Disclosed is a photocatalytic coating sol composition and the method for preparing the same. The photocatalytic coating sol composition comprising 0.1% to 10% by weight of a photo-catalyst, 0.1% to 10% by weight of an inorganic adsorbent, 1% to 20% by weight of an inorganic binder, 55% to 95% by weight of an organic solvent and if necessary 0.1% by weight to 10% by weight of a metal compound. Specifically, the present invention can remove harmful substances by coating photocatalytic coating sol composition prepared from photocatalyst, inorganic adsorbent, inorganic binder, metal compound and organic solvent on metal filter such as aluminum etc., and plastic filter such as polyethylene and polypropylene etc. used in environmental contaminants treatment system or air conditioning plant such as air-conditioner and air-cleaner, according to any one of any ordinary coating techniques such as spray method or dipping method etc. at room temperature.
FIG. 6

- ○ PE Filter coated without Photocatalyst
- ▲ PE Filter Coated with Photocatalyst

Time (minute) vs. Removal Rate (TMA Concentration/Initial Concentration)
PHOTOCATALYTIC COATING MATERIAL HAVING PHOTOCATALYTIC ACTIVITY AND ADSORPTION PROPERTY AND METHOD FOR PREPARING THE SAME

TECHNICAL FIELD

[0001] The present invention relates to a photocatalytic coating sol composition and a method for preparing the same, and more particularly to an application to an environmental purifying system in a manner of coating a photocatalytic coating sol composition, having high adsorption property as well as high photocatalytic activity, on meshes of metal such as stainless steel, non-ferrous metal such as aluminum, non-woven fabric, ceramic filter and plastics such as polyethylene (PE) filter, by means of an inorganic binder, by using common coating techniques such as spraying method or dipping method etc. at room temperature.

BACKGROUND ART

[0002] Previously, the conventional method for treating environmental contaminants could be classified into two methods. One is a physico-chemical method which includes adsorption, cooling condensation, solvent scrubber, catalytic oxidation method. And another is a biological treatment method. However, the adsorption method and the cooling condensation method are ineffective for fundamentally treating the contaminants, and thus there is a limitation on using these methods. The solvent scrubber method is a type of a chemical deodorization method in which the contaminants are neutralized due to chemicals, whereby removal rate of the contaminants is high for limited areas. However, the above methods have several disadvantages, because an additional device is required to spray the chemicals in order to take place the reaction of the chemicals effectively with the contaminants in areas having vast production source of contaminants, and a large amount of chemicals must be used for neutralizing the contaminants in an area having a large amount of contaminants in high concentration. Meanwhile, both in direct combustion method and the catalytic oxidation method, substances causing pollutions are removed through an oxidation process, which show a high removal rate, yet produce secondary contaminants such as NOx and SOx, and require high cost.

[0003] A method for biological treating the contaminants using microorganisms has been widely used in recent years owing to low initial investment costs as well as operating costs, has been studied actively in industrially advanced countries such as Europe and North America, and thus has reached to a commercialization step. According to this method, various microorganisms capable of removing the contaminants are immobilized in a carrier, which is advantageous in removing the contaminants in a high rate. And also, it allows using small-sized equipments. However, the method has technical problems, for example, contaminants used as nutrients for growth of the microorganisms must be continuously administered into a reactor where a substantial contaminants removal is performed, the carrier must be washed periodically, the microorganisms must be well controlled, and process of this method must be operated continuously.

[0004] Recently, in order to solve the above problems, there is an increasing interest in removing contaminants and odor materials using photocatalyst as a high-grade oxidation technique. Specifically, Korean Patent Application No. 1999-0052838 discloses a filter using photocatalyst coated with titanium dioxide (TiO₂), zinc oxide (ZnO) and silver (Ag) etc. on filter such as non-woven fabric, activated carbon and Zeolite etc. Korean Patent Application No. 2000-0034908 discloses a method for treating volatile organic compounds by using photocatalyst, and Korean Utility Model Application No. 2000-0029950 discloses a device for treating water by using titanium oxides.

[0005] The photocatalytic oxidation refers to the decomposing reaction of gaseous or liquid phase organic materials which are adsorbed on the surface of the photocatalyst owing to the strong oxidation of hydroxyl radicals (—OH) generated by a hole, wherein the hole is generated together with an electron when a light energy; more than the bandgap energy, is irradiated on the photocatalyst.

