suds suppressor.

4. The detergent composition of Claim 3 wherein said suds suppressor is at a level of from about 0.0005 to about 0.02, optionally from about 0.001 to about 0.01.

5. The detergent composition of Claim 3 or Claim 4 wherein said suds suppressor comprises a silicone suds suppressor.

6. The detergent composition of any of Claims 1-5 wherein the detergent surfactant has a predominantly linear structure and is optionally selected from the group consisting of straight chain anionic and nonionic detergent surfactants.

7. The detergent composition of any of Claims 1-6 wherein the alkalinity is provided, at least in an effective amount, by volatile alkaline agents which optionally can be an alkanol amine having the formula:



wherein each R is selected from the group consisting of hydrogen and alkyl groups containing from one to four carbon atoms and the total of carbon atoms in the compound is from three to six, said volatile alkaline agent optionally being 2-amino,2-methylpropanol.

8. A kit comprising an implement containing a pad containing superabsorbent material and a detergent composition according to any of Claims 1-7.

WO 98/42819

PCT/IB98/00356

32

9. The detergent composition of any of Claims 1-8 in a container, in association with instructions to use it with a pad containing a superabsorbent material.
10. The process of cleaning a surface, optionally a ceramic surface, comprising applying an effective amount of a detergent composition according to any of Claims 1-8 and absorbing the composition in an absorbent structure comprising a superabsorbent material.

