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(71) Applicant (for all designated States except US): **GLAXO GROUP LIMITED** [GB/GB]; Glaxo Wellcome House, Berkeley Avenue, Greenford Middlesex UB6 0NN (GB).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **KING, Simon** [GB/GB]; GlaxoSmithKline, St George's Avenue, Weybridge Surrey KT13 0DE (GB). **STOVELL, Alex** [GB/GB]; GlaxoSmithKline, St George's Avenue, Weybridge Surrey KT13 0DE (GB).

(74) Agent: **WALKER, Ralph Francis**; GlaxoSmithKline, Global Patents CN925.1, 980 Great West Road, Brentford Middlesex TW8 9GS (GB).

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(54) Title: FILTER MATERIAL AND FACE MASK AGAINST PATHOGENS

(57) Abstract: An air filter material comprising an air permeable substrate having a composition comprising a poly-(carboxylic acid) polymer; a monomeric carboxylic acid; and an anionic and/or non-ionic surfactant deposited on it wherein the weight ratio monomeric carboxylic acid : poly-(carboxylic acid) polymer is in the range 10 : 1 to 2 : 1, and the loading of the composition on the substrate is 1-20 g/m². The air filter material is suitable for a face mask to neutralize airborne viral and bacterial pathogens.



FILTER MATERIAL AND FACE MASK AGAINST PATHOGENS

This invention relates to a novel device being an air filter material able to remove and neutralize harmful airborne pathogens such as viruses and microorganisms from inhaled air contaminated with such pathogens, and from contaminated air exhaled from patients infected with such pathogens. The invention further relates to a face mask incorporating such an air filter material, and a process and materials for making the filter material.

In the course of history pandemics of Influenza have occurred, of which the “Spanish flu” pandemic of 1918 was the largest pandemic of any infectious disease known to medical science (Oxford, J. S., 2000). The three strains which caused these pandemics belong to group A of the influenza virus and, unlike the other two groups (B and C), this group infects a vast variety of animals (poultry, swine, horses, humans and other mammals). Influenza A virus continue to cause global problems, both economically and medically (Hayden, F. G. & Palese, P., 2000). A recent concern has been the avian Influenza A H5N1 virus, so called “bird flu” which first demonstrated its ability to infect birds in China in 1997 and has since spread to other countries in South East Asia, Europe and Africa (Enserink, M, 2006; Guan, Y. *et al.*, 2004; Peiris, J. S. *et al.*, 2004). The ability of H5N1 to cause severe disease in birds was documented by the World Health Organisation during a mild outbreak in South East Asian birds during 2003-2004. H5N1 mutates rapidly and is highly pathogenic. Currently the H1N1 virus, so called “swine flu”, has appeared in humans and risk of an H1N1 virus pandemic is of particular concern.

In addition to these influenza viruses, other viruses and bacteria are of concern in certain environments such as hospitals, where they might infect vulnerable patients. Even the so called “common cold” caused by Human Rhinovirus HRV can cause risks to such patients. Examples of bacteria of concern are gram negative bacteria such as *E. Coli* and gram positive bacteria such as *S.aureus*. It is known that anti-bacterial agents which are effective against gram negative bacteria may not be as effective against gram positive, and vice versa. A need exists for antibacterial materials which are comparably effective against both Gram negative and Gram positive bacteria.

Much has been done to control and prevent another pandemic from occurring with many anti-influenza products (vaccines and treatments) currently on the market. Presently, Amantadine is the principal antiviral compound against Influenza infections,

but its activity is restricted to Influenza A virus. Anti-neuraminidase inhibitors, such as Zanamivir (Relenza) and Oseltamivir (Tamiflu), are a new class of antiviral agents licensed for use in the treatment of both Influenza A and B infections (Carr, J., *et al.*, 2002). The role of these antivirals in a pandemic may be limited due to the time and cost involved in
5 production and the current limited supply. With the recent threat of an H5N1 or H1N1 pandemic the need to prevent any risk of transmission of the virus to or between humans has become particularly important.

The inhalation of air contaminated by harmful virus and/or other micro-organisms is a common route for infection of human beings, particularly health workers and others
10 who work with infected humans or animals. Air exhaled by infected patients is a source of contamination. Face masks incorporating a suitable filter material would be ideal for use as a barrier to prevent species-to-species transmission of such virus and other microorganisms.

Air filters believed to remove such viruses and/or other micro-organisms are
15 known. One type of such a filter comprises a fibrous or particulate substrate on which is deposited a substance which captures or otherwise neutralizes virus and/or other micro-organisms of concern.

Three papers in Journal of Virology: Sept. 1968, p878-885; March 1970, p 313-320 and p 321-328, disclose antiviral activity of various polycarboxylic acids including
20 polyacrylic acid, polymethacrylic acid and polyacetal carboxylic acids. The antiviral activity reported therein appears to be a cell-mediated effect, and the conclusion is expressed that "*PMAA (polymethacrylic acid) did not inactivate the virus particle in its extracellular state*".

Examples of disclosures of such filters are listed below.

25 US-A-3,871,950 and US-A-4,181,694 disclose hollow fibres of acrylonitrile polymers for ultrafilter use, primarily for filtering aqueous media. US-A-4,856,509 discloses a face mask wherein select portions of the mask contain a viral destroying agent such as citric acid. US-A-5,767,167 discloses aerogel foams suited for filtering media for capture of micro organisms such as virus etc. US-A-5,783,502 discloses a fabric substrate
30 with anti viral molecules, particularly cationic groups such as quaternary ammonium cationic hydrocarbon groups bonded to the fabric. US-A-5,851,395 discloses a virus filter comprising a filter material onto which is deposited a virus-capturing material based on

sialic acid (9-carbon monosaccharides having a carboxylic acid substituent on the ring). US-A-6,182,659 discloses a virus-removing filter based on a Streptococcus agalactiae culture product. US-A-6,190,437 discloses an air filter for removing virus from the air comprising a carrier substrate impregnated with "iodine resins". US-A-6,379,794 discloses
5 filters based on glass and other high modulus fibres impregnated with an acrylic latex. US-A-6,551,608 discloses a porous thermoplastic material substrate and an antiviral substance made by sintering at least one antiviral agent with the thermoplastic substance. US-A-7,029,516 discloses a filter system for removing particles from a fluid comprising a non-woven polypropylene base upon which is deposited an acidic polymer
10 such as polyacrylic acid. US-A-2004/0250683 discloses a filter material comprising a network of fibres with an acidic substance deposited thereon, which may be an acrylic polymer. US-A-2005/0247608 discloses a filter block which may be treated with various anti viral polymers, principally cationic polymers.

