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(54) Title: WIPER WITH USE INDICATOR

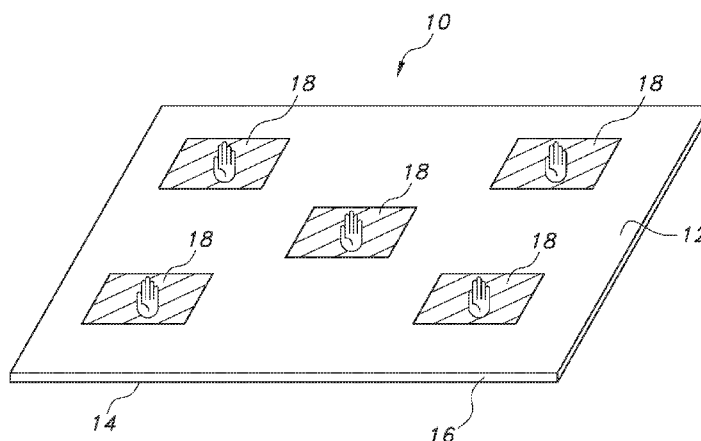


FIG. 1

(57) **Abstract:** Disposable cleaning wipes having a use indicator are provided that are suitable for use in home and industrial cleaning applications. The cleaning wipes comprise cellulosic fibers, an antimicrobial agent and an indicator complex, the indicator complex including (i) a colored compound selected from the group consisting of a phthalocyanine compound, an ultramarine compound, and an iron oxide compound, and (ii) a cationic agent. The indicator complex is releasably attached, by ionic bonding, to a discrete region of the fibrous sheet. The anti-microbial compound is also attached, by ionic bonding, to the fibrous sheet. Thus, in use, the indicator complex is released by the fibrous sheet commensurate with the release of antimicrobial agent. The release and loss of the indicator complex provides the user with an indication of when the antimicrobial agent within the fibrous sheet is substantially depleted and the cleaning wipe should be replaced.

WIPER WITH USE INDICATOR

This application claims the benefit of priority from U.S. Provisional Application No. 62/166,574 filed on May 26, 2015.

FIELD OF INVENTION

- 5 The present invention relates to disposable cleaning articles having a use indicator for use in home and industrial cleaning applications.

BACKGROUND

- Disposable wipers have been used heretofore for various industrial and home cleaning applications. In particular, disposable wipers have been used for cleaning hard surfaces including, for example, 10 countertops, floors, windows, appliances, equipment, tools, and so forth. Numerous different materials are known and used for such cleaning applications. However, depending on the particular cleaning task and the nature of the wiper, often times the wiper can be used for a limited number of times before needing to be disposed of. Further, often times the wiper may still be physically intact but require disposal due to the presence of microorganisms acquired in the prior cleaning tasks.
- 15 In this regard, in many different industries microorganism contamination is a significant problem. For example, in the food service industry, raw food products are often prepared on hard surfaces such as counters, tables, and the like. Microbes (e.g., viruses, bacteria, fungi, and the like) from these products can collect on the surfaces, and later transfer to a cleaning towel or wiper that is used to clean the surfaces. After transfer, the microbes can remain on the wipe and begin to grow in numbers. In an 20 attempt to prevent such contamination, wipers containing certain antimicrobial agents have been employed. For instance, many of these wipers are treated and/or impregnated with anti-microbial agents that help prevent or inhibit the growth of microorganisms within the sheet. Further, in certain instances the applied antimicrobial agents can be released from the wiper to provide the liquid released from the wiper with a certain degree of antimicrobial activity. Quaternary ammonium 25 chlorides have heretofore been used in such applications. By way of example, antimicrobially treated wipes and/or fabrics are described in US4929498 to Suskind, et al., US6916480 to Anderson et al., US7838447 to Clark et al. and US2012/0171267 to Cunningham et al.

In order to help users assess when a particular wiper may need to be discarded, life-span indicators have heretofore been developed. In this regard, various indicators have been applied to a cleaning

fabrics in an effort to provide the user with an indication of when the wipe should be discarded. Various indicators are described in US2005/0125926 to Rekum et al., EP0047101 to Fellows and US4311470 to Fenn et al. However, a significant challenge for these indicators is having them appropriately provide the signal to discard the wiper when the wipers are used in a wide variety of cleaning applications and are exposed to widely different mechanical forces and chemical compounds. In this regard, it will be appreciated that it is quite common to use liquid cleaning compositions in conjunction with wipers. A wide variety of cleaning liquids are known and used in combination with wipers, including the use of highly oxidative or reductive agents such as sodium hypochlorite, hydrogen peroxide, potassium percarbonate, urea-hydrogen peroxide and so forth. Accordingly, it has further proven highly difficult to provide a life-span indicator that is sufficiently durable to withstand the different mechanical forces and cleaning liquids applied to the wiper and yet which is also adequately transient to timely provide the desired signal to consumers to replace the wiper.

Therefore, in order to address the unmet needs associated with prior wipers, the present invention provides a pre-treated wiper which employs a durable life-span indicator that is triggered in direct relation to the loss of antimicrobial activity within the fabric and that functions in the presence of a wide range of cleaning liquids, including highly caustic and oxidative cleaners.