1/6

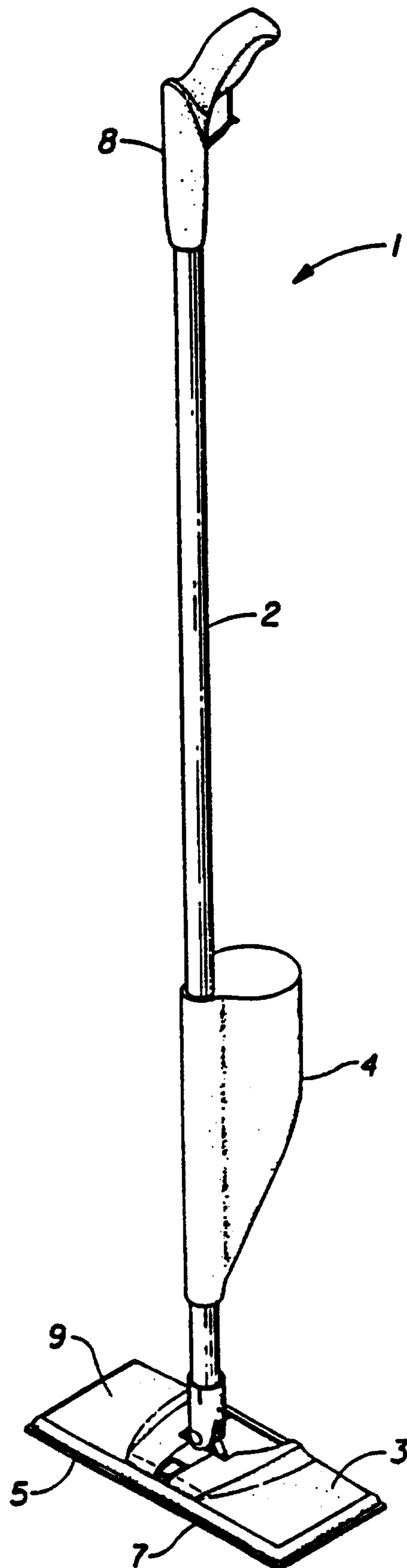


Fig. 1a

2/6

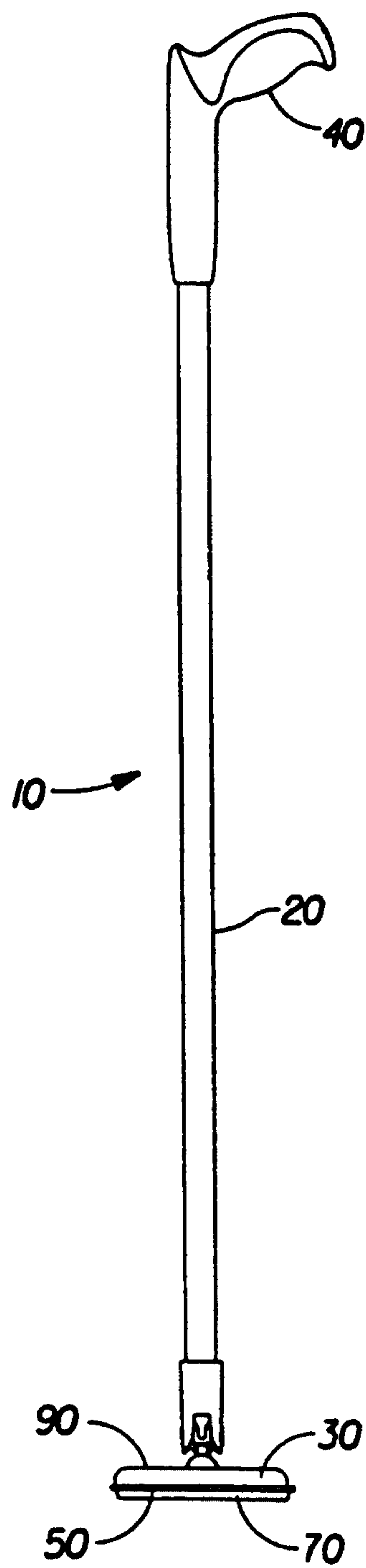