WO-A-2001/07090 discloses a filter for removing micro-organisms comprising a
15 substrate having a reactive surface and a polymer on its surface which includes cationic groups for attracting micro organisms. WO-A-2002/058812 discloses an air filter with micro-encapsulated biocides. WO-A-2003/039713 discloses a filter material said to have an anti pathogenic effect, including an effect against virus, based on a fibrous substrate partly coated with a polymer network containing pendant functional groups which may
20 be acidic groups. WO-A-2005/070242 discloses an inhalation filter made of fibres treated to impart an electrical charge to catch particles such as virus.

GB-A-2035133 discloses a membrane filter with a water-insoluble polymer, preferably a PVA, on its surface. Use of such a filter material in gas mask cartridges is suggested.

25 JP-A-2001/162116 discloses an antibacterial filtration medium in which a self-cross-linking acrylic resin is used to bind a silver-organic iodine antibacterial agent to a fibrous substrate. JP-A-2005/198676 discloses the use of a water-hardenable resin emulsion to bind citric acid to an antiviral face mask.

WO-A-2008/009651 discloses a filter material which comprises an air permeable
30 substrate combined with an acidic polymer which is effective at neutralizing viruses in air passing through the material. This filter material is disclosed as suitable for face masks. A substrate disclosed therein is polyester, and acidic polymers disclosed therein are

polymers of acrylic acid available under the trade name "Carbopol"™, and polymaleic acid polymers available under the trade name "Gantrez"™. In the filter materials disclosed in WO-A-2008/009651 these acidic polymers are made into a solution together with citric acid and a surfactant for deposition onto the substrate. In WO-A-2008/009651 an anionic surfactant is used because ionic surfactants tend to increase the viscosity of such solutions and hinder deposition. WO-A-2010/144643 discloses a further use for such acidic polymers as a pathogen-neutralising surface coating on protective articles such as gloves, clothing etc.

There is an ongoing need to improve such filters. In particular there is a need for lighter weight filters which are effective at neutralizing influenza and other viruses and microorganisms from airstreams. The present invention addresses this need. Other objects and advantages of the present invention will be apparent from the following description.

According to a first aspect of this invention there is provided an air-permeable filter material comprising an air permeable substrate having deposited thereon a composition comprising:

- a poly-(carboxylic acid) polymer;
- a monomeric carboxylic acid;
- an anionic and/or non-ionic surfactant;

wherein the weight ratio of poly-(carboxylic acid) polymer : monomeric carboxylic acid is in the range 1 : 10 to 1 : 2, and the loading of the composition on the substrate is 1-20 g/m².

It is found that the above composition enables effectiveness of neutralization of airborne viruses and other pathogens even at the above-mentioned low loading onto the substrate. In turn this low loading facilitates the use of the filter material to provide a lightweight face mask which for example is suitable for surgical or hospital uses, and which is easier to fold flat.

The air-permeable substrate may comprise a fibrous material, which can be a woven or non-woven material. Examples of woven materials include those natural and synthetic fibers such as cotton, cellulose, wool, polyolefins, polyester, polyamide (e.g. nylon), rayon, polyacrylonitrile, cellulose acetate, polystyrene, polyvinyls and any other synthetic polymers that can be processed into fibers. Examples of non-woven materials

include polypropylene, polyethylene, polyester, nylon, PET and PLA. Non-woven material is preferred. Such a material may be in the form of a non-woven sheet or pad.

Polyester fibre, especially non woven polyester, is a preferred air-permeable substrate because it is found that the poly-(carboxylic acid) polymer of the types described herein adhere better to polyester material. There appears to be less tendency for such polymers to visibly flake or rub off a polyester substrate. Polyester fibres and fabrics made therefrom are well known. The term "polyester" as used herein is a generic name for a manufactured fibre being a polymer with units linked by ester groups. A common polyester used for woven and non-woven fibre manufacture is polyethylene terephthalate, comprising:



units. The fibrous material may comprise such a polyester, or may be a blend of such a polyester and one or more other fibrous material.

The grade of fibrous material used may be determined by practice to achieve a suitable through-flow of air, and the density may be as known from the face-mask art to provide a mask of a comfortable weight.

Typical fibrous, e.g. non-woven materials, e.g. polyester, found suitable for use in this invention have weights 5 – 50 g/m², preferably 10 - 40 g/m², especially 30 - 40 g/m². Such weights are found to facilitate a comfortably lightweight face mask. Such materials are commercially available. Other suitable materials can be determined empirically.

It has been found that poly-(carboxylic acid) polymers are effective at capturing and neutralizing virus in air passing through such a material. Virus particles are believed to be dispersed in the air in small droplets of water. Without being limited to a specific theory of action it is believed that upon contact with the surface of the substrate the virus interacts with the poly-(carboxylic acid) polymer, become entrapped, and then the localised low pH environment (e.g. ca. pH 2.8 to 5) of the poly-(carboxylic acid) polymer inactivates the virus to thereby neutralize it. It is believed that the filter material of this invention may be effective in this manner against, among others, the virus that cause colds, influenza, SARS, RSV, H5N1 and H1N1 and mutated serotypes of these.

Poly-(carboxylic acid) polymers are typically polymers which include –COOH groups in their structure, or derivative groups such as acid-anhydride groups, readily cleavable carboxylic acid ester groups or salified –COOH groups which readily cleave to

yield -COOH groups. A poly-(carboxylic acid) polymer may have its -COOH groups (or derivative groups) directly linked to its backbone, or the polymer may be a so-called grafted or dendritic polymers in which the -COOH (or derivative) groups are attached to side chains branching off from the backbone.

5 Suitable poly-(carboxylic acid) polymers include -CR¹.COOH- units in their structure, wherein R¹ is preferably hydrogen, or R¹ may be C₁₋₃ alkyl, C₁₋₃ alkoxy or C₁₋₃ hydroxy alkyl.

A first type of such a poly-(carboxylic acid) polymer comprises a polymer having units:



in its structure wherein R^2 and R^3 are independently preferably hydrogen, or may be C_{1-3} alkyl or C_{1-3} alkoxy. For example such a polymer may comprise a poly-(carboxyvinyl) polymer, for example a polymer of a monomer compound of formula $CR^2R^3=CR^1.COOH$ wherein the substituents are as defined above. An example of such a poly-(carboxylic acid) polymer is carboxypolymethylene. Such a poly-(carboxylic acid) polymer may comprise a polymer of acrylic acid or methacrylic acid, i.e. polyacrylic or polymethacrylic acid, e.g. linear polyacrylic and polymethacrylic acid homo- or co- polymers. Polyacrylic acid polymers are preferred.

