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(54) **Title:** ACTIVE FILTER LAYERS, FILTER CONSTRUCTS AND METHODS FOR IMPROVING A FILTER'S CAPACITY OF CAPTURING PARTICLES AND NEUTRALIZING PATHOGENIC PARTICLES

(57) **Abstract:** The present disclosure relates to removing and neutralizing pathogenic particles from air by filtration. Especially the disclosure relates to antipathogenic filter layers comprising detonation nanodiamonds and metal ions, filter constructions carrying those and method for improving a filter's capacity of capturing and neutralizing pathogenic particles.

ACTIVE FILTER LAYERS, FILTER CONSTRUCTS AND METHODS FOR IMPROVING A FILTER'S CAPACITY OF CAPTURING PARTICLES AND NEUTRALIZING PATHOGENIC PARTICLES

The present invention relates to an active filter layer, especially air filter layer and a filter construct comprising such a layer. The present invention relates also to a method for improving a filter's capacity of capturing particles and neutralizing pathogenic particles.

Background

A mechanical air filter is a device composed of porous, often fibrous, materials which remove solid particulates such as dust, mold, and bacteria from the air. Particles larger than the pores of the filter layer remain in the pores. Also electrostatic filter layer result is retention of particles without deactivating those. Filters with an adsorbent or catalyst such as charcoal (carbon) may also remove odors and gaseous pollutants. Air filters are used in applications where air quality is important, e.g. in building ventilation systems such as offices, clean rooms, hospitals, nuclear power stations but also in engines. Various filters are used also for personal protection. Some of the most recent filter materials are based on various pore sized PTFE applicable also within HEPA (High Efficiency Particulate Air) and ULPA (Ultra-Low Particulate Air). Conventional face masks comprise a minimum three-ply layer, the active material being made from of a static charge carrying melt-blown polymer, most commonly polypropylene, placed between non-woven fabric. One of the functions of melt-blown polypropylene material is to prevent the flow of microbes through the mask.

Most of the current active filtration solutions are based on electrocharged polymer layer. The mechanism is used in respirator filters that meet the stringent NIOSH filter efficiency and breathing resistance requirements because it enhances particle collection without increasing breathing resistance. There are known means on how to produce the specific, charge carrying filtration layer (electrostatic layer). In addition to melt-blowing processes, many of those are relaying on cumbersome and slow electrospinning processing or materials providing only a moderate charge or said charge lifetime. Melt-blown polypropylene electrostatic charge decays over a period of time.

The N99 and N95 masks present the only available design capable of stopping the COVID-19 virion, because it contains an electrocharged layer or layers capable of attracting and capturing aerosol droplets down to micrometer dimensions, virions, and bacteria in the 100s of nanometer dimensions. An N95 mask or N95 respirator is a particulate-filtering facepiece respirator that meets the U.S. National Institute for Occupational Safety and Health (NIOSH) N95 classification of air filtration, meaning that it filters at least 95% of airborne particles. An N99 mask or N99 respirator is a particulate-filtering facepiece respirator that meets the U.S. National Institute for Occupational Safety and Health (NIOSH) N95 classification of air filtration, meaning that it filters at least 99% of airborne particles. N95 respirators are considered functionally equivalent to certain respirators regulated under non-U.S. jurisdictions, such as FFP2 respirators of the European Union and KN95 respirators of China. N99 respirators are considered functionally equivalent to certain respirators regulated under non-U.S. jurisdictions, such as FFP3 respirators of the European Union and KN99 respirators of China.

HEPA filters are composed of a mat of randomly arranged fibers typically composed of fiberglass with diameters between 0.5 and 2.0 micrometers. The air space between HEPA filter fibers is typically much greater than 0.3 µm. HEPA filters are used in the prevention of the spread of airborne bacterial and viral organisms (infections).

Also metal impregnated filters and face masks are available in the market. Metal ions such as Silver and Copper are known to have antimicrobial activity. The PuraWard fiber (Purafil Filtration Group) product bulletin teaches that copper ions weaken the amino acids of the cell wall, allowing silver to invade the cell resulting in elimination of 99.96% of tested bacteria and 99.98% of tested virus.

WO 2004/024278 discloses an active agent incorporated in the porous dielectric carrier. The active agent may be an antimicrobial or an antitoxin, such as metals including silver and copper.

Nanodiamond (ND) also referred to as ultrananocrystalline diamond or ultradispersed diamond (UDD) is a unique nanomaterial which can be produced by detonation synthesis. The detonation nanodiamonds comprise sp^3 carbon and the non-diamond carbon mainly comprising sp^2 carbon species. Sp^2 carbon provides and active surface to the diamonds. Functionalization of detonation nanodiamonds is discussed in e.g. WO 2014/174150, WO 2014/191633 and WO 2015/092142. The use of nanodiamond particle on various fibrous materials has already been demonstrated in other industrial applications.

Sato K. et al. (Advanced Powder Technology 29 (2018) 972-976) discloses cellulose nanofiller/nanodiamond composite films. Positively charged nanodiamonds (ND) and negatively charged cellulose nano fibrils (CNF) are combined in an aqueous solution. Such films are very dense and coating alike in structure.

There is a need for providing improved active layers with high filtration efficiency and long lifetime. Preferably said layer would be flexible as well as has moderate manufacturing costs. Preferably said layer is not only able to capture particulates but also various pathogens such as bacteria and viruses. Said solutions are desirably available in industrial quantities and able to be scaled up said in short time frame. Moreover, any effective filtration solution with simultaneously reduced pressure drop would result in energy savings within HEPA/ULPA filtration as well as by lower airflow resistance easier breathing when applied in a mask construction.

Summary

The present disclosure generally relates to removal of particles, especially particles having pathogenic properties from air by filtration. In addition, this disclosure relates to neutralizing particles with potentially pathogenic properties.

The first aspect of the present invention is an antipathogenic filter layer comprising filter material. Characteristic features of such filter layer are depicted in claim 1.

The second aspect of the present invention is an antipathogenic filter construct. Characteristic features of such construct are depicted in claim 17.

The third aspect of the present invention is a method for improving a filter's capacity of capturing and neutralizing pathogenic particles. Characteristic features of such method are depicted in claim 23.

The invention enhances efficient removal and neutralizing particles having pathogenic properties, including bacteria and viruses, with a reasonable airflow resistance.

Detailed description

Nanodiamond particles are commercially available both in their positively charged and negatively charged forms which makes them effective species for making electrostatic layers. The inventors have now surprisingly found that they can be applied also for various high-performance filter layers for air including those used in face masks and HEPA filters. Nanodiamonds having a high surface charge (zeta potential are commercially available at brand names uDiamond Hydrogen D (highly zeta positive, hydrogen terminated nanodiamonds in dispersion), uDiamond Vox D (highly zeta negative, carboxylated nanodiamonds in dispersion) or uDiamond Amine D (highly zeta positive nanodiamonds in dispersion).