Fig. 1b

3/6

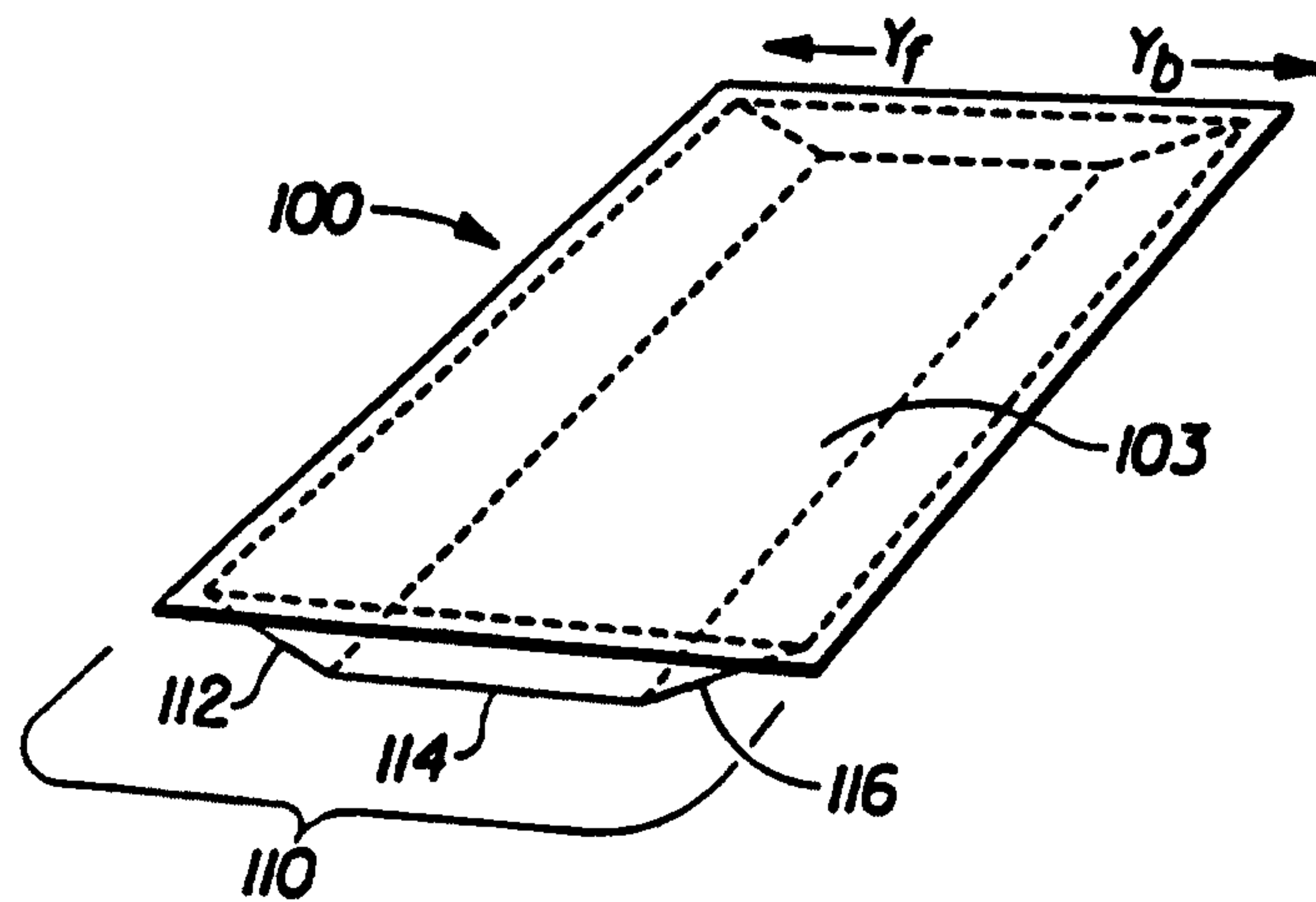