SUMMARY OF THE INVENTION

A cleaning article is provided comprising a fibrous sheet having (i) cellulosic fibers with a cationic antimicrobial agent releasably attached thereto and (ii) cellulosic fibers with a complex releasably attached thereto, the complex comprising a dye and an antimicrobial agent. The fibrous sheet has opposed first and second outer surfaces and, on at least the first surface, the complex is present on less than about 45%, or less than about 30%, of the area of the first surface of the fibrous sheet. Desirably, the complex is present on the first surface of the sheet such that it forms a graphic. In a further aspect, the antimicrobial agent (separate from that contained within the complex) can be present on greater than about 55%, 75% or even 90% of the first surface of the fibrous sheet. Desirably the complex is stable against oxidation and reduction having an ORP of between 0 and 1.61 V. In further aspects the complex is water stable and can comprise an ionic bond between the dye and the antimicrobial agent. In certain embodiments the dye can be selected from the group consisting of metallophthalocyanines, ultramarines, iron oxides, and derivatives thereof. Further, in certain embodiments, the antimicrobial agent can be selected from the group consisting of quaternary ammonium, biguanide compounds, chitosan, and derivatives thereof. Still further, the antimicrobial agent can be ionically bonded to the cellulosic fibers.

In a further aspect, a cleaning article is provided comprising a fibrous sheet of cellulosic fibers having first and second regions wherein the first region includes a complex formed by (i) a colored compound selected from the group consisting of a phthalocyanine compound, an ultramarine compound, an iron oxide compound, and/or a derivative thereof, and (ii) a cationic agent, wherein said complex is
5 releasably attached to said cellulosic fibers by ionic bonding. The second region of the fibrous sheet has a cationic antimicrobial agent releasably attached to the cellulosic fiber by ionic bonding and is substantially free of colored compounds selected from the group consisting of a phthalocyanine compound, an ultramarine compound, an iron oxide compound, and/or a derivative thereof. In certain
10 embodiments, the first region can comprise less than about 45%, about 30% or even about 10% of the surface area of said fibrous sheet. In further embodiments, the second region can comprise at least about 55%, at least about 70%, or even at least about 90% of the surface area of said fibrous sheet. The antimicrobial agent and colored compound can comprise one or more of the agents identified herein. In certain embodiments, the colored compound can comprise a phthalocyanine compound
15 such as, for example, a metallophthalocyanine. Further, in certain additional embodiments, the antimicrobial agent can comprise one or more cationic agents such as, for example, one or more quaternary ammonium, chitosan and/or biguanide compounds.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a top perspective view of a wiper of the present invention.

DETAILED DESCRIPTION

20 Throughout the specification and claims, discussion of the articles and/or individual components thereof is with the understanding set forth below.

(i) As used herein the term "cellulosic" means those materials comprising or derived from cellulose including natural or synthetic cellulose as well as that derived from both woody and non-woody sources.

25 (ii) The term "comprising" or "including" or "having" are inclusive or open-ended and do not exclude additional unrecited elements, compositional components, or method steps. Accordingly, the terms "comprising" or "including" or "having" encompass the more restrictive terms "consisting essentially of" and "consisting of."

(iii) As used herein "continuous fibers" means fibers formed in a continuous, uninterrupted
30 manner having indefinite length and having a high aspect ratio (length to diameter) in excess of 100:1;

in use such fibers having a length substantially the same as the length or width dimension of the wiper itself.

(iv) As used herein "staple fibers" means natural fibers or continuous fibers cut to length, such fibers having a length between about 0.5 mm and about 200 mm.

5 (v) As used herein, unless expressly indicated otherwise, when used in relation to material compositions the terms "percent", "percentage", "weight percent" or "percent by weight" each refer to the quantity by weight of a component as a percentage of the total based upon a dry product.

(vi) As used herein a "phthalocyanine compound" includes molecules having a phthalocyanine ring.

10 (vii) As used herein, the term "wet wipe" refers to a fibrous sheet having had a liquid applied thereto and which is retained therein.

Disposable cleaning wipes having a use indicator are provided that are suitable for use in home and industrial cleaning applications. In one embodiment, as shown in reference to Fig. 1, a wiper 10 is provided having a first outer surface 12, an opposed second outer surface 14 and a side edge 16. As
15 described in more detail below, the wiper 10 comprise cellulosic fibers, an antimicrobial agent and an indicator complex. The cellulosic fibers of the wiper 10 are treated with and contain an antimicrobial compound (not shown) attached to the fibers by ionic bonding. The first outer surface 12 of the wiper 10 also includes graphic elements 18 formed by those areas of the first surface 10 that have been treated with and contain the indicator complex. The indicator complex is likewise releasably attached,
20 by ionic bonding, to cellulosic fibers of the wiper 10. Thus, in use, the indicator complex is released by the wiper 10 commensurate with the release of antimicrobial agent. The release and loss of the indicator complex and the graphic elements 18 provide the user with an indication of when the antimicrobial agent within the wiper 10 is substantially depleted and the used wiper should be replaced.

25 Fibrous Sheet

The cleaning articles of the present invention include a fibrous layer or material. The fibrous material comprises at least a portion of the cleaning substrate and has a porous structure including individual openings or interstitial spaces which, in certain embodiments, collectively form pathways through the thickness of the material via adjacent, inter-connecting spaces or openings. In certain embodiments,
30 the wiping substrate substantially retains its integrity when wet and, in certain aspects, remains resiliently compressible when wet. The fibrous sheets may comprise continuous fibers, staple length fibers, or combinations of the same. In addition, the fibrous sheets may comprise either woven, knit, or

nonwoven fabrics and further the fibrous material or sheets may be used to form laminates with one or more additional materials. Suitable fibrous sheets will typically have a dry basis weight of from about 20 g/m² to about 260 g/m². In certain embodiments, the dry basis weight of the fibrous sheet will be about 30 g/m² to about 190 g/m² and in still further embodiments may be between about 35 g/m² to about 120 g/m².