It is to be noted that nanodiamonds are believed to have certain independent activity against bacteria and viruses. Now the inventors have also found out that when the filter layer is incorporated also by an agent having antipathogenic, such as antimicrobial, antiviral or an antitoxin properties, such as metal ions, the activity of the microbes and many viral particles will be destroyed or reduced.

The small and spherical, highly charged nanodiamond particles applied onto/into the porous substrate can form a three-dimensional structure on nanoscale, effective capturing not only the, particles and bacteria but the smallest of the viruses. The nanodiamond particles provide a non-decaying surface charge which is not affected for example by moisture. The present disclosure allows manufacturing electrostatic layers capturing either negatively or positively charged species, including particles, bacteria and viruses. A filter construct can be designed to comprise either one filter layer capturing oppositely charged species or two oppositely charged filter layers capturing both negatively and positively charged species. Further, the performance of a filter construct can be tailored by modifying the electrostatic layer nanodiamond concentration and/or the thickness of the filter layer containing the nanodiamond particles. The nanodiamond particles can be applied, for example, by drying them from their dispersion form directly onto a fibrous carrier material, allowing them located throughout said fibrous layer material surfaces. The use of 4-6 nm nanodiamond particles in their dispersion form allows also their even spread and adhesion throughout the complex, fine-sized porous structure.

Filter layer

The broadest embodiment of the invention is antipathogenic filter layer. Said filter material has detonation nanodiamonds (NDs) and metal ions incorporated in the filter material layer.

In this connection term “pathogenic” or “a particle having pathogenic properties” includes microbes, fungi, algae, germ and viruses as well as e.g. droplets carrying those. The type or severity of a potential infection caused by the pathogen is nor relevant, it is well known that many pathogens do not harm a subject with strong immune system.

In this connection term “neutralizing” in connection of particles having pathogenic properties means that said pathogenic property will be removed or reduced. For example, a microbial pathogen may be killed or it’s ability to cause an infection in a host may be reduced. This can be done at least by affecting or destroying the bacterial membrane. Viruses may be neutralized e.g. by changing their surface structure (spike proteins, lipid envelope, protein envelope, other membranes) or genetic material. The degree reduction of ability to cause an infection is at least 75%, 90% or 95% when compared to a filter material with respective structure but without nanodiamonds and metal ions described here. In one embodiment the bacteria or microbe is killed or virus loses it’s ability to cause infections.

In one embodiment the ability to cause an infection a pathogenic particle is reduced by at least 95% when compared to a filter material with respective structure but without nanodiamonds and metal ions described here during contact time of 20 minutes.

It is to be noted that a pathogen can be neutralized effectively and rapidly using harsh conditions such as disinfectants, high temperature or a radiation. Many of these are not applicable in air filtration requiring safety, affordable cost and easiness in use.

In one embodiment the antipathogenic filter layer described here is able to neutralize a pathogen, such as virus or bacteria or bout viruses and bacteria in a contact time no longer than 60 minutes, preferably no longer than 30 minutes and most preferably no longer than 20 minutes. Expression “a contact time no longer than 60, 30 or 20 minutes” includes contact times between 0.1 second to said 60, 30 or 20 minutes.

In this connection contact refers to contact between the pathogen and nanodiamond, preferably between the pathogen and nanodiamond.

In one embodiment the pathogen is Influenza A virus, subtype H1N1. In one embodiment the pathogen is *Staphylococcus aureus* or *Escherichia coli*.

The amount of detonation nanodiamonds (NDs) incorporated to the antimicrobial filter layer may be 0.001 to 10 g/m^2 calculated based on the outer surface of the filter material layer. The amount of incorporated nanodiamonds may be 0.001 to 5 g/m^2, 0.001 to 2 g/m^2; 0.01 to 0.1 g/m^2, such as 0.075 g/m^2). The amount of nanodiamonds may be adapted to the properties of the filter material and the needs of the application.

The amount of metal ions incorporated to the antimicrobial filter layer may be at 0.01 to 100 g/m^2 calculated based on the outer surface of the filter material layer.

Examples of suitable metal ions are metal ions such as aluminum, barium, boron, calcium, chromium, copper, iron, magnesium, manganese, molybdenum, nickel, potassium, sodium, strontium, zinc and silver, such as copper and/or silver. In one embodiment the antipathogenic filter layer comprises metal ions of copper, silver, zinc or any mixture thereof. Metal ions can be applied in form of salts. In filter layer they may be at least in form of complex with nanodiamond or in salt form or attached as ions to the charged filter matrix. The metals can also be present as metallic nanoparticles.

The salt may be any non-harmful salt such as sulphate, nitrate, chloride or e.g. salts of organic compound (e.g. citrate, oxalate).

In this connection the term “filter material” means the filter material before incorporating the nanodiamonds. The material may be a mechanical filter without electrostatic charge, it may be charged, it may be functionalized, or it may comprise incorporated active agents such as charcoal. The filter material can be natural polymer based or a synthetic material such as a polymer or a mixture of polymers. The filter material can also be ceramic material or metal based.

In this connection the expression “an outer surface of the filter material” means the outer surface of the sheet excluding the surface of the pores. The term “surface of the filter material” means the whole open surface of the material layer and includes also the (inner) surface of the pores within the material.

The filter material has a continuous porosity. In this context the term continuous porosity means open porosity allowing gas flow through the porous layers. The pores or series of pores form a tubular open-ended structure elongating from the first surface of the filter layer to the second surface of the filter material layer. In this connection the free space within the filter material are referred as “pores”. The pore size can vary from 100 nm to 30 micrometers and the diameter of a pore can vary throughout the pore structure.

Filter material layers may be composed of a mat of randomly arranged fibres or any other porous material such as ceramic of metallic structure. The fibrous material may comprise a synthetic or natural polymer such as nylon, polyethylene, polypropylene, polyester, glass fibre or any cellulosic fibre. The fibrous material is typically a mixture of various polymers, one such representative being marketed as “ES Fiber Cotton”. The microporous structure can also be created by stretching a selected polymer material, for example PTFE, to arrive into desired microporous structure. In PTFE layers typically applied within HEPA and ULPA filters, the micropore diameter varies typically between 0.1 to 10 micrometers.

Another typical representative example is PET based G4 class filters applied as prefilters in HEPA construct. PET based filter may be adhered to separate PTFE layer to form one filter layer. The other representative examples are PET or any other material based G1, G2, G3, M5, M6, F7, F8, F9, E10, E11, E12, H13, H14, U15, U16 and U17 class filters.