Fig. 2

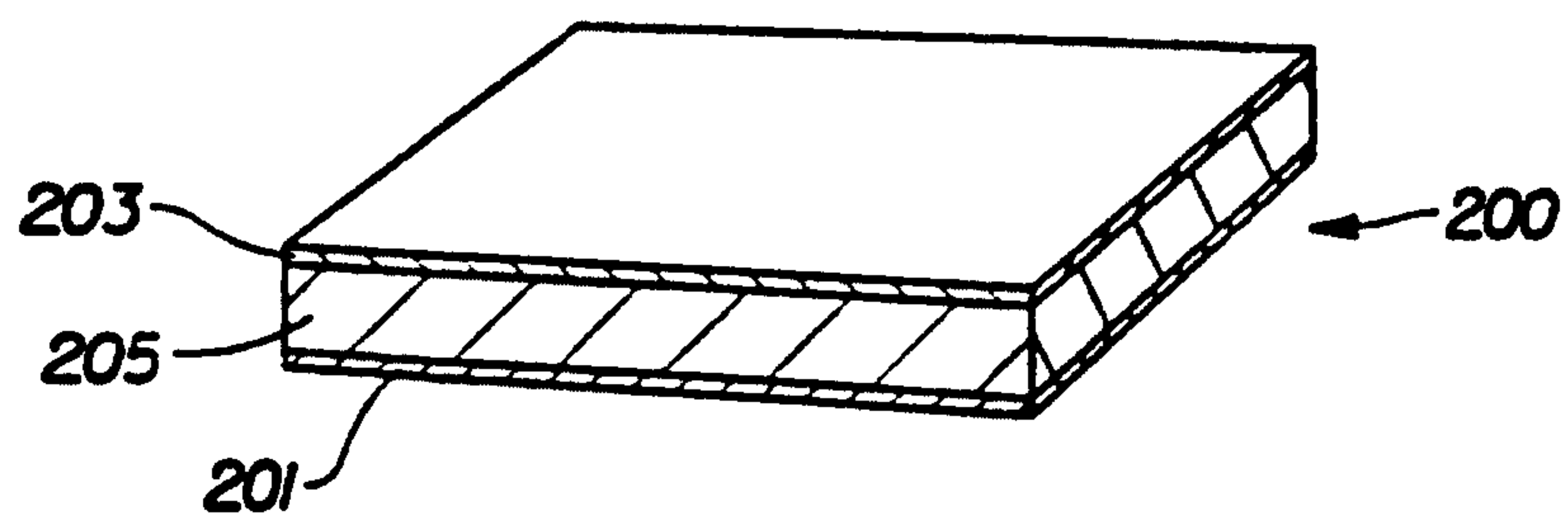


Fig. 3

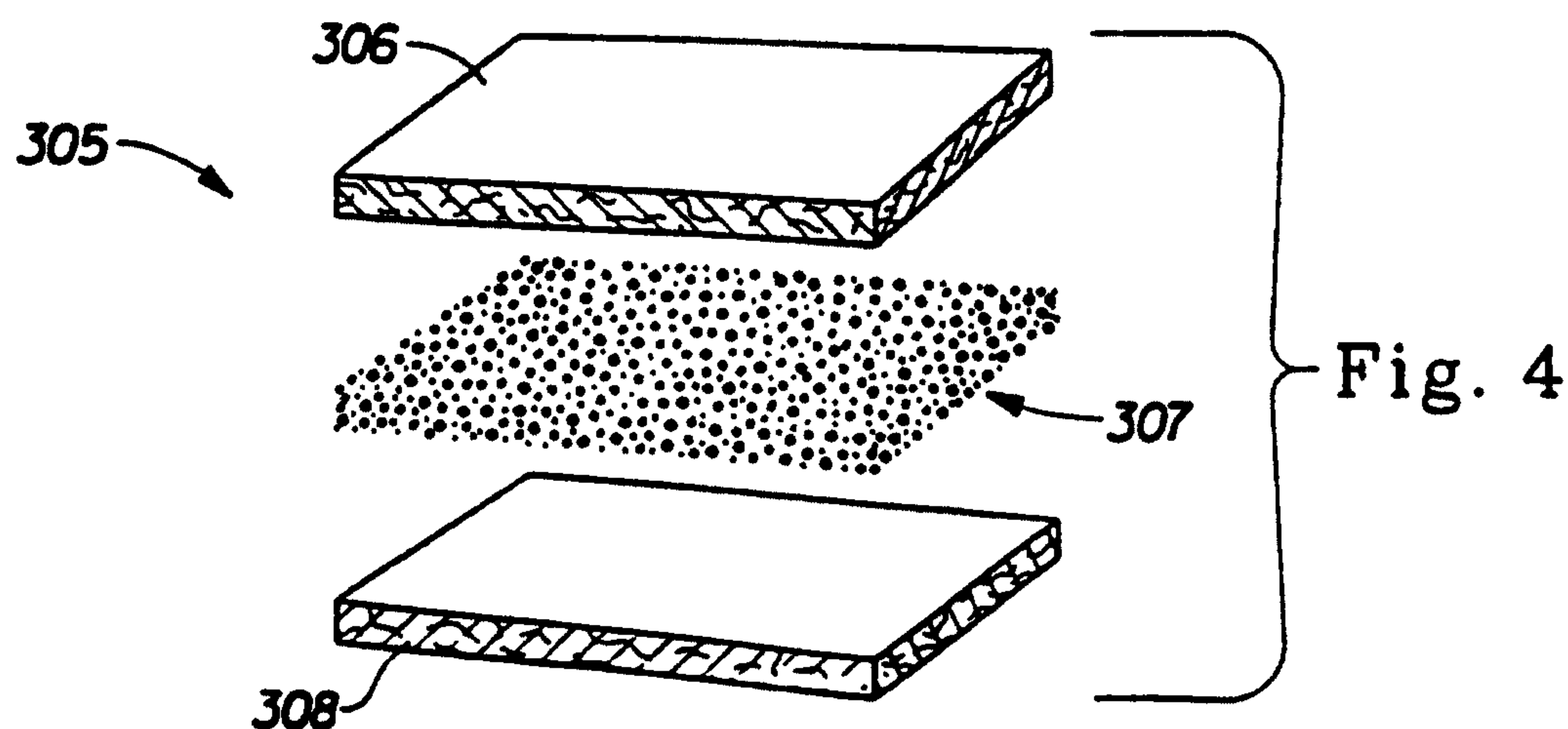