[0006] That is, the photocatalyst shows catalytic activity by absorbing light energy, and the generated oxidation strength is used to decompose environmental contaminants by oxidation. Representative materials inducing photocatalytic reaction may be, for example, TiO₂, ZnO₂, ZnO, SrTiO₃, CdS, GaP, InP, GaAs, BaTiO₃, K₂O·O₂, Fe·O₂, Ta·O₂, WO₃, SnO₂, Bi₂O₃, NiO, Cu·O, SiO₂, SiO₂, MoS₂, InPb, RuO₂, CoO, Fe etc. and could be used by adding metals such like Pt, Rh, Ag, Cu, Sn, Ni, Fe etc. and metal oxide thereof to the above photocatalyst. Among them, titanium dioxide (TiO₂) is mostly used because it is harmless to human body, exhibits excellent photocatalytic activity, good photo-corrosion resistance and requires low cost.

[0007] The titanium dioxide absorbs and reacts at a wavelength less than 388 nm and generates the electron (conduction band) and the hole (valence band). Hereby, glow lamp and mercuric lamp besides solar energy lamp could be used for UV ray as a light source. The electron and the hole generated by the above reaction recombine with each other within 10⁻¹² sec to 10⁻⁹ sec. However, if the contaminants are adsorbed on the surface prior to recombination of the electron and the hole, the contaminants are decomposed by the electron and the hole.

[0008] The reaction mechanism of this photocatalyst can be represented as the following reaction formulas 1 to 5.

\[
\begin{align*}
\text{TiO}_2 + h^+ & \rightarrow e^- + h^+ \quad \text{(Reaction formula 1)} \\
\text{e}^- + \text{O}_2 & \rightarrow \text{O}_2^- \text{radical} \quad \text{(Reaction formula 2)} \\
h^+ & \rightarrow \text{OH} \rightarrow \text{OH radical} \quad \text{(Reaction formula 3)} \\
\text{O}_2^- \text{radical} + \text{A (organics, microorganisms, contaminants)} & \rightarrow \text{A}^- \quad \text{(Reaction formula 4)} \\
-\text{OH radicals} + \text{B (organics, microorganisms, contaminants)} & \rightarrow \text{B}^- \quad \text{(Reaction formula 5)}
\end{align*}
\]

[0009] There have been extensive researches performed in order to develop a method for preparing coating sol composition containing photocatalyst (e.g. titanium dioxide) to provide a photocatalytic active material, which are capable of removing the contaminants by adsorption and decomposition. Specifically, the technique for antifogging is disclosed in PCT Publication No. WO96/029375, wherein the technique prevents substrate from forming haze and water-drop thereon by coating a photocatalyst layer on transparent substrates such as mirror, lens and plate. Also, the technique has been practically used in anti-fouling field, such as a filter for an air cleaner, the filter deodorizing odor components
(e.g. cigarette smoke) by using titanium dioxide as photocatalyst, antibiotic filter having antibacterial function in water or atmosphere, glass and tile. And, a filter being coated with a photocatalyst can be applied to photocatalytic system to decompose the volatile organic compounds. However, since the photocatalytic reaction is a surface reaction, there is a need for developing a technique capable of adsorbing a large amount of organic contaminants or odor materials.

**[0010]** A method for coating photocatalyst via a liquid phase, which is most commonly used, uses titanium alkoxide as a starting material to prepare a solid composition, which coats a carrier (Japanese patent publication No. 5-253544). However, the method requires complex process steps such as generating photocatalytic particles on the carrier after coating, crystallization of anatase type having high photocatalytic activity, and sintering at the temperature range of 400 to 600°C to give adherence to a carrier, resulting in high manufacturing cost.

**[0011]** Also, the application of this method is restricted to coat on polymer materials such as plastics having poor heat resistance. Further, even though a photocatalytic coating on tiles and ceramics having excellent heat-resistance is carried out and then treated at high temperature, there are still problems such as large power consumption.

**[0012]** Meanwhile, photocatalytic coating method via a gaseous phase not using photocatalytic coating sol composition includes spattering method or chemical vapor depositing method disclosed in Japanese Patent publication No. 60-44055. However, there are also problems such as high initial investment cost due to the manufacturing of equipment, high consumption of electric power and manufacturing time due to the increase of coating film thickness.

**[0013]** Also, if titanium dioxide is formed as a thin-film on a support according to the sol-gel method, it requires much time for decomposing contaminants because of limited contact area of contaminants on the thin-film containing photocatalyst. For effective removing of environmental contaminants using photocatalyst, there is a need for enlarging surface area of photocatalyst or increasing the intensity of light source. Specifically, filter for air handling unit such as air purifier, air-conditioner etc. which is used for removing odor material and the like, requires about 10^{-3} sec of treatment time, and thus it requires development to the sol for coating having high adsorption power and high photocatalytic activity.