Thickness of a filter layer may be varied. Typical polymer-based may have weight per m^2 of 30 to 300 g/m^2. When the base material is metal, the weight per m2 will obviously be higher.

The pores can also be manufactured by needle punching, a typical method producing “needle punched nylon” applied widely for example within safety masks.

The metal and ceramic based filter structures are typically manufactured by sintering selected sized metal or ceramic particles to form a filter structure. If applying nanodiamond particles on either metallic or ceramic filter structure, such filters can be re-activated by washing away the trapped species and nanodiamonds, followed by re-introducing a new load of nanodiamond particles to filter pores surfaces.

Nonwoven fiber layers or mats may have a very high proportion of void volume. Non-woven fibrous filter media are formed by the random distribution of fibers in a specific space exhibit a complicated pore size structure. The material may be electrostatically charged. Such static charge decays over a period of time.

The air space between the HEPA filter fibers (as those comprised of glass-fibre) is typically much greater than 0.3 µm. The filter's minimal resistance to airflow, or pressure drop, is usually specified around 300 pascals (0.044 psi) at its nominal volumetric flow rate.

Due to nanoscale size of the detonation nanodiamonds and metal ions, and possible complexes of those, the pressure loss caused by the filter material will not remarkably be increased when nanodiamonds are incorporated. If adhering the nanodiamond particles and metal ions to a filter material with larger pore size, it is possible to reduce the air flow resistance without compromising on the filter particulate capturing performance. Such a feature allows lower pressure drop in

HEPA/ULPA filters and thus, lower overall energy consumption. Such a feature also allows lower air flow resistance within safety masks, making such a mask more user friendly due to easier breathing.

Nanodiamonds create active surface to the filter layer or increase the active surface. They have an ability to capture particles, viruses, bacteria, pollen, allergens and fungus and possibly also at least partially deactivate those. The nanodiamonds may adhered on to the surface of the filter material. The nanodiamonds can also be inside, completely or in part, the filter body material matrix. This allows a direct interaction with the foreign particles, viruses and bacteria, and enhances capturing those. The distribution and thus the particle to particle distance of the nanodiamond particles may be adjusted by selecting suitable application method.

Without binding to the theory, it is believed that organic acid will act as a complexing agent to stabilize metal ions in aqueous suspension and enhance metal distribution on filter material.

Low amount of nanodiamonds and metal ions does not affect on filter layer weight or bendability properties. It does not remarkable increase the production cost or increase air flow resistance. If choosing a cheaper filter material without but applying nanodiamonds thereto, the cost can be even lowered.

The total amount of nanodiamonds and metal ions may be 0.05 to 1.0 wt.-% of the total weight of said layer.

The nanodiamonds may have a surface charge of at least +40 mV or less than -40 mV; preferably at least +50 mV or less than -50 mV. The nanodiamonds may have surface charge of at least +55 Mv or less than -55 mV. When defining less than – 55 mV, it is meant a value like – 56 mV or less.

The nanodiamond surface charges may be measured of nanodiamonds diluted to 0.1 wt.-% aqueous dispersion using Malvern Zetasizer NanoZS according to manufacturer’s instructions. The nanodiamond particle size distributions may be measured of samples diluted to 0.5 wt.-%.

Measuring particle size distribution (PSD) as well as the particles zeta potential has to be carried out with a tool designed for measuring the PSD with a tool designed for defined primary particle size. Malvern Zetasizer Nano ZS is commonly applied for particles sizing less than 10 nm and is thus favored by many working with 4-6 nm sized detonation nanodiamond particles.

When it comes qualifying an acceptable measurement with Malvern Zetasizer Nano ZS tool, the following quality measures have to be passed:

- Z-average size, the best value to report when used in quality control setting as defined in ISO 13321 and more recently in ISO 22412
- Cumulants analysis, as defined in ISO 13321 and more recently in ISO 22412
- Y-intercept or Intercept
- Polydispersity Index, as defined in ISO standard document 13321:1996 E and ISO 22412:2008

It is also possible to change the liquid medium: For example, the zeta positive hydrogenated nanodiamond powder can be suspended directly into water or other liquid mediums. Alternatively, the zeta positive hydrogenated nanodiamond powder can be first suspended into water, then mixing another liquid medium, having boiling point above water and at least partly soluble in water, with the aqueous zeta positive hydrogenated nanodiamond suspension, and then distilling (evaporating) the water out, giving zeta positive hydrogenated nanodiamond particles suspended in the liquid medium other than water.

Nanodiamonds incorporated to the filter material may form complexes with for example metal ions added for improving antibacterial characteristics.

Starting from an active filter layer, it is possible to recover the nanodiamonds by extraction and followed by filtration. Then the surface charge can be measured in concentrated aqueous solution. Solvent change, if necessary, can be done using knowns methods such as evaporation and then adding an aqueous solvent. Alternatively, the filter material can be burnt at temperature reaching max 400 °C, to avoid oxidizing away the nanodiamonds themselves. Then the remaining nanodiamonds are dispersed to an aqueous solution for measurements.

The surface charge relates to the stability of colloidal dispersions. The value indicates the degree of repulsion between adjacent, similarly charged particles in dispersion or suspension. For molecules and particles that are small enough, a high zeta potential will confer stability, i.e., the solution or dispersion will resist aggregation. The higher numeric value the higher is the repulsion between the particles and the better is the stability of a dispersion of particles.

High numeric surface charge value (zeta potential) of a nanodiamond indicates high repulsion forces and enhances forming a two- or three dimensional network of nanodiamond particles on the filter material wherein the nanodiamond particle to particle distance may be tailored to 100 nm or less from each other. This forces viruses or any other particles bypassing the filter layer to a close contact with nanodiamonds and metal ions resulting them to being captured by the oppositely charged nanodiamond particles.

A filter layer may comprise either one surface layer incorporated with nanodiamonds with negative surface charge and metal ion and another surface layer incorporated with nanodiamonds with positive surface charge and metal ions. The surfaces of oppositely charged species adsorb both negatively and positively charged species. Alternatively, both surfaces may have similar charge. If filter layer's both surface layers are incorporated with nanodiamonds and metal ions, the bulky part of the filter layer acts as a dielectric layer between the filter layer two surface layers.

The filter layer electrostatic performance comprised from adhered nanodiamond particles surface charge (measured as zeta potential) may be modified by tailoring the nanodiamond concentration and/or by tailoring the thickness of the fibrous layer containing the nanodiamond particles. The nanodiamond particles strong surface charge warrants also said particles strong adhesion to filter layer body material. This surface charge is so strong that the particles remain adhered despite subjecting the filter layer to strong airflow.