Homopolymers are preferred because copolymers can interact with anionic surfactants to significantly build viscosity. This can cause difficulties in applying the composition to the substrate. Homopolymers do not interact with anionic surfactants to the same degree. Also homopolymers can have a relatively low salt tolerance, which can result in viscosity reduction in the presence of ions such as ions from the monomeric carboxylic acid, e.g. citrate from citric acid. These effects can be advantageous if the composition is applied in aqueous solution form as described below, for which a low solution viscosity, typically that of a mobile watery liquid, is preferred. Such a poly-(carboxylic acid) polymer, e.g. a homopolymer polyacrylic acid, may be cross-linked for example with a polyalkenyl ether, allyl ether, e.g. of pentaerythritol, of sucrose or of propylene. Typically such polymers are those described in the art as “lightly crosslinked”, for example as made by performing the polymerization in ethyl acetate. Typically such poly-(carboxylic acid) polymers may have a molecular weight of 50,000 to 5,000,000, typically around 500,000 – 700,000, e.g. around 600,000.

Suitable polyacrylic acid homopolymers are commercially available under the trade name Carbopol™. Examples of such Carbopol™ polymers are the specific Carbopols 971P and 974P.

A second type of such a poly-(carboxylic acid) polymer is one which includes
 5 adjacent $-\text{CR}^4\text{.COOH}-$ units in its structure wherein R^4 is preferably hydrogen, or R^4 may be C_{1-3} alkyl, C_{1-3} alkoxy or C_{1-3} hydroxy alkyl. Examples of such poly-(carboxylic acid) polymers are those based on maleic acid moieties which typically include $-\text{[CH.COOH-CH.COOH]-}$ units, and/or salts or esters of such units, or such units in anhydride form in which COOH groups on adjacent carbon atoms may be cyclised to form a $-\text{CH.CO-O-}$
 10 CO.CH- ring system, such derivatives being susceptible to hydrolysis to form the corresponding free acid.

One embodiment of this second type of such a poly-(carboxylic acid) polymer comprises units with pairs of carboxylic acid groups on adjacent polymer chain carbon atoms. For example such polymers may comprise units:

15 $-\text{[CR}^5\text{R}^6 - \text{CR}^7\text{R}^8 - \text{CR}^9\text{.COOH} - \text{CR}^{10}\text{.COOH]-}$

in its structure wherein R^5 , R^6 , R^7 , R^8 , R^9 and R^{10} are independently hydrogen (preferred) or C_{1-3} alkyl or C_{1-3} alkoxy, preferably R^5 and R^6 being hydrogen, R^7 being hydrogen R^8 being methoxy, and R^9 and R^{10} being hydrogen, or a derivative thereof retaining COOH groups in its structure, or groups readily hydrolysable to COOH groups. An example of
 20 such a poly-(carboxylic acid) polymer is the polymer based on a copolymer of methyl vinyl ether and maleic anhydride.

An example of this second type of such a poly-(carboxylic acid) polymer comprises:

25 $-\text{[CH}_2\text{-CH.OCH}_3\text{-CH.COOH} - \text{CH.COOH]-}$

units in its structure. Such polymers may be linear polymers or cross linked polymers, and both of such types are commercially available under the Gantrez™ trade name. Linear, non-cross linked, polymers of this type are commercially available under the trade name Gantrez™ S (CAS # 25153-4-69), e.g. Gantrez™ S-96 having a molecular weight ca.700,000, Gantrez™ S-97 having a molecular weight ca. 1,200,000. Such Gantrez™
 30 polymers are preferred. In experiments it was found that that a filter material comprising such a Gantrez polymer retained a surface pH below pH 3.5, suitable to kill viruses, even after 24 hours of immersion in water.

An example of this second type of such a poly-(carboxylic acid) polymer being a derivative of such an acid is an anhydride, i.e. in which the two adjacent –COOH groups are cyclised to form a –CH.CO–O.CO.CH– ring system, such an anhydride is susceptible to hydrolysis to form the corresponding free acids. Such polymers are commercially available under the trade name Gantrez™ AN (CAS # 9011-16-9), e.g. Gantrez™ AN-119, Gantrez™ AN-903, Gantrez™ AN-139, Gantrez™ AN-169.

Another example of this second type of such a poly-(carboxylic acid) polymer is a derivative being a partial salt, e.g. where some of the free –COOH groups are converted into a metal salt of a Group I or Group II metal such as respectively either sodium or calcium, or a mixed sodium-calcium salt. Such a polymer is commercially available under the trade name Gantrez™ MS, e.g. Gantrez™ MS-955 (CAS # 62386-95-2).

Another example of a derivative of such an acid is a partial ester in which some of the free –COOH groups are esterified with C₁₋₆ alkyl e.g. ethyl or n-butyl. Such polymers are commercially available under the trade name Gantrez™ ES, e.g. Gantrez™ ES-225 (CAS # 25087-06-03) or Gantrez™ ES-425 (CAS # 25119-68-0).

Typically polymers of this second type have molecular weights in the range 200,000 – 2,000,000.

Other poly-(carboxylic acid) polymers of this type include copolymers of C₁₀₋₃₀ alkyl acrylates and one or more monomer compound of formula R¹¹R¹²C=CR¹³-COO R¹⁴, wherein each of R¹¹, R¹², R¹³, and R¹⁴ is independently selected from hydrogen or C₁₋₅ alkyl, in particular methyl, ethyl or propyl. Examples of such monomer compounds include esters of acrylic acid and methacrylic acid.

The term “monomeric carboxylic acid” used herein includes aliphatic saturated and unsaturated, and aromatic, carboxylic acids, hydroxy-carboxylic acids and amino-carboxylic acids. Suitable aliphatic monomeric carboxylic acids comprise a C₁₋₄ alkylene moiety substituted with at least one –CO.OH group, and optionally one or more –OH and/or –NH₂ group. The monomeric carboxylic acid is preferably a solid acid. Examples of such solid monomeric carboxylic acids include salicylic, fumaric, benzoic, glutaric, lactic, citric, malonic, acetic, glycolic, malic, adipic, succinic, aspartic, phthalic, tartaric, glutamic, pyroglutamic, gluconic acid, and mixtures of two or more thereof. Citric acid is preferred.