The fibrous material includes cellulosic fibers. In this regard, the fibrous material includes greater than about 15% by weight cellulosic fibers and in certain embodiments at least about 30% cellulosic fibers and in still further embodiments at least about 50% cellulosic fibers. By way of example, the fibrous material may comprise between about 15% and 98% cellulosic fibers, or between about 30% and 95% cellulosic fibers or even between about 55% and 90% cellulosic fibers.

The cellulosic fibers may include traditional paper making fibers including woody fibers such as those obtained from deciduous and coniferous trees, including, but not limited to, softwood fibers, such as northern and southern softwood kraft fibers, and also hardwood fibers, such as eucalyptus, maple, birch, and aspen. Other papermaking fibers that can be used in the present disclosure include paper broke or recycled fibers and high yield fibers. Various pulping processes believed suitable for the production of cellulosic fibers include bleached chemithermomechanical pulp (BCTMP), chemithermomechanical pulp (CTMP), pressure/pressure thermomechanical pulp (PTMP), thermomechanical pulp (TMP), thermomechanical chemical pulp (TMCP), high yield sulfite pulps, and high yield Kraft pulps, all of which leave the resulting fibers with high levels of lignin. In this regard, high yield fibers are well known for their stiffness in both dry and wet states relative to typical chemically pulped fibers. In addition, the cellulosic fibers may comprises non-woody fibers, such as cotton, abaca, bamboo, kenaf, sabai grass, flax, esparto grass, straw, jute hemp, bagasse, milkweed floss fibers, pineapple leaf fibers and so forth. Still further, the cellulosic fibers may comprise synthetic fibers derived from cellulosic materials such as, for example, viscose, Rayon, lyocell or other comparable fibers. Moreover, if desired, secondary fibers obtained from recycled materials may be used, such as fiber pulp reclaimed from sources such as, for example, newsprint, paperboard, office waste, etc. The fibrous sheet material can comprise a single variety of cellulosic fibers or alternatively can comprise mixture of two or more different cellulosic fibers. As is known in the art, it is often desirable to employ mixtures of fibers especially when utilizing recycled or secondary fibers.

In addition to cellulosic fibers, the fibrous material may also comprise non-cellulosic fibers such as synthetic polymer fibers including those formed from polyolefin, polyester, polyamide, polylactic acid, or other fiber forming polymers. Preferred polymeric fibers include, but are not limited to, those

comprising polypropylene and/or polyethylene. The non-cellulosic fibers may be formed according to one or more various processes including, but not limited to, those formed by melt-extrusion processes such as, for example, spunbonding, meltblowing, and so forth. Methods of making such fibers and related webs are described in, for example, US3498874 to Evans et al., US3849241 to Butin et al., US 5 4340563 to Appel et al., US4443513 to Meitner et al.; US4853281 to Win et al.; US5382400 to Pike et al., US6200669 to Marmon et al., US6224977 to Kobylivker et al., and so forth. In this regard, in certain embodiments, the fibrous material may comprise between about 85% and 2% non-cellulosic fibers, or between about 70% and 5% non-cellulosic fibers or even between about 45% and 10% non-cellulosic fibers. In certain embodiments, the non-cellulosic or synthetic polymer fibers can comprise 10 continuous fibers.

Wet-laid or hydroentangled nonwoven sheet materials are particularly well suited for use in the present invention. Hydroentangling is a process of forming a nonwoven web which generally includes the steps of (i) depositing loose fibers on a porous belt or patterned screen and (ii) subjecting the fibers to one or more rows of fine high-pressure jets of water so that the fibers become sufficiently entangled 15 with one another to form a coherent nonwoven web. In certain aspects, hydroentangling readily allows for the combination of different fiber types, such as combining fibers of distinct composition (e.g. polymeric fibers and wood pulp fibers) or fibers of distinct size (e.g. continuous length and staple length fibers). By way of non-limiting example, suitable hydroentangled materials, and methods of making the same, are described in greater detail in US3485706 to Evans, US3620903 to Bunting et al., US4925722 to Jeffers et al., US5009747 to Viazmsensky et al., US5284703 to Everhart et al. and 20 US2010/0279085 to Adam et al. In one embodiment, the fibrous sheet can comprise a mixture of pulp fibers and continuous polyolefin spunbond fibers.

In further embodiments, the fibrous sheet of the present invention can comprise an air-laid nonwoven web. In the air-laying process, fibers are entrained in an air stream, intermingled and then deposited 25 onto a forming screen or wire, usually with the assistance of a vacuum supply. The randomly deposited fibers are then bonded to one another autogenously, such as through the use of heat and/or pressure, or through the use of a binder, such as by the inclusion of binder fibers or the application of adhesive to the web. By way of non-limiting example, various specific examples of suitable air-laid nonwoven sheets, and methods of making the same, are described in US4548856 to Ali Kahn et al., 30 US6811638 to Close et al., US6946413 to Lange et al., US2004/0192136 to Gusky et al., US2006/0008621 to Gusky et al. and so forth.

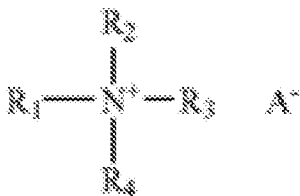
Coformed materials are also particularly well suited for use in the present invention. Coform nonwoven webs are formed by the comingling of polymeric fibers and absorbent fibers, such as polyolefin fibers and cellulosic fibers, as the fibers are entrained by a common airstream before they are deposited onto a forming surface. Examples of such coform sheets materials, and methods of making the same, are described US4100324 to Anderson et al., US5350624 to Georger et al., and US2011/0151196 to Schmidt et al. In certain embodiments such coform sheets can comprise air-formed matrix of thermoplastic polyolefin meltblown fibers and wood pulp fibers.