Fig. 4

4/6

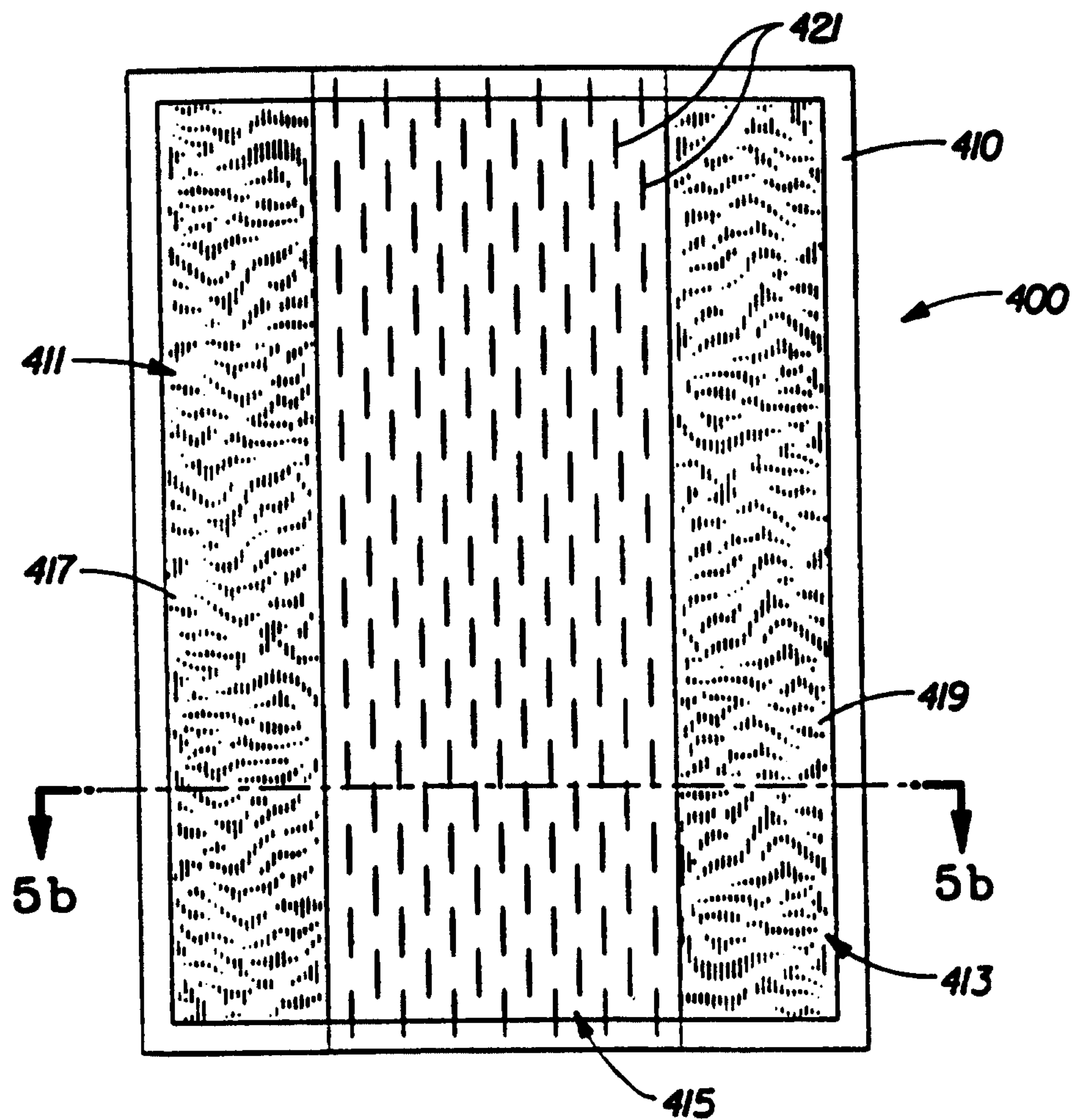


Fig. 5a