**[0014]** Conventionally, in order to uniformly disperse different kinds of particles between different kinds of particles in solution state, different kinds of sol composition were physically mixed with each other (U.S. Pat. No. 5,591,380), or two kinds of alkoxides as starting materials were dissolved simultaneously into the solvent to prepare sol composition (U.S. Pat. No. 4,176,089). However, in case of mixing two kinds of sol composition, the stability of sol composition decreases and turns into gel in short time. During the coating process, the coating film becomes thick and is delaminated from the carrier after the heating treatment. And, the methods have the disadvantage in that the condition of the manufacture process must be controlled accurately when sol particles are dispersed by dissolusion start materials simultaneously.

**[0015]** The present inventors have made a research to develop a photocatalytic coating composition having high adsorption and high photocatalytic activity, and as a result, the present invention has been completed on the basis of the discovery described below.

**DISCLOSURE OF INVENTION**

**[0016]** An object of the present invention is to provide a photocatalytic coating sol composition and method for preparing the same, capable of preventing delamination of secondary contaminants generated by transient photocatalytic reaction and having high photocatalytic activity.

**[0017]** Another object of the present invention is to provide a method capable of decomposing and removing environmental contaminants and harmful microorganisms etc. by coating filters with the photocatalytic coating sol composition for water treatment and air treatment coated according to a method such as spray method or dipping method.

**[0018]** Therefore, in one aspect of the present invention, there is provided a photocatalytic coating sol composition comprising 0.1% to 20% by weight of a photocatalyst, 0.1% to 10% by weight of an inorganic adsorbent, 1% to 20% by weight of an inorganic binder and 55% to 95% by weight of an organic solvent.

**[0019]** In another aspect of the present invention, there is provided a photocatalytic coating sol composition comprising 0.1% to 20% by weight of a photocatalyst, 0.1% to 10% by weight of an inorganic adsorbent, 1% to 20% by weight of an inorganic binder, 55% to 95% by weight of an organic solvent and 0.1% to 10% by weight of a metal compound.

**[0020]** In a further aspect of the present invention, there is provided a method for preparing the photocatalytic coating sol composition comprising the steps of mixing 1% to 20% by weight of an inorganic binder, 55% to 95% by weight of an organic solvent and if necessary, 0.1% to 0.5% by weight of a strong acid or a strong base and then stirring at 1000 to 1500 rpm for 10 to 30 min at room temperature, adding 0.1% to 20% by weight of a photocatalyst powder and 0.1% to 10% by weight of an inorganic adsorbent into the mixture and then treating for 10 to 50 min in an ultrasonic device, and if necessary, adding 0.1% to 10% by weight of a metal compound into the mixture.

**[0021]** The photocatalyst may be used either alone or mixture of at least two kinds of photocatalytic metal oxides selected from TiO_2, ZnO, ZnO, CaTiO_3, WO_3, SrO, MoO_3, Fe_2O_3, InP, GaAs, BaTiO_3, K_2O, Fe_3O_4, and Ta_2O_5, preferably TiO_2 and/or ZnO. Also, a small sized photocatalyst particle shows more excellent photocatalytic property. Therefore, the average diameter of particle should be from 1 to 50 nm, and preferably 1 to 10 nm.

**[0022]** Meanwhile, the reaction rate of the photocatalyst is increased by adding 0.01% to 5% by weight of a metal or a metal oxide, for example, palladium, platinum, rodium, tungsten, gold, silver and copper etc. of the total weight of the photocatalyst. Also, the durability of the photocatalyst can be improved by combining the photocatalyst with hindered amine type photo-stabilizer and triazole-based UV adsorbent to inhibit deterioration of photocatalytic coating film due to photocatalytic reaction.

**[0023]** The inorganic adsorbent in accordance with the present invention is not particularly limited, but preferably high adsorbent inorganic material which is capable of
adsorbing odor material and harmful materials during photocatalytic reaction, and more preferably, for example, magnesium or calcium-containing silicates, talc, diatomite, zeolite coated with silver or copper ion.

[0024] As the inorganic binder in accordance with the present invention may be used, for example, isopropoxide compound, silane compound etc., preferably isopropoxide compound such as titanium isopropoxide. Also, in order to control hydrolysis rate of the inorganic binder, acid or base catalyst may be added in small amounts.

[0025] The organic solvent used in the present invention may be alcohol having lower alkyl group, preferably anhydride ethanol or isopropanol etc.

[0026] Meanwhile, the metal compound in the present invention is not particularly limited, but preferably the materials capable of improving antibiotic function and color of the materials may preferably be used either alone or as a mixture of more than two species selected from a copper compound such as acetylacetone (copper (I)), copper acetate monohydrate (copper (II)) etc., a silver compound such as silver acetate etc., bengala, vermilion, cadmium red, yellow earth, cadmium yellow, emerald rock, chromium oxide green, Prussian blue, cobalt blue, manganese or carbon black, and more preferably a copper compound.