If desired, the nonwoven web may also be further treated by one or more techniques as is known in the art to improve the durability, strength, hand, aesthetics, texture, and/or other properties of the fibrous sheet material. For instance, the nonwoven web may be pattern bonded or embossed by the use of heat, pressure and/or ultrasonic energy. By way of non-limiting example, various suitable pattern embossing and/or bonding techniques are described in US3855046 to Hansen et al., US5620779 to Levy et al., US5962112 to Haynes et al., US7252870 to Anderson et al. and so forth. The fibrous sheet materials may be embossed and/or bonded by continuous and/or discontinuous lines, by patterns of numerous discrete elements, or other patterns as may be desired. As additional examples, the nonwoven web may be embossed and/or bonded uniformly across the surface or regionally such as along the periphery or edge of the sheet. The fibrous sheets may also, if desired, be treated by various other known techniques such as, for example, stretching, needling, creping, and so forth.

20 Antimicrobial Agent

The fibrous sheet includes one or more antimicrobial agents that are releasably bound to the cellulosic fiber through ionic bonding. Thus, the antimicrobial agent(s) is an ionic antimicrobial agent and, in certain embodiments, can comprise a cationic antimicrobial agent. Ionic antimicrobial agents believed suitable for use in the present invention include those in the following families: quaternary ammonium compounds, bis(biguanide)s, chitosans, and the like. In certain embodiments, the cationic antimicrobial agent can be highly ionic (N^+ , X^-) with less than about 10% covalent content.

An antimicrobial agent well suited for use in the present invention includes one or more a quaternary ammonium compound having the following formula:



wherein,

R1, R2, R3, and R4 are independently selected from the group consisting of H, C₁-C₃₀ alkyl, C₁-C₃₀ alkenyl, C₁-C₃₀ alkylethoxy, C₁-C₃₀ alkylphenoethoxy, and the like; and A is selected from the group consisting of halogens (e.g., chlorine, bromine, fluorine, etc.), methosulfates, phosphates, and the like.

For instance, suitable quaternary ammonium compounds that may be used in present invention include, but are not limited to, benzalkonium chloride (BZK) or other benzalkonium halides, benzethonium chloride or other benzethonium halides, cetylpyridinium chloride, dequalinium chloride, N-myristyl-N-methyl-morpholinium methyl sulfate, poly-N-3-(dimethylammonio)propyl-N-3-(ethyleneoxyethelene dimethylammonio)propylurea dichloride, alpha-4-1-tris(2-hydroxyethyl)ammonium chloride-2-butenyl-omega-tris(2-hydroxyethyl)ammonium chloride, polyoxyethylene (dimethyliminio)ethylene(dimethyliminio)-ethylene dichloride. Additional quaternary ammonium compounds believed suitable for use in the present invention include those described in US6712121 to Clark et al. and US7838447 to Clark et al., the contents of which are incorporated herein to the extent consistent herewith. Various quaternary ammonium antimicrobial agents are commercially available from Lonza Group Ltd including BARDAC 208M (a blend of alkyl dimethyl benzyl ammonium chlorides), BARDAC 2080 (based on dialkyl(C 8-C 10)dimethyl ammonium chloride); BARDAC 2250 (didecyl dimethyl ammonium chloride); BARQUAT MB-50 and BARQUAT MB-80 (blends of alkyl dimethyl benzyl ammonium chlorides); and BARQUAT MS-100 (based on myristyl dimethyl benzyl ammonium chloride), and others.

An additional antimicrobial agent believed suitable for use with the present invention includes one or more agents from the bis(biguanide) family. Biguanide antimicrobial actives including, but not limited to, polyhexamethylene biguanide hydrochloride, poly[oxyethylene(dimethyliminio)ethylene(dimethyliminio)ethylene dichloride], p-chlorophenyl biguanide, 4-chlorobenzhydryl biguanide, halogenated hexidine such as, but not limited to, chlorohexidine (1,1'-hexamethylene-bis-5-(4-chlorophenyl biguanide) and its salts. Additional biguanide antimicrobial

actives believed suitable for use in the present invention include those disclosed in US4655756 to Fawkes, US4615937 to Bouchette, US5141803 to Pregozen, and US5993840 to Fawkes et al..

Commercially available biguanide antimicrobial agents are also commercially available from Lonza Group Ltd under the trade names COSMOCIL CG, SPECTRADYNE and VANTOCIL IB.