A filter layer may comprise either one surface layer incorporated with nanodiamonds with negative surface charge and metal ions and the other surface layer incorporated with nanodiamonds with negative surface charge and metal ions. The surfaces of same charged species both adsorb positively charged species and thereby further improve the efficiency.

A filter layer may comprise either one or both surface layers incorporated with positively or negatively charged nanodiamonds and metals (metal ions). The surfaces of same charged species both adsorb oppositely charged species and thereby further improve the efficiency. The surfaces of oppositely charged species adsorb both negatively and positively charged species and thus, improve the efficiency in case wherein both positively and negatively charged species need to be filtered.

A filter layer may comprise the nanodiamonds and metals (metal ions) throughout the filter porous structure. The nanodiamonds can carry either positive or negative surface charge. The effectivity can be tailored by adjusting the nanodiamond and metals (metal ions) concentration and or the filter layer thickness and pore size.

Evidently, it is also possible to apply nanodiamonds to one side of the filter and metal ions (in form of dissociated salts in aqueous solution) to the opposing side.

The net charge of a particle may be determined by the sum of the charges exposed on the surface. This may be calculated from the protein structure(s) at the surface. There are several tools available online to calculate net charges of folded protein structures as well as their surface charge distribution.

The filter material described here may further comprise organic acid incorporated therein at amount of 0.05 to 1000 g/m^2 calculated based on the outer surface of the filter material layer. The organic acid may be malic acid, citric acid or a mixture thereof. The use of organic acids may improve the adhesion of metal ions to the filter material.

The filter material described here may further comprise quaternary ammonium compounds therein at amount of 0.05 to 500 g/m^2 calculated based on the outer surface of the filter material layer. The quaternary ammonium compound may be didecyldimethylammonium chloride. The quaternary ammonium salts may complex with metal ions.

The nanodiamonds may have an average primary particle diameter of 4 to 6 nm. Nanoscale size increases the active, highly charged area and provide their good adhesion to the filter layer base material. In addition, nanodiamonds do not substantially lower the gas flow throughout the filter layer. They are not detached as subjected to airflow.

Preferably the nanodiamond is also a single digit nanodiamond. Single digit nanodiamonds provide a large active surface and do not aggregate. In addition, they have a minimal effect to the air flow properties of the filter layer. By term “single digit nanodiamond” is meant a nanodiamond particle substantially in its primary particle form. The average size of a single digit nanodiamond particle is 10 nm or less.

Filter construct

The present invention relates also to a filter construct. An essential feature of such construct is that it comprises at least one filter layer described here. In addition, the construct may comprise one or more selected from the following

- one or more pre-filter layer; and
- one or more filter layer(s); and

- one or more electrostatic layers;
- one or more ePTFE layers;
- one or two protective layers; and
- any combination of those.

Prefilter layers may be used for removal most of the larger particles such as dust, hair, and pollen. These are commonly used in e.g. HEPA filtration constructs and may be e.g. coarse mechanical filters. The nanodiamond particles as well as metal ions, can also be on a prefilter, either on one or both outer surface layers or impregnated throughout the prefilter porous structure.

Protective layers may be used to protect either the active filtration layer from external factors (such as abrasion, touch or oily skin) or to protect skin from the active filtration layer and increase comfort of e.g. a face mask.

Separate electrostatic layers may be included to further improve the filtration efficiency.

In addition, the filter construct may comprise filter layers with charcoal or any other active ingredient.

Filter properties may be discussed based on Under European normalization standards EN 779. As an example, a HEPA filter may remove at least 99.97% of airborne particles 0.3 micrometers (µm) in diameter which complies with the retention capacity of HEPA claim H13 defined by the United States Department of Energy (DOE) standard and averaged retention of > 99.95%.

The filter construct described here may increase the retention may to averaged retention of 99.995% (H14) or even higher.

One advantage of the present invention is that an excellent retention of particles may be achieved by using even a coarse filter material, such as material of G4 class, as a filter material into which nanodiamonds are incorporated. As an example, G4 class filter used as a primary filter removes particles of >5 µm with substantially 100% retention. When a coarse filter material is used, the air flow resistance is low thereby saving energy and/or improving comfort of a face mask. Similarly, as applied as a part of HEPA construct, the pressure drop can be dramatically reduced resulting in great energy savings and the HVAC device lower noise level. In addition, such material is cheaper than finer filter materials. It may also be possible to reach an excellent particle retention even using only a prefilter and one nanodiamond incorporated layer.

Another advantage is that incorporated metal ions are active in neutralizing the particles with pathogenic properties, such as bacteria and viruses.

The filtration construct may be a face mask, a safety cloth or curtain or a HEPA filter construct.

The general structure of a face mask is known. One example of the construction, also used in the experimental section here, is a mask called 4 PLY N95 face comprising total of 4 layers: outside and inside are standard polypropylene (PP) layer, 2nd from outside is the layer comprised of ES Fiber Cotton with incorporated nanodiamonds and 3rd layer is melt brown PP layer (an electrostatic layer).

Another example of the construction, also used in the experimental section here, is a mask called 4 PLY N95 face comprising total of 4 layers: outside and inside are standard polypropylene (PP) layer, 2nd from outside is the layer comprised of ES Fiber Cotton with incorporated nanodiamonds and 3rd layer is F8 level PTFE layer (a filter layer). With F8 level filter layer is meant a filter capable of trapping particles sized 1 to 10 micrometers, according EN 779 standard.

Still another example of the construction, also used in the experimental section here, is a mask called 4 PLY N95 face comprising total of 4 layers: outside and inside are standard polypropylene (PP) layer, 2nd from outside is the layer comprised of G4 glass filter comprised of polyethylene terephthalate with incorporated nanodiamonds and 3rd layer is F8 level PTFE layer (a filter layer).

Further example of the construction is also 4 ply face mask: outside and inside are non-woven fabric, 2nd from outside is the filter layer constructed from G4 class PET incorporated with nanodiamonds and metal ions adhered to F9 Class Polytetrafluoroethylene (PTFE) layer (comprising 2nd layer) and 3rd layer is so called “hot air cotton” (a filter layer as ES Cotton fibre).

Use of low melt PET in part or as whole of the layer may enhance adhesion of said PET layer to PTFE layer. PTFE typically has better performance in filtration as such and nanodiamonds are incorporated in the PET layer

The filter construct may comprise two or more active filter layers described here. Said layers may be incorporated with nanodiamonds with opposite surface charges in combination with metal ions.