[0027] The method for preparing the photocatalytic coating sol composition in the present invention can be explained as follows:

[0028] First, after mixing 1% to 20% of an inorganic binder with 55% to 95% of an organic solvent and if necessary 0.1% to 0.5% of a strong acid or a strong base, is followed by the step of stirring the mixture at 1000 to 1500 rpm for 10 to 30 min at room temperature. Then, 0.1% to 20% of a photocatalyst powder is added in the mixture.

[0029] In the mixture, 0.1% to 10% by weight of an inorganic adsorbent is added and treated for 10 to 50 min in an ultrasonic device to obtain the coating sol composition according to the present invention. At this time, the inorganic adsorbent is adsorbed on the coating film while harmful materials such as odor materials, primarily decomposable materials are decomposed by the photocatalyst, secondary contaminants are adsorbed on the coating film after photocatalyzing primarily decomposable materials and thus the harmful materials will be less emitted into the atmosphere by photo-decomposition of the photocatalyst.

[0030] Also, if necessary, 0.1% to 10%, preferably 0.2% to 5% of a metal compound may be used to enhance antibiotic function of the photocatalytic coating sol composition according to the present invention or to enhance color development of the coating film by irradiating ultraviolet light on the coating film.

[0031] Since the photocatalytic coating sol composition according to the present invention may be uniformly dispersed with different kinds of oxides onto the coating film, the method can be more easily and commercially used than the prior methods. Also, in order to control hydrolysis rate of inorganic binder, small amounts of acid or base catalyst may be added.

[0032] The photocatalytic coating sol composition according to the present invention may be coated on the desired substrate according to a printing method, a spraying method, a dipping method etc. and dried, and preferably the spraying method or the dipping method may be used. Wherein the drying temperature in the spraying and dipping method depends on solvents, it is generally 50 to 200°C., preferably 100 to 150°C.

[0033] The substrate is not particularly limited, but any material capable of being coated with the photocatalytic coating sol composition prepared according to the present invention is preferred. For example, the substrates include various carriers which require effects of antibiotic, deodorization, pollution control etc., or filters for water treatment and air pollution preventing equipment, metal, alloy, glass, curtain, wall paper, package, plastics and papers.

[0034] For coating the photocatalytic coating sol composition on the substrate, the thickness of the coating film must be controlled according to use. If the thickness of the coating film is larger than 0.1 μm, the photocatalytic layer is firmly adherent on the substrate and thus the coating structure having high durability is obtained, and furthermore as the thickness of the coating film increases, the photocatalytic activity increases too.

[0035] On the other hand, if the thickness is larger than 5 μm, the photocatalytic activity does not increase accordingly because the light source can not be sufficiently transmitted into the bottom of the photocatalyst layer. Because the photocatalytic activity is high if the thickness is less than the size of 5 μm, it is preferable that the photocatalytic coating film is selected taking into account of the light transmission properties.

[0036] Also, it is effective to control the thickness of the coating film in the range of 20 to 50 μm to enhance adsorbent property of the contaminants. Therefore, the thickness of the photocatalytic layer can be determined in the range of 5 to 50 μm.

[0037] The photocatalytic coating sol composition in accordance with the present invention can be applied to various carriers which require an effect of antibiotic, deodorization, pollution control for example interior goods such as curtain, wall paper, commodities such as tent, umbrella, scarf etc., packaging vessel such as food package etc., agricultural field such as raising seedling sheet etc., Also the metal including photocatalytic function may be used as substrate with single metal of aluminum iron, copper etc. and further all kinds of alloy such as stainless, pearl brass, aluminum alloy, titanium alloy etc.

[0038] Meanwhile, the coating film consisting of the photocatalytic coating sol composition according to the present invention can be formed onto the metal sheet or plate coating with common paint and colored copperplate according to the shape or quality of the used metal. If the adherent layer and the coating film of the photocatalyst have high photo-transmission rate and transparency, its applicability can be improved because the color tone of basic paint is not damaged.

[0039] Photocatalyst substrate structure according to the present invention makes it possible to function simultaneously such as decomposition, antibiotic and deodorization of harmful materials by applying to window glass of automobile or all kinds of conveyance, window glass of architecture, filter for refrigeration chilling showcase or environ-
mental purifying system by utilizing the functions and enhance pollution prevention function of glass surface.

[0040] Specifically, it is used to coat plastic filters (e.g. polyethylene filter, polypropylene filter etc.) for environmental purifying systems, air handling purifier and air-cleaner.