- 5 Additionally, further antimicrobial agents believed suitable for use with the present invention include chitosan and derivatives thereof including, for example, modified chitosans, crosslinked chitosans and chitosan salts. Chitosan is a partially or fully deacetylated form of chitin, a naturally occurring polysaccharide. Chitin occurs widely in nature, for example, in the cell walls of fungi such as mushrooms and the hard shell of insect and crustaceans such as shrimp. Exemplary commercially
- 10 available chitosan compounds include, but are not limited to, the following: 417963 Chitosan from shrimp shells, practical grade; 448877 Chitosan medium molecular weight; 746134 Chitosan from white mushrooms, all from Sigma-Aldrich Chemical Company, Milwaukee, Wisconsin. In addition, examples of chitosan derivatives suitable for use in the present invention includes chitosan glycolate and gauternized chitosan compounds.
- 15 The amount of the antimicrobial agent applied to the cellulosic fiber and contained within the cleaning article can vary in accordance with various factors including, the intended function of the antimicrobial agent, the intended end-use of the article, the desired longevity of the article, the relative amounts of the other components present within the formulation, the weight percent of cellulosic fiber in the sheet, etc. A significant factor in determining suitable add-on levels for the antimicrobial agent is whether the
- 20 antimicrobial agent is intended to sanitize hard surfaces wiped by the fibrous sheet or whether the antimicrobial is merely intended to limit or prevent the growth of microbes within the sheet itself. It will be readily appreciated that applications intended to sanitize hard surfaces wiped by the fibrous sheet will require significantly higher add-on levels of the antimicrobial agent(s). The amount of antimicrobial agent applied to the cellulosic fibers can be between about 0.01% and about 10% by weight (based
- 25 upon the weight of the dried treated cellulosic fibers). In certain embodiments intended to sanitize hard surfaces, the antimicrobial agent is present in the sheet in amounts between about 0.1% and about 8% by weight, or between about 0.5% and about 4% by weight (based upon weight of the dry wipe). In still other embodiments in which the antimicrobial agent is merely intended to limit or prevent microbial growth within the sheet, the antimicrobial agent is present in amounts between about 0.01%
- 30 and about 0.1% by weight (based upon the weight of the dry wipe).

The antimicrobial agent is desirably present on between about 55% and 100% of the area of the fibrous sheet. In certain embodiments, a first outer surface of the sheet can have the antimicrobial

agent applied thereto and/or present on at least 55%, 70% or 90% of the surface area of said first surface or of the entire sheet surface area. In certain embodiments, the antimicrobial treatment can be present upon 100% of the surface area of the first surface and/or all surfaces of the fibrous web.

Further, as applied, the antimicrobial agent may also be present through the entire thickness of the sheet.

The cellulosic fibers of the cleaning sheet may be treated with the antimicrobial agent in one or more ways known in the art. In one aspect, an antimicrobial agent can generally be combined with the cellulosic fibers as part of the papermaking process. For example, the antimicrobial agent can be added during the preparation of the fibrous slurry used to form the web or a pre-cursor material used to form the web. In one embodiment, a conventional papermaking fiber stock prep beater or pulper is initially provided with a liquid (e.g. water) to which the antimicrobial agent is added. The amount of antimicrobial agent added to the pulper can generally vary to achieve the various loadings noted above. In some embodiments, the antimicrobial agent may be added to the pulper in an amount up to about 5 percent by weight of the treated fibrous material, in other embodiments between about 0.04 percent to about 1.0 percent by weight of the treated fibrous material.

While present within the pulper, the antimicrobial agent can become releasably attached to the cellulosic fibrous material. Specifically, partially charged groups present on cellulosic fibers (e.g., hydroxy moieties) can form ionic and/or associative bonds with the positively charged portion of the antimicrobial agent. Moreover, when subjected to continuous agitation, such as occurs in a typical pulping operation, a greater likelihood exists that the antimicrobial agent will be brought into contact with any free partially charged groups on the cellulosic fibers. Thus, substantially all of the antimicrobial agent present within the pulper can become associatively bonded to the fibrous material. As such, any liquid that is later removed during the papermaking process, such as through gravity, vacuum boxes or shoes, dryer, and the like, can be substantially free of the antimicrobial agent. After the antimicrobial agent is mixed with the fibrous material within the pulper, the resulting fibrous slurry can optionally be diluted and readied for formation into a layer of fibrous material or cellulosic web utilizing conventional wet-laying or papermaking techniques.

In addition, the cellulosic fibers may be treated with the various agents by means known in the art such as, for example, spraying, printing, etc. In this regard, the antimicrobial agents may be applied across the surface of the sheet in one or more patterns as desired such as through the use of rotogravure or gravure printing (direct or indirect), flexographic printing, screen printing, digital, spray, stencil application and so forth.

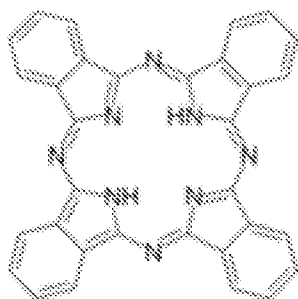
Indicator

Dyes suitable for use with the present invention are capable for preferentially forming a complex with the antimicrobial agent relative to the cellulosic material and further are highly resistant to oxidation and reduction. Preferably the dye will be color stable resistant to oxidation and reduction and have an

5 ORP of between 0 and 1.61 V. In certain embodiments the dye may have an ORP of between 0.5 and 1.6 V. As used herein, ORP values of agents are determined under standard conditions (e.g. 1 molar concentration, 25°C, 1 ATM). Dyes suitable for use in the present invention include

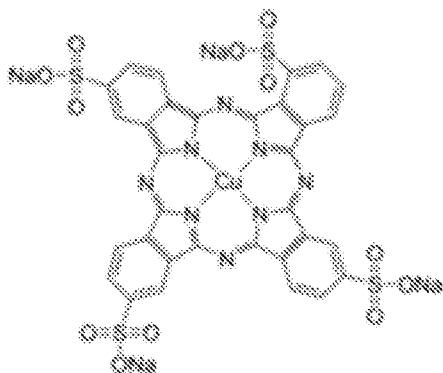
metallophthalocyanines. The phthalocyanine ring, as shown below, is an intensely blue-green-colored aromatic macrocyclic compound, however other colors can be achieved by the formation of

10 coordination complexes with one or more elements, particularly metals.