Typically the weight ratio of poly-(carboxylic acid) polymer : monomeric carboxylic acid is in the range 1 : 6 to 1 : 3. For example the poly-(carboxylic acid) polymer may be

one as mentioned above which includes $-CR^1.COOH-$ units in its structure, such as the above mentioned polyacrylic acid homopolymer poly-(carboxylic acid) polymers or poly-(carboxylic acid) polymers based on maleic acid moieties, and the monomeric carboxylic acid may be citric acid, and may be used in the above mentioned ratio range 1 : 6 to 1 : 3.

5 The surfactant can facilitate wetting of the filter material. Airborne pathogens such as viruses are known to be carried in small droplets of water, and consequently enhanced wetting of the filter material can enhance the effective contact between the pathogen and the active materials on the filter material. Furthermore surfactants are known to be effective in disrupting the membranes of virus and bacteria.

10 The surfactant(s) in the composition may comprise solely one or more anionic surfactant, or solely one or more non-ionic surfactant, or a mixture of one or more anionic surfactant and one or more non-ionic surfactant. It is found that a composition according to this invention containing one or more non-ionic surfactant may be effective in neutralizing viruses. However it is found that a composition containing a combination
15 of one or more anionic surfactant with one or more non-ionic surfactant may be effective in neutralizing both viruses and bacteria. Also a non-ionic surfactant has been found to stabilise the anionic surfactant in such a combination. At relatively high surfactant concentration levels, particularly in the presence of high ionic strength, ionic surfactants can precipitate out due to a phenomenon called the "Krafft Point"; inclusion of a non-
20 ionic co-surfactant can help prevent this occurring.

Preferred anionic surfactants are selected from alkali metal alkyl sulphates of general formula $(C_nH_{2n+1})-SO_4^- M^+$ where n is 8-20, preferably 10-15 especially 12, and M is an alkali metal, especially sodium. A preferred anionic surfactant of this type is sodium lauryl sulphate $C_{12}H_{25}SO_4Na$.

25 Examples of non-ionic surfactants include fatty alcohols such as cetyl alcohol, stearyl alcohol, cetostearyl alcohol, oleyl alcohol; polyoxyethylene ether type surfactants such as polyoxyethylene glycol alkyl ethers; polyoxypropylene glycol alkyl ethers; polyoxyethylene glycol octylphenol ethers such as Triton X-100™; polyoxyethylene glycol alkylphenol ethers; glycerol alkyl esters and sorbitan alkyl esters.

30 Preferred non-ionic surfactants include polyoxyethylene ether type surfactants such as polyoxyethylene sorbitan monolaurate, e.g. the commercially available materials sold under the name Polysorbate™, such as Polysorbate 20™, and the polyethylene glycol

p-(1,1,3,3-tetramethylbutyl) phenyl ether (Octoxynol) materials sold under the name Triton™, such as Triton X-100™.

When a combination of one or more anionic surfactant with one or more non-ionic surfactant is used a suitable weight ratio of anionic surfactant : non-ionic surfactant is in the range 4 : 1 – 1 : 4, preferably around 1 : 1 e.g. 1+/- 0.1 : 1+/- 0.1. A suitable combination of anionic surfactant and non-ionic surfactant is anionic sodium lauryl sulphate and a non-ionic polyoxyethylene ether type surfactant such as Triton X-100™.

Typically the weight ratio of poly-(carboxylic acid) : surfactant(s) in the filter material may be in the range 4 : 1 to 1 : 4, preferably 2 : 1 to 1 : 2, especially 2 : 1 – 1 : 1.

Additional substances may be incorporated into the filter material, for example additional substances to optimize the properties and anti-viral and/or antibacterial effectiveness of the filter material.

For example the composition may contain an alkali. An alkali in the composition can help to achieve a suitable pH environment for neutralization of pathogens. A suitable alkali is an alkali metal hydroxide such as sodium hydroxide. As described below the composition may be applied to the substrate as a dispersion or solution in a liquid vehicle, and the quantity of alkali used may conveniently be determined based on the pH of such a dispersion or solution.

For example the filter material may incorporate one or more metal salt, for example selected from salts of silver, zinc, iron, copper, tin and mixtures thereof. Such salts may have antibacterial activity. These may be inorganic salts such as those of mineral acids such as chloride, nitrate or sulphate, or organic salts. An example of a metal salt of this type is zinc chloride.

For example the filter material may incorporate one or more antimicrobial compound. Suitable examples of such compounds include quaternary ammonium compounds such as benzalkonium chloride or cetrimide; phenolic compounds such as triclosan or benzoic acid; biguanides such as chlorhexidine or alexidine; or mixtures thereof.

Although in general a high loading of the poly-(carboxylic acid) polymer on the substrate is desirable to achieve high effectiveness against pathogens, it is found that this needs to be balanced against the disadvantage that too high a loading can result in blockage of the passage of air through the filter material. Also when the filter material is

used in a face mask too high a loading can make the mask bulky, and in particular difficult to fold flat. The present loading of the composition on the substrate of 1-20 g/m² is found to combine antiviral efficacy with flexibility and a suitably low bulk that facilitates folding a mask flat. Preferably the loading of the composition on the substrate is 5-15 g/m² especially around 5-10 g/m².

A preferred filter material according to this invention comprises a non-woven polyester substrate of weight 30 - 40 g/m², e.g. around 34 g/m², having deposited thereon a composition comprising a poly-(carboxylic acid) polymer selected from polyacrylic acid homopolymer cross-linked with allyl pentaerythritol or allyl sucrose, with a molecular weight of 50,000 – 5,000,000 such as Carbopol 971P or 974P; citric acid, at a poly-(carboxylic acid) : citric acid ratio 1:6 - 1:3; and a surfactant being either sodium lauryl sulphate, or a mixture of sodium lauryl sulphate : Triton X-100 (Octoxynol); at a ratio of poly-(carboxylic acid) : surfactant of 2:1 – 1:1; at a loading of the composition of around 5 - 15 g/m².

Another preferred filter material according to this invention comprises a non-woven polyester substrate of weight 10 - 40 g/m², e.g. around 34 g/m² having deposited thereon a composition comprising a poly-(carboxylic acid) polymer based on maleic acid moieties which include $[-CH.COOH-CH.COOH-]$ units, with a molecular weight of 200,000 – 2,000,000 such as Gantrez S97; citric acid, at a poly-(carboxylic acid) citric acid ratio 1:6 - 1:3; and a surfactant being either sodium lauryl sulphate, or a mixture of sodium lauryl sulphate : Triton X-100 (Octoxynol) at a ratio of poly-(carboxylic acid) : surfactant of 2:1 – 1:1; at a loading of the composition of around 5 - 15 g/m².