The surfaces incorporated with oppositely charged nanodiamonds and metal ions in one embodiment are not facing directly each other. They may be incorporated on opposite surfaces on one filter material layer. This protects the charge of each surface. Alternatively, they may be separated by a dielectric spacer known within the filed. A spacer may be an air cavity between the layers. Alternatively, said opposite charged surfaces may be applied on the opposite sides of a single filter material layer. Unless the nanodiamonds and metal ions are applied in excess, the filter material acts as an insulator or a dielectric layer. The advantage of using a dielectric spacer that it prevents neutralization of the charge(s).

Hence, a dielectric spacer can also be applied between the surface of filter material layer incorporated with nanodiamonds and metal ions and a filter layer with static charge. Here, the incorporation of such a spacer will prevent the static charged filter layer charge from decaying unwantedly.

The nanodiamond and metal ion enhanced filter material can be made on any available solid substrate, synthetic or natural, allowing the airflow through the filter media. The filtering efficiency can be tailored and further increased by adjusting the nanodiamond content per filter surface area. The nanodiamonds can be adhered and metal ions either on one side of the filter layer, on both sides of the filter layer or throughout the filter material porous structure. The latter is easy to gain by for example immersing the entire filter cloth into selected nanodiamond dispersion in either water or any other applicable solvent, followed by drying said filter cloth material essentially free from applied nanodiamond dispersion contained liquid media. If applying the nanodiamond particles and metal ions only on one side of the filter media, the other, non-treated side stays essentially free of any charge. This invention is facilitating making filter structures having several charged layers separated from each other by the non-charged bulky filter material, without increasing the HEPA filter or safety mask airflow resistance too high. Due to performance improvement it is also possible to carry out high efficiency filtration with filter materials having larger pore sizes and thus, lower airflow resistance.

The filter material charged surfaces can be tuned to carry either non-decaying positive or non-decaying negative charge by selecting the nanodiamond particles from either those with high positive surface charge (zeta potential) or high negative surface charge (zeta potential) (such as Carbodeon uDiamond Vox D in water (5 wt.%), said product being comprised of carboxylated detonation nanodiamond particles exhibiting (zeta potential) surface charge of ≥ - 50 mV i.e. – 50 mV or more negative than – 50 mV).

Respectively, metal ions can be applied in the same solution as nanodiamonds or using a separate aqueous suspension. This allows applying metal ions independently from nanodiamond, to a same or another surface.

The nanodiamond and metal ion contained filter materials show excellent virucidal, bactericidal as well as fungicidal performance, with remarkable short contact time. With contact time is meant time required killing the viruses, bacteria and fungus. High virucidal, bactericidal and fungicidal efficiency combined with short contact time provides aseptic filter materials applicable both within air filtration such as HEPA and ULPA but also aseptic filter materials for PPE's (Personal Protection Equipment) such as safety masks and respirators as well as other safety materials, safety curtains and clothes.

Combining the aseptic property with said technology provided lower air flow resistance in safety masks and respirators, the present invention provides high efficiency personal protection equipment with low breathing resistance and thus, easiness to use. Opposite to using melt blown polypropylene as PPE's active filter material (decaying charge), the nanodiamond and metal(s) containing filter's exhibit permanent, tunable (highly positive or highly negative) charge providing excellent stability over long periods of time.

Manufacturing

The nanodiamond and metal (typically metal ions) containing filter material can be made on any available solid substrate, synthetic or natural, allowing the airflow through the filter media. The filtering efficiency can be tailored and further increased by adjusting the nanodiamond and metal content per filter surface area. Advantageously, the nanodiamond concentration can be bigger and the metal content can be further reduced. The nanodiamonds and metal(s) can be adhered either on one side of the filter layer, on both sides of the filter layer or throughout the filter material porous structure. The latter is easy to gain by for example immersing the entire filter cloth into selected nanodiamond and metal(s) containing suspension in either water or any other applicable solvent, followed by drying said filter cloth material essentially free from applied nanodiamond and metal(s) containing suspension contained liquid media. If applying the nanodiamonds and metal(s) only on one side of the filter media, the other, non-treated side stays essentially free of any charge. This invention is facilitating making filter structures having several charged layers separated from each other by the non-charged bulky filter material, without increasing the HEPA filter or safety mask airflow resistance too high. Due to performance improvement it is also possible to carry out high efficiency filtration with filter materials having larger pore sizes and thus, lower airflow resistance.

The filter material charged surfaces can be tuned to carry either non-decaying positive or non-decaying negative charge by selecting the nanodiamond particles from either those with high positive or high negative surface charge (zeta potential) (such as Carbodeon uDiamond Vox D in water (5 wt.%), said product being comprised of carboxylated detonation nanodiamond particles exhibiting (zeta potential) surface charge of ≥ - 50 mV i.e. – 50 mV or more negative than – 50 mV).

The present invention relates also to method for improving a filter’s capacity of capturing and neutralizing pathogenic particles. The method is characterized by

a) providing aqueous suspension comprising nanodiamond dispersion, metal salts and optionally organic acid and/or quaternary ammonium compound; and

(b) providing at least one filter layer; and

(c) applying said dispersion to at least one side of the filter layer,

wherein such formed layer comprises detonation nanodiamonds (ND) at amount of 0.001 to 10 g/m^2, metal salts at amount of 0.01 to 100 g/m^2 and optionally organic acid at amount of 0.05 to 1000 g/m^2 and/or quaternary ammonium compound at amount of 0.05 to 500 g/m^2 calculated based on the outer surface of the filter material layer. Metal salts are in ionic form as dissociated in aqueous suspension of step (a).

The nanodiamonds applied may have surface charge of at least +40 mV or less than -40 mV measured as an aqueous dispersion, optionally before diluted to be applied. The surface charge may also be at least +50 mV or more negative than (less than) -50 mV or at least +55 mV or more negative than -55 mV.

The nanodiamond and metal containing suspension may be applied by spraying on to at least one side of the filter layer and drying. Spray application allows producing filter layers which carry charged nanodiamonds and metal ions only at one surface. In addition, drying step after spraying may be easier than after immersion.

The nanodiamond and metal containing suspension may be applied by immersing the filter to said suspension followed by drying the filter by evaporating the solvent. An immersion application results in substantially uniform spread of nanodiamonds and metal ions on the surface of the filter and pores throughout the filter structure (planar directions as well as z-axis direction). It will also allow a higher nanodiamond load and thereby enhanced adsorption capacity.

The drying step (evaporation of the solvent used in dispersion) can be made using known methods, such as high-speed dryer applying heat. Also passive evaporation may be used, especially when the dispersion with high nanodiamond content and thus relatively low solvent content has been used. If desired, the nanodiamond dispersion may be diluted before the application. An active filter layer can be dried to desired moisture content.