Many derivatives of the parent phthalocyanine are known, such as where either carbon atoms of the macrocycle are exchanged for nitrogen atoms or where the hydrogen atoms of the ring are substituted by functional groups like halogens, hydroxy, amino, alkyl, aryl, thiol, alkoxy, nitro, sulfonic acid groups

15 and so forth. As a specific example, metallophthalocyanines such as copper (II) phthalocyanine tetrasulfonic acid tetra sodium salt (Acid Blue 249, shown below), is intensity colored and chemical resistant.



Other indicator agents believed suitable for use with the present invention include ultramarines and iron oxides. Ultramarines comprise complex aluminum sulfosilicate lattices having a general formula of $\text{Na}(\text{AlSiO})\text{S}$, the proportions varying with color. Ultramarine blue, for example, has the following approximate formula: $\text{Na}_7\text{Al}_6\text{Si}_6\text{O}_{24}\text{S}_3$

- 5 Ultramarine blue can, in one aspect, be obtained by calcining a mixture of kaolin, sulfur, sodium carbonate, and carbon at temperatures above 700°C . Various ultramarines include CAS nos. 1317-97-1; 1345-00-2; 11116-33-55; 12703-66-1; 12769-96-9; 57455-37-5 and so forth. These are available as violet, pink, green and orange colors.

- Iron oxides include, for example, FeO ; FeOOH ; Fe_2O_3 ; Fe_3O_4 and mixtures thereof. Various iron oxides
10 include CAS Nos. 1345-25-1; 1309-37-1; 1309-38-2; 1332-37-2; 12227-89-3; 20344-49-4; 51274-00-1; 64294-91-3 and so forth. The hydrated forms of iron oxides are also believed suitable for use herein.

- The indicator agent is desirably applied to less than the entire cleaning sheet. In certain embodiments, a first planar surface of the sheet can have the indicator agent applied thereto covering less than about 50% of the surface area of the entire fibrous sheet or less than about 50% of the surface area of the
15 first surface of the sheet. In certain other embodiments, the indicator agent may be applied to and present on between about 1% and about 45% of the surface area of the first surface, or between about 2% and 30% of the surface area of the first surface of the sheet or even between about 5% and about 20% of the surface area of the first surface of the sheet. In further embodiments, the indicator agent may be applied in such a manner to both the opposed first and second surfaces of the web and, in
20 certain embodiments, also through the entire depth of the sheet. When applied to both the first and second planar surfaces of the cleaning article, the graphics may be the same or different from one another. The indicator agent can be applied as a single contiguous graphic or, alternatively, as a plurality of discrete graphics. The indicator can be applied in any one of various graphics including, but not limited to, a pattern of contiguous or discrete lines, circles, dots, icons, images, characters, etc.
- 25 In addition, more than one indicator dye may be used to provide a graphic with a plurality of visually distinguishable colors. In particular embodiments, indicator agent may be applied by depositing the same upon a preformed sheet or fabric containing the cellulosic material with the antimicrobial agent bonded thereto. The indicator may be applied to present the desired graphic or visual by the use of rotogravure or gravure printing (direct or indirect), flexographic printing, screen printing, stencil
30 application and so forth.

With regard to application of the indicator agents, the method also includes a drying step. The indicator agents as applied to the cellulosic fibers, together with the associated solvents, may be dried using one or more means known in the art such as, for example, heating by conveying the treated sheet material over heated cans or roller (e.g. a Yankee dryer), passing hot dry air through the treated sheet material (e.g. through air dryer), and other forms of heating (e.g. use of infrared heaters, UV lights, etc.).

Additional Treatments

The base sheet and fibers therein may optionally contain and/or be treated with one or more components to improve or modify certain attributes or functions of the cleaning sheet. In one aspect the base sheet may further contain one or more surfactants or detergents. Such compounds are known to improve the wettability of fabrics, aid various aqueous cleaning actions and in certain instances can also aid in the effectiveness of the antimicrobial agent. In addition, the fibrous sheet and/or fibers may optionally contain and/or be treated with other additives including, but not limited to sequestrants, solvents, pH modifiers, wet strength resins, binders, antistatic agents, fragrances, and so forth. By way of example, various additives believed suitable for use in combination with the present invention are described in US7838447 to Clark et al., the entire contents of which are incorporated herein to the extent consistent herewith.

Examples

Example 1

X-80 HYDROKNIT® wipes (Kimberly-Clark Professional, Roswell, Georgia) comprising wood pulp fibers and polypropylene spunbond fibers, were cut into 6 inch x 6 inch squares. The wiper sheets were treated with a 0.5% wt/wt solution of water and Chitosan (Sigma-Aldrich Chemical Company, Milwaukee, Wisconsin). The chitosan solution was applied to the wiper sheets drop-wise in discrete locations via a Pasteur pipette. The wiper sheets were then dried in an oven at 85°C for 5 minutes. The dried wiper sheets were then dipped into a solution of 5% wt/wt copper phthalocyanine tetrasulphonic acid, tetra sodium salt (Sigma-Aldrich Chemical Company, Milwaukee, Wisconsin) in water and placed onto a paper towel. The treated wiper sheets were blue in color although they were darker blue in the areas treated with the chitosan solution. The wiper sheets were then rinsed in room temperature water; the rinsed wiper sheets retained the blue color only in the areas treated with the chitosan solution evidencing that the coloring agent preferentially binds with the applied chitosan and not the wood pulp or polyolefin fibers. The rinsed wiper sheets were dried and then placed for 5 hours

into a container of undiluted household bleach (Clorox Concentrated Regular-Bleach, from Clorox Company of Oakland, CA). No discharge of the blue color or leaching of the blue color was observed evidencing the stability of both the coloring agent and chitosan-coloring agent complex.