BRIEF DESCRIPTION OF THE DRAWINGS

[0041] Further objects and advantages of the invention can be more fully understood from the following detailed description taken in conjunction with the accompanying drawing in which:

[0042] FIG. 1 shows a graph of photocatalytic activity of metal mesh coated with a photocatalytic coating sol composition prepared without adding inorganic adsorption and metal compound;

[0043] FIG. 2 shows a graph of photocatalytic activity of metal mesh coated with a photocatalytic coating sol composition according to Example 6 of the present invention;

[0044] FIG. 3 shows a graph of photocatalytic activity of metal mesh coated with a photocatalytic coating sol composition according to Example 7 of the present invention;

[0045] FIG. 4 shows a graph of antibiotic experiment results of metal mesh coated with a photocatalytic coating sol composition prepared according to the present invention and photocatalytic coating sol composition prepared without adding inorganic adsorbent and metal ions, respectively;

[0046] FIG. 5 shows a graph of de-colorization experiment result of polyethylene filter coated with a photocatalytic coating sol composition prepared according to the present invention;

[0047] FIG. 6 shows a graph of activity experiment result of polyethylene filter coated with a photocatalytic coating sol composition prepared according to the present invention;

[0048] FIG. 7 shows the graph of saturated activity experiment result of polyethylene filter coated with a photocatalytic coating sol composition prepared according to the present invention;

[0049] FIG. 8 shows an electron microscope photograph taken from the surface of polyethylene filter coated with a photocatalytic coating sol composition prepared according to the present invention; and

[0050] FIG. 9 shows an electron microscope photograph taken from section of polyethylene filter coated with a photocatalytic coating sol composition prepared according to the present invention.

BEST MODE FOR CARRYING OUT THE INVENTION

[0051] The present invention will now be described in detail in connection with the preferred embodiments with reference to the accompanying drawings. The examples should not be construed as a limitation upon the scope of the present invention.

EXAMPLE 1

[0052] 5% by weight of titanium isopropoxide [Junsei Chemical Co., Ltd.], 78.8% by weight of anhydrous ethanol and 0.2% by weight of hydrochloric acid were mixed and then stirred with 1200 rpm for 20 min at room temperature. Next, 10% by weight of titanium dioxide powder [Degussa P25, Germany] was added into the mixture.

[0053] In the mixed solution, 6% by weight of talc [DUKSAN PURE CHEMICAL Co., Ltd.] was added and then treated for more than 30 min in a ultrasonic device [BRANSON Ultrasonic Co., DHA-1000], to obtain sol composition for coating.

EXAMPLE 2

[0054] 5% by weight of titanium isopropoxide [Junsei Chemical Co., Ltd.], 78.5% by weight of anhydrous ethanol and 0.2% by weight of hydrochloric acid were mixed and then stirred with 1200 rpm for 20 min at room temperature. Next, 10% by weight of titanium dioxide powder [Degussa P25, Germany] was added into the mixture.

[0055] In the mixed solution, 6% by weight of talc [DUKSAN PURE CHEMICAL Co., Ltd.] was added and then treated for more than 30 min in an ultrasonic device [BRANSON Ultrasonic Co., DHA-1000], followed by adding 0.3% by weight of copper acetate hydrate [Junsei chemical Co., Ltd., Japan] in the solution, to obtain sol composition for coating.

EXAMPLE 3

[0056] The same process as in Example 1 was carried out, except that, instead of 6% by weight of talc, 5% by weight of diatomite [DUKSAN PURE CHEMICAL Co., Ltd.] was used.

EXAMPLE 4

[0057] The same process as in Example 2 was carried out, except that, instead of 0.3% by weight of copper acetate hydrate, 0.3% by weight of hydrate silver acetate [Junsei Chem. Co., Ltd., Japan] was used.

EXAMPLE 5

[0058] 3% by weight of titanium dioxide [Degussa P25, Germany], 93% by weight of ethanol and 0.2% by weight of hydrochloric acid were mixed and then stirred with 1200 rpm for 20 min at room temperature.

[0059] In the mixed solution, 3.8% by weight of magnesium silicate [Aldrich, U.S.A.] was added and treated for more than 30 min in an ultrasonic device [BRANSON Ultrasonic Co., DHA-1000], followed by adding 0.3% by weight of copper acetylacetate [Junsei chemical Co., Ltd., Japan] in the solution, to obtain sol composition for coating.

EXAMPLE 6

[0060] The sol composition for coating prepared according to Example 1 was coated on a metal mesh [Al salongs 4x8 mm, 0.4 T, Hyungjei Metalas Co., Korea] according to the spraying method (diameter: 1.5, pressure: 4 KG) at room temperature and then dried at the temperature of 120 to 150°C, to obtain metal mesh coated with photocatalyst.

EXAMPLE 7

[0061] The same process as in Example 6 was carried out, except that, instead of the sol composition for coating
prepared by Example 1, the sol composition for coating prepared by Example 2 was used.

EXAMPLE 8

[0062] The same process as in Example 6 was carried out, except that, instead of the sol composition for coating prepared by Example 1, the sol composition for coating prepared by Example 3 was used.