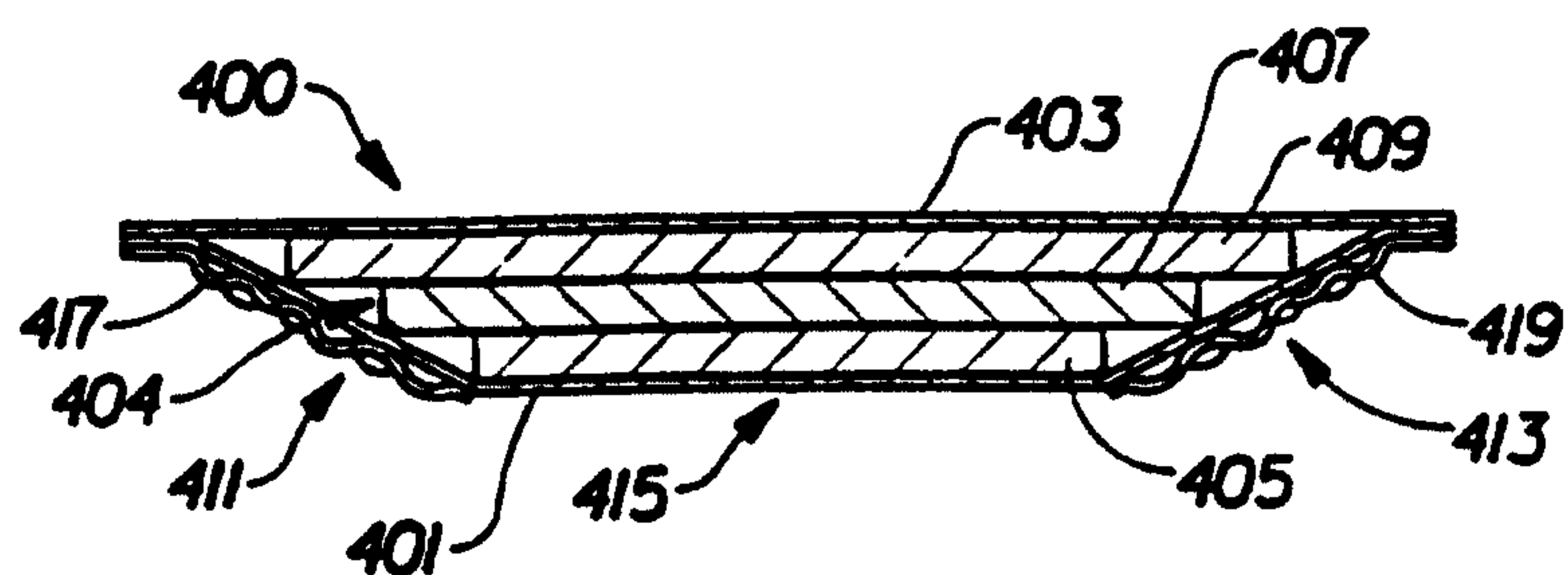
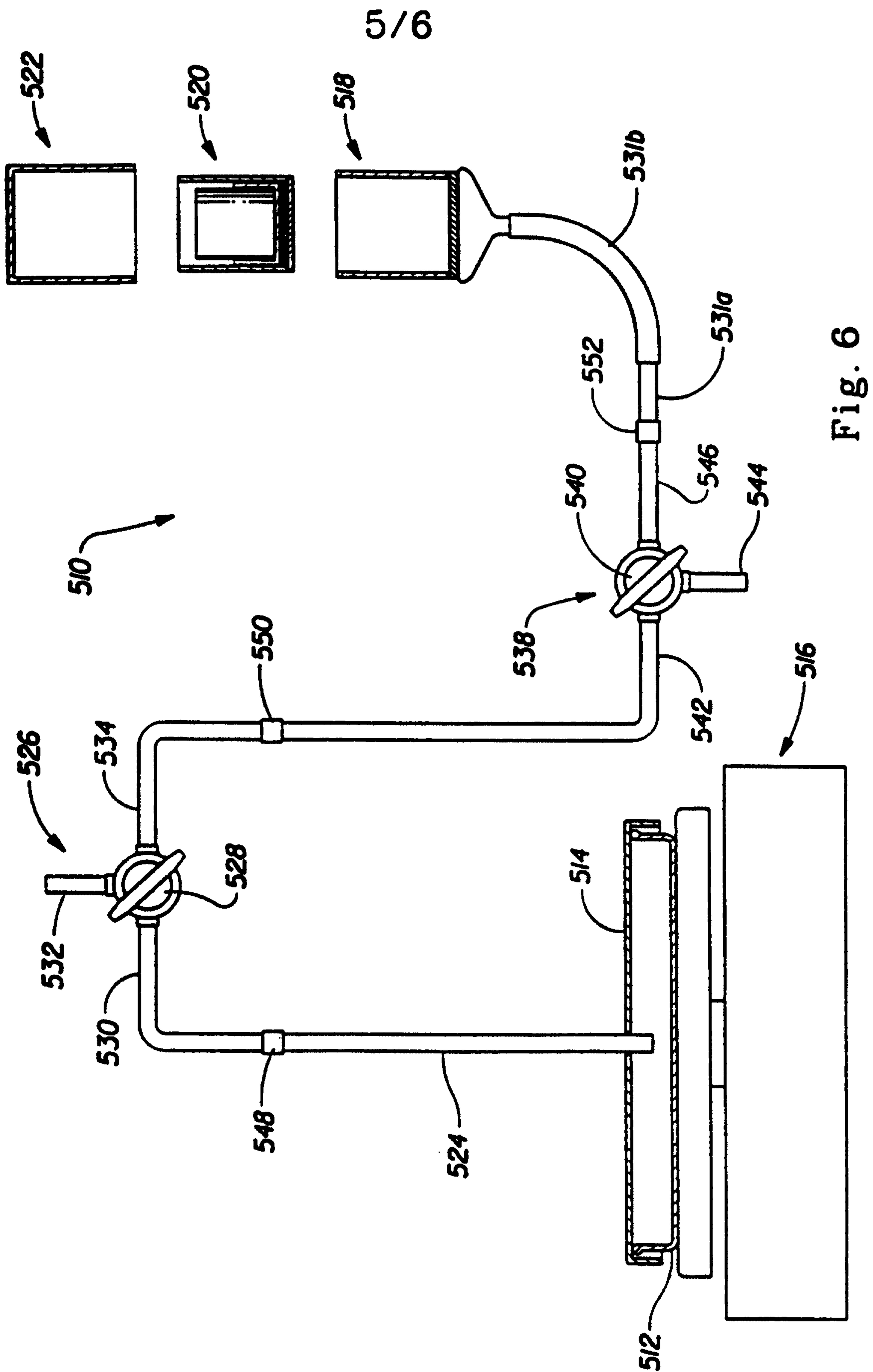