Example 2

5 X-80 HYDROKNIT® wipes were also obtained for use in this example. Wiper sheets were set aside untreated ("control samples") and other wiper sheets were treated with an aqueous solution of CARBOQUAT® H (from Lonza of Allendale, New Jersey) to provide a wiper sheet having 0.5% by weight quaternary ammonium antimicrobial agent therein ("treated samples"). A 0.1% wt/wt water solution of ultramarine blue (from Hilton Davis, Cincinnati Ohio) was made and applied to both control
10 samples and treated samples. The samples were then dried in a convection oven at 85°C for 10 minutes. The dried samples were then subjected to 3 minutes of hand washing in a cleaning solution followed by drying in a convection oven. The cleaning solution consisted of 5 ml household dishwashing liquid (AJAX® dishwashing soap, Colgate-Palmolive Company of New York, New York) in 1 liter of room temperature water. On visual inspection after the hand washing, the control samples
15 had lost all of the color whereas the treated samples had retained the blue color of the ultramarine blue. The treated samples were then subjected to multiple 3-minute hand wash cycles with drying after each washing. Upon visual inspection after each washing cycle, it could be seen that the blue color slowly faded evidencing that the antimicrobial/dye complex was slowly washed out from the treated samples.

20 Example 3

The control and treated samples described in Example 2 were again made and used in this example. A 0.1% wt/wt solution of water and iron oxide (BF Goodrich, Cincinnati, Ohio) was made and applied to both the treated and control samples. These wipes were dried in a convection oven at 85°C for 10 minutes. The cleaning solution described in Example 2 was again prepared and used to subject the
25 samples to 3 minutes of hand washing followed by drying in a convection oven. On visual inspection the control samples had lost all of the black color whereas the treated samples retained the black color of the iron oxide. The treated samples were subjected to multiple 3-minute hand wash cycles with drying after each washing. Upon visual inspection after each washing cycle, it could be seen that the black color slowly faded evidencing that the antimicrobial/dye complex was slowly washed out from the
30 treated samples.

Example 4 (Comparative)

- X-80 HYDROKNIT® wipers were also obtained for use in this example. Wiper sheets were treated with 0.5% wt/wt solution of water and Mackamine CO-SP (Lauramine oxide from Rhodia Group, St Louis, Missouri). The antimicrobial agent was applied to the wiper sheets drop-wise in discrete locations via a Pasteur pipette. The treated wiper sheets were then dried in the oven at 85° C for 10 minutes. The dry wipes were then dipped into a 0.1% wt/wt solution of water and copper phthalocyaninetetrasulfonic acid tetrasodium salt (Sigma-Aldrich Chemical Company, Milwaukee, Wisconsin). The treated wiper sheets were then rinsed with water. After rinsing, upon visual inspection it could be seen that the dye had been removed from both locations treated with the lauramine oxide as well as those locations lacking the lauramine oxide treatment.
- 10 The cleaning articles can, optionally, include one or more additional elements or components as are known in the art. Thus, while the invention has been described in detail with respect to specific embodiments and/or examples thereof, it will be apparent to those skilled in the art that various alterations, modifications and other changes may be made to the invention without departing from the spirit and scope of the same. It is therefore intended that the claims cover or encompass all
- 15 such modifications, alterations and/or changes.

CLAIMS

What is claimed is:

1. A cleaning article comprising:

5 a fibrous sheet comprising cellulosic fibers, said fibrous sheet having opposed first and second outer surfaces;

a cationic antimicrobial agent releasably attached to said cellulosic fiber;

a complex comprising a dye and said antimicrobial agent and wherein said complex is stable against oxidation and reduction having an ORP of between 0 and 1.61 V; and

10 wherein said complex forms a graphic and is present on less than about 25% of the area of the first outer surface of said sheet.

2. The cleaning article of claim 1 wherein said dye comprises a phthalocyanine compound and/or a derivative thereof.

3. The cleaning article of claim 1 wherein said dye is selected from the group consisting of metallophthalocyanines, ultramarines, iron oxides, and derivatives thereof.

15 4. The cleaning article of claim 1 wherein said dye comprises a metallophthalocyanine.

5. The cleaning article of claim 1 wherein said complex is water insoluble.

6. The cleaning article of claim 1 wherein said antimicrobial agent is selected from the group consisting of quaternary ammonium, biguanide compounds, chitosan, and derivatives thereof.

20 7. The cleaning article of claim 5 wherein the antimicrobial agent is ionically bonded to the cellulosic fibers.

8. The cleaning article of claim 1 wherein said fibrous sheet comprises at least 50% by weight cellulosic fibers, on a dry basis.