The filter material described herein may be made by a method of dissolving or dispersing the component poly-(carboxylic acid) polymer(s), the monomeric carboxylic acid(s) and the anionic and/or non-ionic surfactant(s), wherein the weight ratio of poly-(carboxylic acid) polymer : monomeric carboxylic acid is in the range 1 : 10 to 1 : 2; and any other components as mentioned herein such as one or more alkali, metal salt or antimicrobial agent, in a liquid vehicle, wetting the substrate material with the so-formed solution or dispersion (a so-called "loading solution") and causing or allowing the liquid vehicle to evaporate to thereby leave the composition deposited on the substrate at the loading of 1-20 g/m².

Suitable and preferred components, combinations of components and ratios of components of such a loading solution are as for the filter material described above, as the components are deposited upon the substrate in the same ratios on evaporation of the liquid vehicle.

5 A suitable pH of the loading solution is pH 2-3, e.g. 2.3+/-0.1, and this may be achieved by means of alkali such as sodium hydroxide in the loading solution.

Preferably the components of the composition are made into a solution in the liquid vehicle.

10 The liquid vehicle may be aqueous, e.g. water or a mixture of water and an alcohol (e.g. methanol, ethanol, propanol), water being preferred.

Wetting of the substrate may be achieved by coating the substrate material with the loading solution for example by dipping the substrate into the loading solution, or spraying the substrate with the loading solution. On an industrial scale dipping is preferred for convenience. The wetted substrate may then be pressed to squeeze out
15 excess loading solution to facilitate achieving the defined loading. A suitable degree of pressing to achieve the desired loading can be determined experimentally. The wet substrate may then be dried e.g. by evaporation in the ambient air or in a drying tunnel. A suitable drying temperature, for example in such a tunnel, is ca. 70°C.

20 A loading solution suitable for use in the process for making the filter material is a further aspect of this invention.

An example of a loading solution according to this aspect of the invention comprises a solution of a poly-(carboxylic acid) polymer selected from polyacrylic acid homopolymer cross-linked with allyl pentaerythritol or allyl sucrose, with a molecular weight of 50,000 – 5,000,000 such as Carbopol 971P or 974P; citric acid, at a poly-
25 (carboxylic acid) citric acid ratio 1:6 - 1:3; and a surfactant being either sodium lauryl sulphate, or a mixture of sodium lauryl sulphate : Triton X-100 (Octoxynol); at a ratio of poly-(carboxylic acid) : surfactant(s) of 2:1 – 1:1; at a solution pH of 2.3+/-0.1.

Another example of a loading solution according to this aspect of the invention comprises a solution of a poly-(carboxylic acid) polymer based on maleic acid moieties
30 which include $[-CH.COOH-CH.COOH-]$ units, with a molecular weight of 200,000 – 2,000,000 such as Gantrez S97; citric acid, at a poly-(carboxylic acid) citric acid ratio 1:6 - 1:3; and a surfactant being either sodium lauryl sulphate, or a mixture of sodium lauryl

sulphate : Triton X-100 (Octoxynol); at a ratio of poly-(carboxylic acid) : surfactant(s) of 2:1 – 1:1; at a solution pH of 2.3+/-0.1.

In such loading solutions a suitable solution pH may be achieved by the addition of the above-mentioned alkali, such as sodium hydroxide, to the loading solution.

5 Loading solutions containing poly-(carboxylic acid) polymer based on maleic acid moieties which include $[-CH.COOH-CH.COOH-]$ units such as the Gantrez™ materials may benefit from the presence of a stabilizer in the loading solution for the Gantrez™ material. A suitable stabilizer is EDTA disodium salt at 100 ppm.

The concentration of the poly-(carboxylic acid) polymer, the monomeric
10 carboxylic acid and the anionic surfactant, and any other components such as the above-mentioned alkali, metal salts and other antimicrobial substances in the liquid vehicle, suitable methods of applying the loading solution onto the substrate, and pressing conditions to remove excess, drying conditions etc. necessary to achieve the above-mentioned loading of the composition on the substrate of $1-20 \text{ g/m}^2$ may be determined
15 experimentally. On a laboratory scale typically loading solutions containing 1-5 wt/% of dissolved solids, preferably 2-4 wt% have been found suitable. On a commercial production scale it is likely that 10-30 wt% of solids will be suitable to achieve such loadings.

Typically the filter material may be in sheet or pad form, generally corresponding
20 to the shape of a starting sheet or pad of the fibrous substrate. Such sheet or pad form filter materials are suitable for use in the above-mentioned face mask. Such sheet or pad form materials can be made into a suitable shape for a face mask of generally known shape in a known manner. Face masks can be made from filter materials of this invention using known mask-making processes, e.g. moulding or folding.

25 The present invention also provides a method of reducing the concentration of airborne pathogens, being virus or microorganisms, in air contaminated by such pathogens, by passing such contaminated air through a filter material as described herein.

Accordingly in a further aspect of this invention a face mask is provided
30 incorporating a filter material as described herein. The overall shape and construction of the face mask may be generally conventional in the field of face masks, and the means to

hold the mask in place on the user's face may for example comprise one or more elastic strap to be passed behind the user's head.

A face mask of this invention may comprise one, two, three or more layers of a sheet or pad form filter material of this invention. The filter material of the invention in sheet form can be adapted easily to the convex shape appropriate for fitting to a user's face. The face mask may additionally comprise one or more layer of a further material, e.g. one layer backing the filter material, or two layers sandwiching the filter material, optionally with one or more further layer. Such a further layer of material may be situated in the face mask such that when the mask is used the layer of further material is positioned between the filter material and the user's skin, as so called "comfort layer" to thereby reduce any irritation to the user's skin. Typically a lightweight face mask of the invention, suitable for use by a physician, may comprise an outer layer, an inner comfort layer, and between them a layer of a filter material of the invention. The construction of the outer and comfort layers may be generally conventional in the field of surgical face masks.