The nanodiamonds and metal ions (together or separately) may be applied as 0.01 to 5 wt.-% (total weight of ND & metal), such as about 0.5 wt.-% nanodiamond dispersion. The nanodiamonds may be applied as 0.1 to 3 wt.-%, as or as 0.1 to 1 wt.-%.

The higher nanodiamond and metal content, the easier is the drying step. A person skilled in the art is able to adapt the application speed and distance for spray application.

The solvent in said dispersion may be any solvent with a boiling point of 250 °C or less, such as 200 °C or less or 150 °C or less. The boiling point should be reasonable to allow evaporating the solvent after the nanodiamond dispersion is applied to the filter material. Low evaporation temperature requires less energy and is gentle to the filer material. Preferably the solvent is an aqueous solution such as deionized water.

The invention is illustrated below by the following non-limiting examples. It should be understood that the embodiments given in the description above and the examples are for illustrative purposes only, and that various changes and modifications are possible within the scope of the invention.

Materials

The detonation nanodiamond material used is Carbodeon commercial hydrogenated nanodiamond dispersion in water “uDiamond® Hydrogen D in water”, containing 2.5 wt.% of highly zeta positive, hydrogen terminated 4-6 nm nanodiamond particles. Said product features zeta potential ≥ + 50 mV and is free from surfactants. The product stability and high, non-decaying charge are both based on hydrogen termination covalently bound to nanodiamond particle.

The applied deionized water features specific resistance of 18 megaohm.

The $CuSO_4 \cdot 5H_2O$ and $Ag_2SO_4 \cdot H_2O$ salts, $C_6H_8O_7 \cdot H_2O$ (organic acid) as well as Didecyldimethylammonium chloride (quaternary ammonium compound) were purchased from Sigma Aldrich and applied as received.

The filter substrate material used is commercial, pigmented G4 filter class non-woven PET (polyethylene terephthalate) material (137 g/m2), comprised of 35% colored PET, 15% of 3 D PET white and 50% of a mixture of low melting point PET (27.5% of compound total weight; melting point) and of high melting point PET (22.5% of compound total weight). With D is meant Denier which a unit of weight used to measure the fineness of silk and man-made fibers. One Denier is equal to one gram per 9000 meters of fiber.

Applied G4 class filter materials are typically applied to trap fine dust with particle size of 1 to 10 micrometers and typical use includes pre-filters and circulation filters for civil defense shelters, exhaust filters for spray painting booths, kitchens etc., inlet air filters for air conditioners and compact machines (e.g. window air conditioners, ventilators as well as pre-filters for filter classes M6 to F8.

Equipments

The commercial “uDiamond® Hydrogen D nanodiamond in water 2.5 wt.% dispersion”, metal salts, organic acid as well as Didecyldimethylammonium chloride were diluted with deionized water manufactured with Millipore Mini-Q deionized water manufacturing unit. The mixing was carried out by using mechanical stirrer.

The nanodiamond, metal salt, organic acid and Didecyldimethylammonium chloride containing diluted aqueous suspension was sprayed onto non-woven PET filter material surface on an industrial fiber cloth processing machine mounted with fine spray nozzles to allow even spread of nanodiamond, metal salts organic acid and Didecyldimethylammonium chloride containing diluted aqueous suspension mist onto non-woven PET filter material surface. The nanodiamond, metal salt, organic acid and Didecyldimethylammonium chloride sprayed non-woven PET filter material was dried with an industrial High-Speed Dryer designed to dry fiber cloths, to provide a ready filtering medium.

The filter media microbicidal activity was tested both at GMicro Testing (Guangdong detection center of microbiology (adds.: Bldg 66, No. 100 Central Xianlie Rd, Guangzhou, China; tel.: 86 20 87137666; web: www.gddcm.com), and

SGS-CSTC Standards Technical Services Co., Ltd. Guangzhou Branch (web: www.sgsgroup.com.cn, tel.: 86 20 82075027).

Experimental work

Example 1. Preparation of diluted nanodiamond, metal salt, organic acid and Didecyldimethylammonium chloride containing aqueous suspension

Fill in a 50 kg barrel with 40 kg's of deionized water and dissolve 49.5 grams of $CuSO_4 \cdot 5H_2O$ as well as 384.8g of $C_6H_8O_7.H_2O$ therein, under gentle mechanical agitation. Introduce 50 grams of uDiamond Hydrogen D 2.5 wt.% highly zeta positive nanodiamond particle dispersion (1.25 grams of nanodiamond solids), under continued gentle agitation. Dissolve 6.57g of Ag_2SO_4 in 500 grams of boiling DI water (100°C) and load the resulting dispersion in the barrel, under continued gentle agitation for an hour. Load 56.3g of Didecyldimethylammonium chloride in the solution of barrel and add fill the barrel with 8953 grams of deionized water and continue stirring for 24 hours. The suspension will turn into a blue colored emulsified solution. Hence, the resulting suspension nanodiamond content is 0.0025 wt.%; copper content 0.0252 wt.% and silver content 0.00454 wt.%. From herein we refer the manufactured suspension as nanodiamond-metal complex suspension.

Example 2. Preparation of nanodiamond-metal complex containing PET filter material

The nanodiamond-metal complex suspension containing 0.0025 wt.% of hydrogenated highly zeta positive nanodiamond particles; 0.0252 wt.% of copper and 0.00454 wt.% of silver was sprayed evenly onto a moving G4 class PET filter substrate (137 g/m^2), followed by drying the resulting filter material in a high-speed dryer unit. The speed of the ES Fiber Cotton Surface was adjusted to adhere approximately 0.0075 g of detonation nanodiamond solids on square meter(m^2) of PET filter material, by coating approximately 83.3 m^2 of PET filter material with, by applying 25 kg's of prepared 50 kg's of nanodiamond-metal complex suspension.

The process was repeated with the remaining 25 kg's of nanodiamond-metal complex by spraying and drying said complex suspension on PET substrate media pristine side (83.3 m^2), to arrive onto 0.015 g of detonation nanodiamond solids and complex other components on one square meter(m^2) of PET filter material, the complex being thus adhered on both sides of the filter material.

Microbicidal and virucidal efficiency measurements

Example 3: Anti-bacterial anti-fungal tests

GMicro Testing (Guangdong detection center of microbiology)

The following data in Table 1 represents the nanodiamond-metal complex containing PET filter material bactericidal and fungicidal performance.