Fig. 5b



6/6

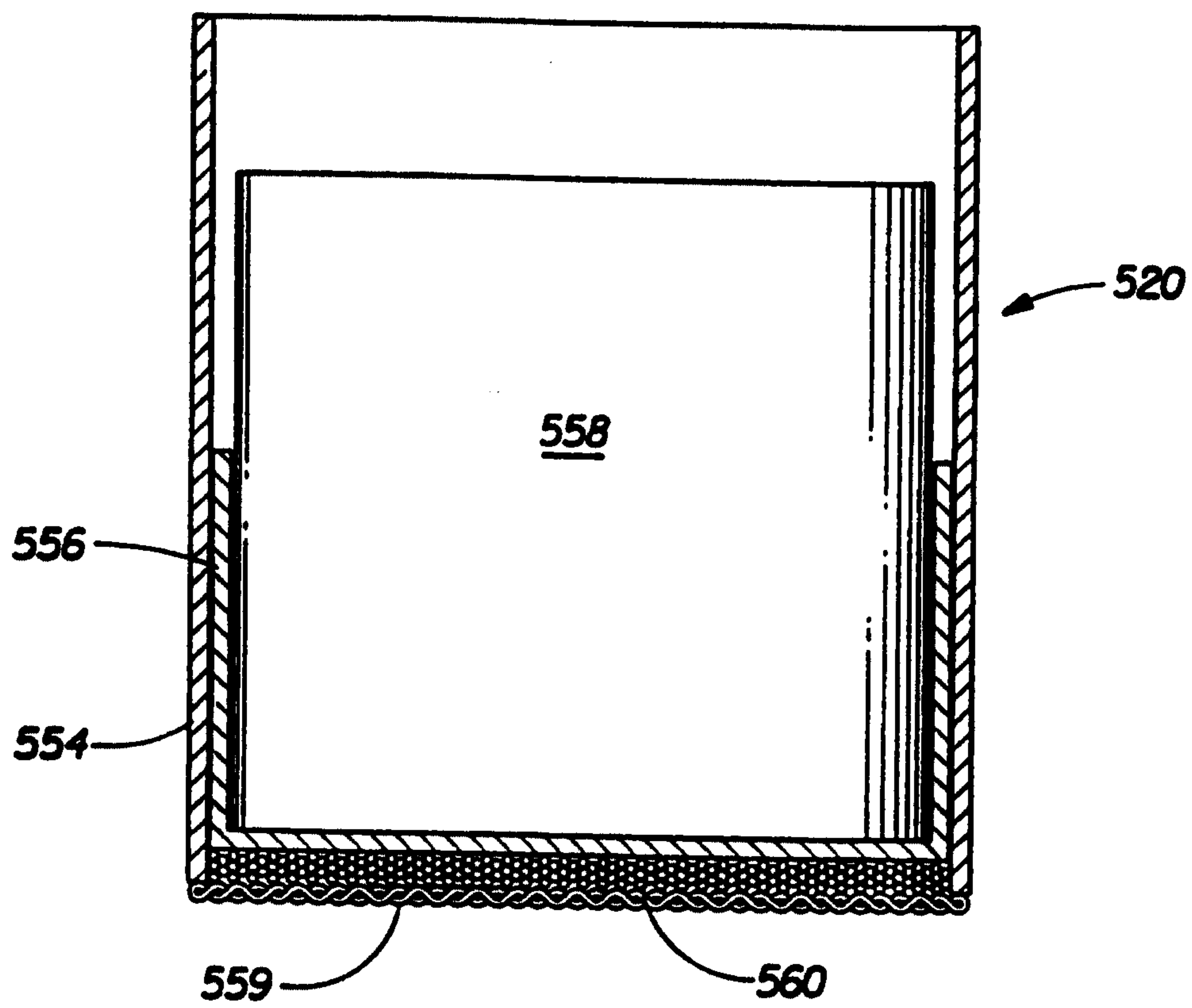


Fig. 7