Such further material may be woven or non-woven material. Examples of woven materials include those natural and synthetic fibers such as cotton, cellulose, wool, polyolefins, polyesters, nylon, rayon, polyacrylonitrile, cellulose acetate, polystyrene, polyvinyls and any other synthetic polymers that can be processed into fibers. Examples of non-woven materials include polypropylene, polyethylene, polyester, nylon, PET and PLA. Non-woven is preferred, and such a material may be in the form of a non-woven sheet or pad. A suitable material for this further material is polyester, cellulose or non-woven polypropylene of the type conventionally used for surgical masks and the like. Suitable grades of non-woven polypropylene include the well known grades commonly used for surgical face masks and the like.

A layer of the filter material of the invention and a layer of such further material may for example be welded together, e.g. around their respective edges, e.g. by ultrasonic welding.

Generally face masks of this invention should be constructed to meet European Standard EN 14683:2005.

The filter materials of this invention may be used in other types of breathing air filter such as nose plugs. Such a filter may be of generally conventional form, incorporating the filter material of the invention.

The present invention will now be described by way of example only with
5 reference to the accompanying drawings.

Fig. 1 shows a perspective view of an oral and nasal filter in use.

Fig. 2 shows the filter of Fig. 1 unattached to the user.

Fig. 3 shows a section through the material of the face mask of Figs. 1-2.

Referring to Figs. 1, 2 and 3, a face mask for inhaled or exhaled air comprising
10 such a filter material of this invention is shown. The face mask 10 (overall) is of generally conventional construction comprising a pad (11) which may be attached over the nose and mouth of a user (12) by a conventional strap (13). The pad (11) comprises an outer layer (14) of the filter material of the invention welded to an inner polyester fibre pad (not visible), the outer layer (14) being in a position to intercept a stream of inhaled or
15 exhaled breathing air.

Fig. 3 shows a suitable layered construction of the mask of Figs 1- 2. There is a layer 91 of the filter material, an inner layer 92 of a non-woven polypropylene material which in use is against the user's skin, and an outer layer 93, of a non-woven polyester material. There may be plural layers 91, 92, 93.

20 In the laboratory scale Examples below loading solutions as indicated were used to deposit compositions onto a non-woven polyester substrate of weight 34 g/m^2 . The solutions were prepared in water, loaded onto the substrate by dipping into the solution, pressing to squeeze out excess solution, and then drying in air at 70°C . Suitable loading solution concentrations and process conditions to achieve the indicated loadings can be
25 determined experimentally.

Example No	Loading solution	Loading gm ⁻²	Kill data at (time)
1	Total solids 2.5 wt% Carbopol 974P 0.5 wt% Citric acid 1.63 wt% Sodium lauryl sulphate 0.37 wt% Sodium hydroxide qs to pH 2.3	5	<i>E.coli</i> 7.5 log (1 minute) <i>S. aureus</i> 7.4 log (1 minute) H1N1 3.6 log (1 minute)
2	Total solids 4.0 wt% Carbopol 974P 0.8 wt% Citric acid 2.61 wt% Sodium lauryl sulphate 0.59 wt% Sodium hydroxide qs to pH 2.3	10	<i>E.coli</i> 7.5 log (1 minute) <i>S. aureus</i> 7.4 log (1 minute) H1N1 6.2 log (1 minute) HRV-42 4.9 log (15 minutes)
3	Total solids 4.0 wt% Gantrez S97 0.8 wt% Citric acid 2.61 wt% Sodium lauryl sulphate 0.59 wt% Sodium hydroxide qs to pH 2.3	10	<i>E.coli</i> 6.3 log (1 minute) <i>S. aureus</i> 6.5 log (1 minute)
4	Total solids 4.0 wt% Gantrez S97 0.57 wt% Citric acid 2.86 wt% Sodium lauryl sulphate 0.57 wt% Sodium hydroxide qs to pH 2.3	10	<i>E.coli</i> 6.5 log (1 minute) <i>S. aureus</i> 6.2 log (1 minute) HRV-42 3.4 log (15 minutes)
5	Total solids 4.0 wt% Gantrez S97 0.57 wt% Citric acid 2.86 wt% Sodium lauryl sulphate 0.286 wt% Triton X-100 0.268 wt% Sodium hydroxide qs to pH 2.3	10	<i>E.coli</i> 6.0 log (1 minute) <i>S. aureus</i> 6.0 log (1 minute) HRV-42 2.7 log (15 minutes)

Virucidal and Bactericidal Efficacy Test Methods

The bactericidal and virucidal efficacy were assessed using protocols based on the AATCC Test Method 100-2004 Assessment of Antibacterial Finishes on Textile Materials, and were performed by challenging 2.5 cm x 2.5 cm squares of each coated substrate sample directly.

Two bacteria were tested separately, a gram negative bacteria *E.coli* (NCTC 10788) and a gram positive bacteria *S.aureus* (NCTC 12923).

Samples loaded with the composition of the invention, and respective non-loaded controls were exposed to 0.1ml of bacterial suspension containing around 8 log₁₀ using standard protocols. Each of the two selected bacteria was exposed for one minute. All tests were run in duplicate and survivors from samples were compared to survivors on samples of the same material without coating. The final log reduction results were calculated based on log₁₀ reduction. Reference uncoated substrate material was seen to

have no bactericidal activity.

Coated substrate materials were tested separately for two viruses, Influenza Type A virus H1N1 assessed by egg culture (EID₅₀/mL reduction) and Human Rhinovirus HRV-42 assessed by tissue culture (TCID₅₀/mL reduction). The tests were performed by

5 independent laboratories according to standard protocols.

The coated samples and respective controls were exposed to 0.2ml of viral suspension containing around 7 log₁₀ TCID₅₀/mL or 7 log₁₀ EID₅₀/mL. Each of the two viruses was exposed for the specified period of time. The survivors from samples were compared to survivors on samples of the same material without coating. The final log
10 reduction results were calculated based on log₁₀ reduction. Reference uncoated substrate material was seen to have no virucidal activity.

Claims.

1. An air-permeable filter material comprising an air permeable substrate having deposited thereon a composition comprising:

a poly-(carboxylic acid) polymer;

5 a monomeric carboxylic acid;

an anionic and/or non-ionic surfactant;

wherein the weight ratio of monomeric carboxylic acid : poly-(carboxylic acid) polymer is in the range 10 : 1 to 2 : 1, and the loading of the composition on the substrate is 1-20 g/m².

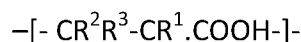
10 2. A filter material according to claim 1 wherein the air-permeable substrate comprises a fibrous material.