9. The cleaning article of claim 8 wherein said fibrous sheet comprises between 5% and 45% by weight polyolefin fibers.

10. The cleaning articles of claim 8 wherein said cationic antimicrobial agent is present on at least 50% of the area of the first outer surface of said sheet.
11. A cleaning article comprising:
- a fibrous sheet comprising cellulosic fibers;
- 5 a first region of the fibrous sheet having a complex formed by (i) a colored compound selected from the group consisting of a phthalocyanine compound, an ultramarine compound, an iron oxide compound, and/or a derivative thereof, and (ii) a cationic agent, wherein said complex is releasably attached to said cellulosic fibers by ionic bonding and further wherein said first region comprises less than about 45% of the area of said fibrous sheet;
- 10 a second region of the fibrous sheet having a cationic antimicrobial agent releasably attached to said cellulosic fiber by ionic bonding and being substantially free of colored compounds selected from the group consisting of a phthalocyanine compound, an ultramarine compound, an iron oxide compound, and/or a derivative thereof, said second region comprising greater than about 55% of the area of said fibrous sheet.
- 15 12. The cleaning article of claim 11 wherein said phthalocyanine compound comprises a metallophthalocyanine.
13. The cleaning article of claim 12 wherein said metallophthalocyanine is copper (II) phthalocyanine tetrasulfonic acid tetra sodium salt.
14. The cleaning article of claim 11 wherein said antimicrobial agent is selected from the group
20 consisting of quaternary ammonium, biguanide compounds, and chitosan.
15. The cleaning article of claim 11 wherein the cationic agent is selected from the group consisting of quaternary ammonium and biguanide compounds.
16. The cleaning article of claim 11 wherein said fibrous sheet comprises at least 50% by weight cellulosic fibers, on a dry basis.
- 25 17. The cleaning article of claim 16 wherein said fibrous sheet comprises between about 5% and about 45% by weight polyolefin fibers.

18. The cleaning articles of claim 17 wherein said cellulosic fibers are selected from the group consisting of hardwood and softwood pulps.

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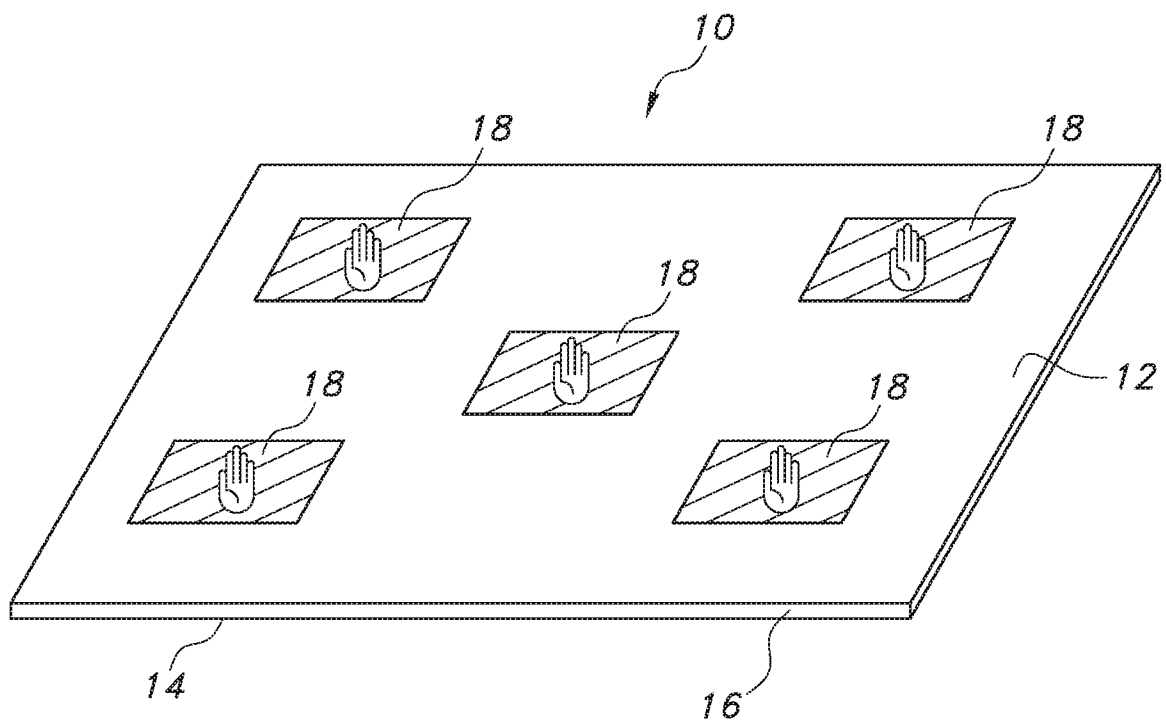


FIG. 1

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2016/034189**A. CLASSIFICATION OF SUBJECT MATTER****B08B 1/00(2006.01)I, A47L 13/16(2006.01)I, D01F 1/10(2006.01)I, D01F 2/00(2006.01)I**

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)

B08B 1/00; A01N 59/08; A47L 13/10; A47L 13/17; A61L 2/00; B32B 27/00; A47L 13/16; D01F 1/10; D01F 2/00

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

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

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

eKOMPASS(KIPO internal) & keywords: wiper, indicator, sheet, fiber, cationic antimicrobial agent, dye, oxidation, reduction, phthalocyanine

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4678704 A (FELLOWS, ADRIAN N.) 07 July 1987 See column 1, line 24 - column 3, line 2 and claims 1, 6, 11.	1-18
Y	EP 0047101 A2 (VEDALE LIMITED) 10 March 1982 See abstract, page 2, lines 20-26 and claim 1.	1-10
Y	US 7008600 B2 (KATSIGRAS et al.) 07 March 2006 See abstract and column 1, lines 15-32; column 13, line 60 - column 14, line 11.	2-4, 11-18
A	US 2005-0160543 A1 (CATALFAMO et al.) 28 July 2005 See paragraphs [0043]-[0052].	1-18
A	US 2005-0125926 A1 (REKUM et al.) 16 June 2005 See abstract and claim 1.	1-18

☐ 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 but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"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

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2016/034189

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