EXAMPLE 9

[0063] The same process as in Example 6 was carried out, except that, instead of the sol composition for coating prepared by Example 1, the sol composition for coating prepared by Example 4 was used.

[0064] Initial concentration of the trichloroethylene was about 2000 ppm, volume of reactor was 125 cm³, the metal mesh was irradiated by black light lamp (wavelength 300 nm to 368 nm, maximum wavelength 400 nm) [4W BLB, Sankyo denki, Japan], and then decomposition rate of the trichloroethylene was measured with FTIR spectrometer [Perkin Elmer, Spectrum one FT-IR spectrometer].

[0065] The measurement results are shown in FIG. 1 to 3.

[0066] FIG. 1 shows the activity of metal mesh coated with photocatalytic coating sol composition prepared without adding inorganic adsorbent and metal compound according to the Comparative Example. FIG. 2 shows the activity of metal mesh coated with photocatalytic coating sol composition prepared according to Example 6 of the present invention, and FIG. 3 shows the activity of metal mesh coated with photocatalytic coating sol composition prepared according to Example 7 of the present invention.

[0067] As shown in FIG. 1, it could be seen that as a result of decomposition by the photocatalyst, the trichloroethylene was decomposed within several minutes (10 min to 20 min), but the peak of hosen as intermediate was detected (C==C: 856 cm⁻¹, C==O: 1825 cm⁻¹) using trichloroethylene (TCE) as reactant.

[0068] It means that trichloroethylene could be rapidly decomposed by the photocatalytic coating sol composition, but harmful hosen could be emitted into the atmosphere.

[0069] Therefore, it is not suitable to use photocatalytic coating sol composition being prepared without adding inorganic adsorbent and metal compound on photocatalyst filter for air-conditioner and air-purifier.

[0070] In contrast, as shown in FIGS. 2 and 3, it is observed that photocatalytic activity was decreased by half and after trichloroethylene was decomposed, peak of hosen corresponding to secondary contaminants (by-product) are not detected, compared to the result obtained from the metal mesh according to the Comparative Example. That means that the secondary contaminants was not emitted into the Initial concentration of the trichloroethylene was about 2000 ppm, volume of reactor was 125 cm³, the metal mesh was irradiated by black light lamp (wavelength 300 nm to 368 nm, maximum wavelength 400 nm) [4W BLB, Sankyo denki, Japan], and then decomposition rate of the trichloroethylene was measured with FTIR spectrometer [Perkin Elmer, Spectrum one FT-IR spectrometer].

[0071] The measurement results are shown in FIG. 1 to 3.

[0072] FIG. 1 shows the activity of metal mesh coated with photocatalytic coating sol composition prepared without adding inorganic adsorbent and metal compound according to the Comparative Example. FIG. 2 shows the activity of metal mesh coated with photocatalytic coating sol composition prepared according to Example 6 of the present invention, and FIG. 3 shows the activity of metal mesh coated with photocatalytic coating sol composition prepared according to Example 7 of the present invention.

[0073] As shown in FIG. 1, it could be seen that as a result of decomposition by the photocatalyst, the trichloroethylene was decomposed within several minutes (10 min to 20 min), but the peak of hosen as intermediate was detected (C==C: 856 cm⁻¹, C==O: 1825 cm⁻¹) using trichloroethylene (TCE) as reactant.

[0074] It means that trichloroethylene could be rapidly decomposed by the photocatalytic coating sol composition, but harmful hosen could be emitted into the atmosphere.

[0075] Therefore, it is not suitable to use photocatalytic coating sol composition being prepared without adding inorganic adsorbent and metal compound on photocatalyst filter for air-conditioner and air-purifier.

[0076] In contrast, as shown in FIGS. 2 and 3, it is observed that photocatalytic activity was decreased by half and after trichloroethylene was decomposed, peak of hosen corresponding to secondary contaminants (by-product) are not detected, compared to the result obtained from the metal mesh according to the Comparative Example. That means that the secondary contaminants was not emitted into the atmosphere because it was adsorbed by adding high adsorptive inorganic.

[0077] Antibiotic Test

[0078] Two petri dishes containing cultured Escherichia coli therein (diameter: 100 mm, height: 15 mm) and two 3 cm×6 cm sized samples of the metal mesh prepared according to Example 8 of the present invention were prepared. Then, each sample was placed in the inside of each petri dish containing the Escherichia coli, wherein one petri dish was irradiated with black light lamp [4W BLB, Sankyo Denki, Japan] of wavelength of 300 nm to 368 nm, maximum wavelength of 400 nm, and 4W equipped at a distance of 5 cm, whereas the other petri dish was not irradiated with L. Colony number of initial Escherichia coli used in the experiment was 70 per petri dish.

[0079] The result is shown in FIG. 4.