3. A filter material according to claim 1 or 2 wherein the fibrous material comprises non-woven polyester.

4. A filter material according to claim 1, 2 or 3 wherein the fibrous material has a weight 5 – 50 g/m².

5. A filter material according to any one of the preceding claims wherein the poly-(carboxylic acid) polymer includes -CR¹.COOH- units in its structure, wherein R¹ is hydrogen C₁₋₃ alkyl, C₁₋₃ alkoxy or C₁₋₃ hydroxy alkyl.

6. A filter material according to claim 5 wherein the poly-(carboxylic acid) polymer comprises a polymer having units:



in its structure wherein R² and R³ are independently hydrogen, C₁₋₃ alkyl or C₁₋₃ alkoxy.

7. A filter material according to claim 6 wherein the poly-(carboxylic acid) polymer comprises a poly-(carboxyvinyl) polymer.

25 8. A filter material according to any one of claims 5 to 7 wherein the poly-(carboxylic acid)polymer comprises a homopolymer of acrylic acid cross-linked with a polyalkenyl ether or allyl ether with a molecular weight of 500,000 – 700,000.

9. A filter material according to claim 5 wherein the poly-(carboxylic acid) polymer includes adjacent -CR⁴.COOH- units in its structure wherein R⁴ is hydrogen, C₁₋₃ alkyl, C₁₋₃ alkoxy or C₁₋₃ hydroxy alkyl.

10. A filter material according to claim 9 wherein the poly-(carboxylic acid) comprises:



units in its structure.

11. A filter material according to any one of the preceding claims wherein the monomeric carboxylic acid is citric acid.
12. A filter material according to any one of the preceding claims wherein the weight ratio of poly-(carboxylic acid) polymer : monomeric carboxylic acid is in the range 1 : 6 to 1 : 3.
13. A filter material according to any one of the preceding claims wherein the one or more anionic surfactant is selected from alkali metal alkyl sulphates of general formula $(C_nH_{2n+1})-SO_4^- M^+$ where n is 8-20 and M is an alkali metal.
- 10 14. A filter material according to claim 13 wherein the anionic surfactant is sodium lauryl sulphate $C_{12}H_{25}SO_4Na$.
15. A filter material according to any one of the preceding claims wherein the non-ionic surfactant is selected from fatty alcohols; polyoxyethylene ether type surfactants; polyoxypropylene glycol alkyl ethers; polyoxyethylene glycol octylphenol ethers; polyoxyethylene glycol alkylphenol ethers; glycerol alkyl esters and sorbitan alkyl esters.
- 15 16. A filter material according to claim 15 wherein the non-ionic surfactant is selected from polyoxyethylene sorbitan monolaurate, and a polyethylene glycol p-(1,1,3,3-tetramethylbutyl) phenyl ether.
17. A filter material according to any one of claims 1-16 wherein the composition contains a combination of one or more anionic surfactant with one or more non-ionic surfactant.
- 20 18. A filter material according to claim 17 wherein the weight ratio of anionic surfactant : non-ionic surfactant is in the range 4 : 1 – 1 : 4.
19. A filter material according to any one of the preceding claims wherein the weight ratio of poly-(carboxylic acid) : surfactant in the filter material is in the range 4 : 1 to 1 : 4.
- 25 20. A filter material according to any one of the preceding claims wherein the composition contains an alkali.
21. A filter material according to any one of the preceding claims wherein the loading of the composition on the composition on the substrate is 5-15 g/m².
- 30 22. A filter material according to claim 1 comprising a non-woven polyester substrate of weight 30 - 40 g/m², e.g. around 34 g/m², having deposited thereon a composition comprising a poly-(carboxylic acid) polymer selected from polyacrylic acid homopolymer

cross-linked with allyl pentaerythritol or allyl sucrose, with a molecular weight of 50,000 – 5,000,000; citric acid, at a poly-(carboxylic acid) polymer : citric acid ratio 1:6 - 1:3; and a surfactant being either sodium lauryl sulphate, or a mixture of sodium lauryl sulphate : Octoxynol at a ratio of poly-(carboxylic acid) polymer : surfactant(s) of 2:1 – 1:1; at a loading of the composition of 5 - 15 g/m².

23. A filter material according to claim 1 comprising a non-woven polyester substrate of weight 10 - 40 g/m² having deposited therein a composition comprising a poly-(carboxylic acid) polymer based on maleic acid moieties which include $[-CH.COOH-CH.COOH-]$ units, with a molecular weight of 200,000 – 2,000,000 such as Gantrez S97; citric acid, at a poly-(carboxylic acid) citric acid ratio 1:6 - 1:3; and a surfactant being either sodium lauryl sulphate, or a mixture of sodium lauryl sulphate : Octoxynol at a ratio of poly-(carboxylic acid) polymer : surfactant(s) of 2:1 – 1:1; at a loading of the composition of around 5 - 15 g/m².

24. A face mask incorporating a filter material as claimed in any one of claims 1 to 23.

25. A method of making a filter material according to any one of claims 1 to 23, comprising dissolving or dispersing the poly-(carboxylic acid) polymer, the monomeric carboxylic acid and the anionic and/or non-ionic surfactant, wherein the weight ratio of monomeric carboxylic acid : poly-(carboxylic acid) polymer is in the range 10 : 1 to 2 : 1; and any other components as mentioned herein such as one or more alkali, metal salt or antimicrobial agent, in a liquid vehicle, wetting the substrate material with the so-formed solution or dispersion and causing or allowing the liquid vehicle to evaporate to thereby leave the composition deposited on the substrate at the loading of 1-20 g/m².

26. A solution or dispersion suitable for a method according to claim 25, comprising the poly-(carboxylic acid) polymer, the monomeric carboxylic acid and the anionic and/or non-ionic surfactant, wherein the weight ratio of monomeric carboxylic acid : poly-(carboxylic acid) polymer is in the range 10 : 1 to 2 : 1, dissolved or dispersed in a liquid vehicle.

27. A solution or dispersion according to claim 26 containing one or more anionic surfactant in the absence of any non-ionic surfactant.

28. A solution or dispersion according to claim 26 containing a combination of one or more anionic surfactant with one or more non-ionic surfactant.

29. A solution or dispersion according to claim 26, 27 or 28, wherein the weight ratio of poly-(carboxylic acid) : surfactant(s) is in the range 4 : 1 to 1 : 4.

30. A solution or dispersion according to any one of claims 26 to 29 having a pH of 2-3.

5 31. A solution or dispersion according to any one of claims 26 to 30 wherein the liquid vehicle is water.