Table 1

Action, concentration and action time	**The tested organism**	**The number of bacteria in control sample**	**The average number of bacteria in the test sample**	**Sterilization rate (%)**
20 minutes	*Staphylococcus aureus* (ATCC 6538)	5.3 X 10^4	< 5	> 99.99%
	Candida albicans (ATCC 10231)	3.5 X 10^4	< 5	> 99.98%

The nanodiamond-metal complex bactericidal performance was >99.99% and the studied bacterial were killed in up to 20 minutes contact time. The nanodiamond-metal complex containing filter material fungicidal performance was >99.98% and the tested fungus were killed in up to 20 minutes contact time.

SGS-CSTC Standards Technical Services Co., Ltd. Guangzhou Branch

The following data in Table 2 represents the nanodiamond-metal complex containing PET filter material bactericidal and fungicidal performance, as analyzed by SGS-CSTC Technical Services Co., Ltd.

Table 2.

Test organism	**Escherichia Coli 8099**	**Candida albicans (ATCC 10231)**
Concentation of inoculum (CFU/mL)	1 X 10^5	1.4 X 10^5
F	2.9	2.3
Ct (CFU)	1.6 X 10^7	5.2 X 10^6

C0 (CFU)	2.2×10^4	2.5×10^4
Tt (CFU)	4.8×10^3	$< 2.0 \times 10^1$
A: antibacterial activity value	3.5	> 5.4
Percentage of antibacterial activity (%)	>99	>99

Notes:

1) Ct: the number of bacteria obtained from the control sample after 24h incubation (CFU)
2) C0: the number of bacteria obtained from the control sample immediately after incubation (CFU)
3) F: The growth value on the control sample, F = lgCt-lgC0
4) Tt: the number of bacteria obtained from the antimicrobial-treated sample after 24 h incubation CFU)
5) The control sample is 100% cotton fabric, provided by SGS lab
6) The sterilization method was autoclave sterilization method (121 C, 15 min)

The tests were carried out by applying test method GB/T 20944.2-2007 (Textiles-Evaluation for antibacterial activity-Part 2: Absorption method). The nanodiamond-metal complex containing filter material bactericidal performance was > 99%. The nanodiamond-metal complex containing filter material fungicidal performance was > 99%.

Example 4. Anti-viral tests

GMicro Testing (Guangdong detection center of microbiology)

The antiviral tests conducted on ND-metal complex containing PET filter material at GMicro Testing are depicted in Table 3 below.

Table 3.

Test item: evaluation of virucidal activity							
Virus and host cell	**Action, concentration and time**	**Group**	**Logarithm of inefectivity titre of virus lgTCID$_{50}$/mL**	**Average titre inefectivity of virus lgTCID$_{50}$/ml**	**Average inefectivity titre of virus TCID$_{50}$/mL**	**Average logarithm reduction value (KL)**	**Virus inactivation ratio (%)**

H1N1 (A/PR/8/34) MDCK Influenza A virus H1N1 (A/PR/8/34) Host cell: MDCK	Original sample, 20 minutes	Control group 1	5.57	5.58	$3.85x10^5$	>4.08	>99.99
		Control group2	5.50				
		Control group 3	5.67				
		Test group 1	<1.5	<1.5	<31.6		
		Test group 2	<1.5				
		Test group 3	<1.5				

The nanodiamond-metal complex containing filter material virucidal performance was >99.99%, and the tested viruses were killed in up to 20 minutes contact time.

SGS-CSTC Standards Technical Services Co., Ltd. Guangzhou Branch

The antiviral tests conducted on nanodiamond-metal complex containing PET filter material at SGS-CSTC Standards Technical Services., Ltd. are depicted in Table 4 below.

Table 4.

Virus and host cell	No.	The logarithm of inefectivity titre value immediate after inoculation of the specimen ($lgTCID_{50}$/bottle)	The logarithm of inefectivity titre value after 2h contacting with reference specimen ($lgTCID_{50}$/bottle)	The logarithm of inefectivity titre value after 2h contacting with the test specimen ($lgTCID_{50}$/bottle)
	1	7.2	6.80	2.80

Influenza A virus H1N1 (A/PR/8/34) Host cell: MDCK	2	7.1	6.80	2.80
	3	7.1	6.87	2.80
lgTCID$_{50}$/bottle Average		7.13	6.82	2.80
Logarithm of antiviral activity	4.02			
Antiviral activity rate (%)	99.99			

The tests were carried out by applying test method ISO 18184:2014 (E), nanodiamond-metal complex containing filter material virucidal performance was >99.99%.

Example 5. Neutralization of SARS-COV-2 Virus

The tests were carried out by University of Helsinki and performed according to the principles of Good Laboratory Practice (GLP) and the ISO 17025 standard. The testing was performed in a biosafety-level-3 (BSL-3) laboratory in accordance with the ISO 35001 standard on biorisk management.

The tested filter material referred in the test as “DiamondTrap material” is a filter construct comprising nanodiamond-metal complex containing PET filter material adhered to ePTFE (expanded PTFE) filter material. The applied PET filter material was G4 class filter media typically applied as a prefilter to protect and support ePTFE membrane.

Test Procedure

In the test, approximately 50 000 infectious SARS-CoV-2-virus particles were dried onto the PET side of the material that had been placed in a sterile 35/10 MM cell culture dish. Virus pipetted on the surface of the cell culture dish was used as a positive control and material without the virus as a cytotoxicity control. Samples were taken after 0 min, 10 min, 20 min, 1 h, and 2 h in the following way: 1 ml of culture media (Minimun essiantial Ea- gle’s medium (MEM) with 2 % fetal bovine serum and antibiotics) was pipetted onto the Petri dish and incubated at RT for 2 min with occasional mixing after. Undiluted samples and 1:10, 1:100, and 1:1000 dilutions were cultured in 96-well plates in two parallel reactions and incubated at 37 °C for 4 days. Samples from 0 min and 2 h time points were also taken and tested for SARS-CoV-2 RNA with PCR to ensure the detachment of the virus RNA from the test material.

Results

Based on microscopic observation of the cytopathic effect (CPE), no signs of virus growth was observed in 1:10, 1:100, or 1:1000 dilutions at any time point. Culturing results from undiluted samples were not used due to the cytotoxicity to the cells. Virus growth was detected in samples taken from plastic surface with all dilutions and at all time points. SARS-CoV-2 RNA was detected in PCR with Ct values 20.18 (test material, 0 min) , 22.93 (test material, 2 h), 18.44 (plastic, 0 min), and 19.20 (plastic, 2 h) indicating that protocol to detach the virus from the material was sufficient. The lack of virus growth in 0 min sample of the test material can be explained by the time it took to take the sample, including 2 min incubation with culture media, after applying the virus onto the surface which indicates that the inactivating effect took place within minutes.

Table 5: CPE caused by virus growth in different time points.