[0080] As shown in FIG. 4, after irradiating with UV for 6 hours, it could be seen that Escherichia coli in the petri dish was completely removed. And for the experiment under the same condition without irradiation, it could be seen that the colony number of Escherichia coli was not decreased.

[0081] ii) Experiment Using Polyethylene Filter

[0082] De-Colorization Test

[0083] For measuring adsorption activity of polyethylene filter coated with photocatalytic coating sol composition...
prepared according to Example 10, 25 ml of aqueous methylenblue solution (M.B.)[ethylene blue 2-3hydrate, Junsei Chen, Co., Ltd. Japan] of 0.8 ppm was added into the petri dish (diameter: 100 mm, height: 15 mm), and the polyethylene filter coated with photocatalyst prepared according to Example 10 was dipped in the petri dish, and then, de-colorization degree of aqueous solution was observed by irradiation with black light lamp[4W BLB, Sankyo Denki, Japan] of wavelength of 300 to 368 nm, maximum wavelength of 400 nm, and 4W equipped at a distance of 15 cm from the petri dish.

The result is shown in FIG. 5. As shown in FIG. 5, it could be seen that the removal rate of aqueous methylene blue (M.B.) solution after 30 min was 84.4%.

Decolorization Test

For decolorization test in gas state, the polyethylene filter coated with photocatalyst prepared by Example 10 was placed in the center of closed SUS reactor having a volume of 125 L and then trimethylamine (TMA) as odor material was poured into the reactor at a rate of 0.83 m/s. After pouring the trimethylamine (TAM), removal rate depending on time was measured, as shown in FIG. 6.

As shown in FIG. 6, removal rate of the trimethylamine was 82.2% after 10 min and 90.41% after 30 min, respectively.

Saturated-Activity Experiment

In the inside of closed SUS reactor having a volume of 125 L, polyethylene filter coated with the photocatalytic coating sol composition prepared according to Example 10 was placed and circulation fan was equipped, and 20 ppm of trimethylamine (TMA) as odor material was poured into the reactor.

Then inner air was circulated by the circulation fan at a rate of 0.83 m/s and left to stand for about 1 hour. Next, concentration of the trimethylamine (TMA) in the inside of the reactor was measured.

The experiment was set as 1 cycle and after completing the 1 cycle, light was irradiated for 1 hour with black light lamp [4W BLB, Sankyo Denki, Japan] on the polyethylene filter coated with the photocatalyst, and followed by repeating the same process as described above. The second experiment was set as 2 cycle and the cycles were repeated.

The result is shown in FIG. 7. As shown in FIG. 7, removing performance of trimethylamine was 1002.7 ppm during 53 cycles, and removing efficiency of trimethylamine (TMA) was maintained for about 90%.

Antibiotic Test

Antibiotic property of polyethylene filter coated with photocatalytic coating sol composition prepared according to Example 10 by using Shake Flask Method was measured.

Herein, the Shake Flask Method can be performed as follows:

First, after samples (30 square shaped pieces of 1 cm x 1 cm) and control samples (30 square shaped pieces of l-methyl) were inoculated with known bacteria, inoculation liquid and a certain amount of neutralization solution were blended followed by extracting the incubated bacteria, and when the number of bacteria in the neutralization solution was measured, bacteria decreasing rate between the sample and the comparative sample was measured by the following equation 1.

Phosphoric acid buffer solution (pH 7.0±0.2) was used as the neutralization solution, Tween 80 (0.05%) was used as surfactant, and after blending and incubating at 150 times/min for 24 hours at a temperature of 35 ±1°C, the bacteria number of test bacteria solution was measured.

\[
\text{Bacteria Decreasing Rate} = \left[ \frac{\text{bacteria of blank after 24 hours} - \text{bacteria number of coated goods after 24 hours}}{\text{bacteria number of blank after 24 hours}} \right] \times 100 \quad \text{[Equation 1]}
\]

Wherein the blank was the original sample without coating, for example polyethylene filter without the photocatalytic coating sol composition coating.

The known bacteria strains used in the Shake Flask method were Staphylococcus aureus ATCC 6538 and Escherichia coli ATCC 25992.

The result is shown in following Table 1.

As shown in the Table 1, microorganisms increasing rate in Examples 7 and 10 using polyethylene filter coated with photocatalytic coating sol composition was very low, while bacteria was increased by 30% to 40% in the blank sample.