32. A method of reducing the concentration of airborne pathogens, being virus or microorganisms, in air contaminated by such pathogens, by passing such contaminated air through a filter material as claimed in any one of claims 1 to 23.

10

Fig. 1.

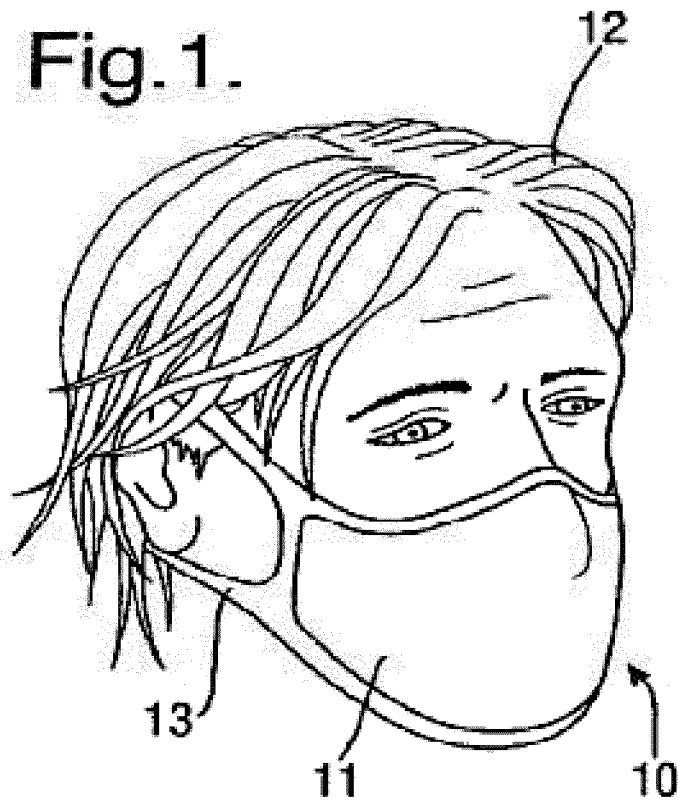


Fig. 2.

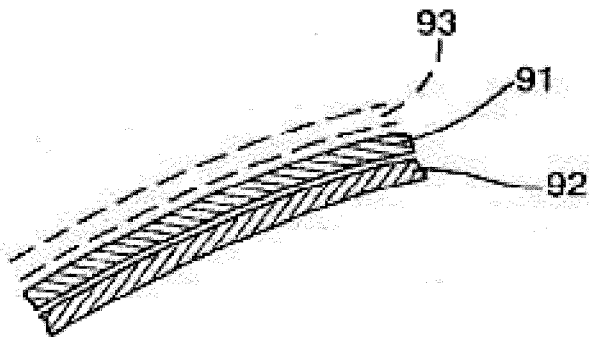
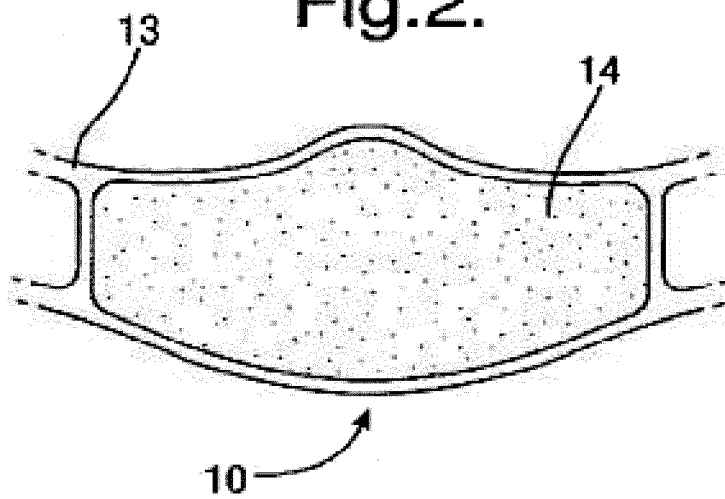


Fig. 3.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2012/054369

A. CLASSIFICATION OF SUBJECT MATTER INV. A41D13/11 D06M15/263 D06M13/184 A62B23/02 B01D46/00 ADD.											
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) D06M A41D A62B B01D A01N A61M Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal, WPI Data											
C. DOCUMENTS CONSIDERED TO BE RELEVANT <table border="1"> <thead> <tr> <th>Category*</th> <th>Citation of document, with indication, where appropriate, of the relevant passages</th> <th>Relevant to claim No.</th> </tr> </thead> <tbody> <tr> <td>X</td> <td>WO 2004/016087 A1 (RECKITT BENCKISER INC [US]; CUSACK TIMOTHY MICHAEL [US]; MCCUE KAREN A) 26 February 2004 (2004-02-26) page 3, line 32 - page 6, line 25 page 22, line 24 - page 23, line 5 claims 1-4,15-17,34-36,39,50-52,65-67,99-102,113-115,125-</td> <td>26-31</td> </tr> <tr> <td>X</td> <td>WO 96/17918 A1 (UNILEVER PLC [GB]; UNILEVER NV [NL]; ALLAN ALEXANDER [GB]; RABONE KENN) 13 June 1996 (1996-06-13) tables 1.1, 2.1, 3.1 ----- -/--</td> <td>26-31</td> </tr> </tbody> </table>			Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.	X	WO 2004/016087 A1 (RECKITT BENCKISER INC [US]; CUSACK TIMOTHY MICHAEL [US]; MCCUE KAREN A) 26 February 2004 (2004-02-26) page 3, line 32 - page 6, line 25 page 22, line 24 - page 23, line 5 claims 1-4,15-17,34-36,39,50-52,65-67,99-102,113-115,125-	26-31	X	WO 96/17918 A1 (UNILEVER PLC [GB]; UNILEVER NV [NL]; ALLAN ALEXANDER [GB]; RABONE KENN) 13 June 1996 (1996-06-13) tables 1.1, 2.1, 3.1 ----- -/--	26-31
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X	WO 2004/016087 A1 (RECKITT BENCKISER INC [US]; CUSACK TIMOTHY MICHAEL [US]; MCCUE KAREN A) 26 February 2004 (2004-02-26) page 3, line 32 - page 6, line 25 page 22, line 24 - page 23, line 5 claims 1-4,15-17,34-36,39,50-52,65-67,99-102,113-115,125-	26-31									
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☒ 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											
Date of the actual completion of the international search		Date of mailing of the international search report									
18 June 2012		22/06/2012									
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Fiocco, Marco									

INTERNATIONAL SEARCH REPORT

International application No
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