Material		Time	Undiluted	1:10	1:100	1:1000
DiamondTrap material	Virus	0 min	X	-	-	-
		10 min	X	-	-	-
		20 min	X	-	-	-
		1 h	X	-	-	-
		2 h	X	-	-	-
Plastic	Virus	0 min	+	+	+	+
		10 min	+	+	+	+
		20 min	+	+	+	+
		1 h	+	+	+	+
		2 h	+	+	+	+
DiamondTrap material	No virus	2 h	X	-	-	-
Plastic		2 h	-	-	-	-

+: CPE detected as a sign of infectious virus

-: CPE not detected

X: CPE caused by cytotoxicity of the sample detected

Together these findings may be taken to show that in the conditions tested the amount of infectious virus decreased below the detection limit within minutes.

Claims

1. An antipathogenic filter layer comprising filter material characterized by said filter material having detonation nanodiamonds (NDs) incorporated therein at amount of 0.001 to 10 g/m^2 calculated based on the outer surface of the filter material layer and metal ions incorporated therein at amount of 0.01 to 100 g/m^2 calculated based on the outer surface of the filter material layer, wherein the nanodiamonds have surface charge of at least +40 mV or more negative than -40 mV measured as a water dispersion by dynamic light scattering microscopy.

2. The antipathogenic air filter layer of claim 1, wherein the contact time to neutralize the pathogen, such as viruses or bacteria or viruses and bacteria is no longer than 60 minutes, preferably no longer than 30 minutes and most preferably no longer than 20 minutes.

3. The antipathogenic filter layer of claim 1 and 2, wherein the pathogen is Influenza A virus, subtype H1N1.

4. The antipathogenic air filter layer of claim 1 and 2, wherein the pathogen is *Staphylococcus aureus* or *Escherichia coli*.

5. The antipathogenic air filter layer of claim 4, wherein the metal ions comprise copper, silver, zinc or any mixture thereof.

6. The antipathogenic air filter layer of any of the preceding claims, wherein said filter material further comprises organic acid incorporated therein at amount of 0.05 to 1000 g/m^2 calculated based on the outer surface of the filter material layer.

7. The antipathogenic air filter layer of claim 8, wherein the organic acid is malic acid, citric acid or a mixture thereof.

8. The antipathogenic air filter layer of any of the preceding claims, wherein said filter material further comprises quaternary ammonium compounds therein at amount of 0.05 to 500 g/m^2 calculated based on the outer surface of the filter material layer.

9. The antipathogenic air filter layer of claim 8, wherein the quaternary ammonium compound is didecyldimethylammonium chloride.

10. The antipathogenic air filter layer of any of the preceding claims, wherein the nanodiamonds and metal ions are adhered on to the surface of the filter material layer.

11. The antipathogenic air filter layer of any of the preceding claims, wherein the nanodiamonds and metal ions are incorporated onto one surface or wherein the nanodiamonds and metal ions are incorporated onto both surfaces of the filter material layer.

12. The antipathogenic air filter layer of any of the preceding claims, wherein the nanodiamonds and metal ions are adhered throughout the filter material layer.

13. The antipathogenic air filter layer of any of the preceding claims, wherein the filter material is fiber based.

14. The antipathogenic air filter layer of any of the preceding claims, wherein the filter material is non-woven.

15. The antipathogenic air filter layer of any of the preceding claims, wherein the nanodiamonds have surface charge of at least +50 mV or more negative than -50 mV.

16. The antipathogenic air filter layer of any of the preceding claims, wherein the nanodiamonds have an average primary particle diameter of 4 to 6 nm.

17. An antipathogenic air filter construct characterized by comprising:

- at least one antipathogenic filter layer of claims 1 to 16; and optionally one or more selected from
- one or more pre-filter layer; and
- one or more electrostatic layers; and
- one or more ePTFE layers; and
- one or two protective layers; and
- any combination of those.

18. The antipathogenic filter construct of claim 17, wherein the construct is a face mask.

19. The antipathogenic filter construct of claim 17, wherein the construct is a safety cloth or curtain.

20. The antipathogenic filter construct of claim 17, wherein the construct is a HEPA or ULPA filter construct.

21. The antipathogenic filter construct of any of claims 17 to 20, wherein the construct comprises two or more antipathogenic filter layers described in any of claim 1 to 18, preferably when said layers are incorporated with nanodiamonds with opposite surface charges.

22. The antipathogenic filter construct of claim 21, wherein the surfaces incorporated with oppositely charged nanodiamonds are separated by a spacer.

23. A method for improving a filter's capacity of capturing and neutralizing pathogenic particles characterized by

(a) providing aqueous suspension comprising nano diamond dispersion, metal salts and optionally organic acid and/or quaternary ammonium compound; and

(b) providing at least one air filter layer; and

(c) applying said dispersion to at least one side of the filter layer,

wherein such formed layer comprises detonation nanodiamonds (ND) at amount of 0.001 to 10 g/m^2, metal salts at amount of 0.01 to 100 g/m^2 and optionally organic acid at amount of 0.05 to 1000 g/m^2 and/or quaternary ammonium compound at amount of 0.05 to 500 g/m^2 calculated based on the outer surface of the filter material layer, wherein the nanodiamonds applied have surface charge of at least +40 mV or more negative than -40 mV measured as a water dispersion before diluted to be applied by dynamic light scattering microscopy.

24. The method of claim 23, wherein the nanodiamonds applied have surface charge of at least +40 mV or less than -40 mV measured as a water dispersion before diluted to be applied.

25. The method of any of claims 23 or 24, wherein the suspension is applied by spraying said suspension on to at least one side of the filter layer and drying.

26. The method of claim 23, wherein the suspension is applied by immersing the filter to said suspension followed by drying.

27. The method of claim 23, wherein the suspension is applied by evaporating said suspension by ultrasonic nebuliser on to at least one side of the filter layer.

INTERNATIONAL SEARCH REPORT

International application No
PCT/FI2022/050024

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01D39/16 B01D39/18 A62B23/02 A41D13/11 B01D39/20
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)
B01D A62C A62B A44C A41D A61K A01N

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

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 2013 127372 A (VISION DEV CO LTD) 27 June 2013 (2013-06-27) paragraphs [0027] - [0034], [0042], [0053], [0055], [0070], [0081] - [0088], [0093], [0109] - [0114]; claims 1-16; example 1	1-27
A	JP 2009 045287 A (BANDO CHEMICAL IND) 5 March 2009 (2009-03-05) paragraphs [0014] - [0017], [0055]; example comparative 4	1-27
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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

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

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Date of the actual completion of the international search 12 April 2022	Date of mailing of the international search report 25/04/2022
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 Focante, Francesca

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INTERNATIONAL SEARCH REPORT

International application No
PCT/FI2022/050024

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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