<table>
<thead>
<tr>
<th>Strain</th>
<th>Staphylococcus aureus ATCC 6538</th>
<th>Staphylococcus aureus ATCC 6538</th>
<th>Escherichia coli ATCC 25992</th>
<th>Escherichia coli ATCC 25992</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample</td>
<td>Immediately after inoculation</td>
<td>After 24 hours from inoculation</td>
<td>Decreasing rate of bacteria (%)</td>
<td>Increasing rate (ratio)</td>
</tr>
<tr>
<td>6538</td>
<td>blank</td>
<td>1.8 x 10⁵</td>
<td>1.7 x 10⁵</td>
<td>1.7 x 10⁵</td>
</tr>
<tr>
<td>6538</td>
<td>Example 7</td>
<td>1.8 x 10⁵</td>
<td>&lt;100</td>
<td>&lt;100</td>
</tr>
<tr>
<td>25992</td>
<td>blank</td>
<td>1.7 x 10⁵</td>
<td>99.9</td>
<td>99.9</td>
</tr>
<tr>
<td>25992</td>
<td>Example 10</td>
<td>1.7 x 10⁵</td>
<td>—</td>
<td>37.1</td>
</tr>
</tbody>
</table>

[0092] The result is shown in FIG. 7. As shown in FIG. 7, removing performance of trimethylamine was 1002.7 ppm during 53 cycles, and removing efficiency of trimethylamine (TMA) was maintained for about 90%.

[0093] Antibiotic Test

[0094] Antibiotic property of polyethylene filter coated with photocatalytic coating sol composition prepared according to Example 10 by using Shake Flask Method was measured.

[0095] Herein, the Shake Flask Method can be performed as follows:

[0096] First, after samples (30 square shaped pieces of 1 cm x 1 cm) and control samples (30 square shaped pieces of l-methyl) were inoculated with known bacteria, inoculation liquid and a certain amount of neutralization solution were blended followed by extracting the incubated bacteria, and when the number of bacteria in the neutralization solution was measured, bacteria decreasing rate between the sample and the comparative sample was measured by the following equation 1.

[0097] Phosphoric acid buffer solution (pH 7.0±0.2) was used as the neutralization solution, Tween 80 (0.05%) was used as surfactant, and after blending and incubating at 150 times/min for 24 hours at a temperature of 35 ±1°C, the bacteria number of test bacteria solution was measured.

\[
\text{Bacteria Decreasing Rate} = \left[ \frac{\text{bacteria of blank after 24 hours} - \text{bacteria number of coated goods after 24 hours}}{\text{bacteria number of blank after 24 hours}} \right] \times 100 \quad \text{[Equation 1]}
\]

Wherein the blank was the original sample without coating, for example polyethylene filter without the photocatalytic coating sol composition coating.

[0099] The known bacteria strains used in the Shake Flask method were Staphylococcus aureus ATCC 6538 and Escherichia coli ATCC 25992.

[0100] The result is shown in following Table 1.

[0101] As shown in the Table 1, microorganisms increasing rate in Examples 7 and 10 using polyethylene filter coated with photocatalytic coating sol composition was very low, while bacteria was increased by 30% to 40% in the blank sample.
Antimicrobial Test

Antimicrobial property for polyethylene filter coated with photocatalytic coating sol composition prepared according to the Example 10 was tested by using ASTM G-21 as test standard.

Known strain used in the ASTM G-21 test standard was Aspergillus niger ATCC 0.962, Penicillium pinophilium ATCC 11797, Chaetomium globosum ATCC 6205, Gliocladium vires ATCC 9645 and Aureobasidium pullulans ATCC 15233.

As a result, it was obtained as 0 grade of the ASTM G-21 test standard. Wherein, the 0 grade refers to no growth of the known strain.

Meanwhile, electron microscope photographs taken from surface and section of polyethylene filter prepared according to Example 10 are shown in FIGS. 8 and 9, respectively.

As shown in FIGS. 8 and 9, surface coated with photocatalytic coating sol composition was confirmed as being very porous, and the thickness of coating layer was about 20 µm.

Industrial Applicability

As described above, the present invention uses an inorganic adsorbent, and includes effective techniques used in environmental contaminants treatment system or air conditioning plant such as air-conditioner and air-cleaner.

1. A photocatalytic coating sol composition comprising 0.1% to 20% by weight of a photocatalyst, 0.1% to 10% by weight of an inorganic adsorbent, 1% to 20% by weight of an inorganic binder, and 55% to 95% by weight of an organic solvent.

2. The photocatalytic coating sol composition according to claim 1, further comprising 0.1% to 10% by weight of a metal compound.

3. The photocatalytic coating sol composition according to claim 2, wherein the metal compound is selected from the group consisting of copper compound, silver compound, bengala, vermilion, cadmium red, yellow earth, cadmium yellow, emerald rock, chromium oxide green, Prussian blue, cobalt blue, manganese and carbon black.

4. The photocatalytic coating sol composition according to claim 1, wherein the photocatalyst is selected from the group consisting of TiO₂, ZnO₂, ZnO, CaTiO₃, WO₃, SnO₂, MoO₃, Fe₂O₃, InP, GaAs, BaTiO₃, KNbO₃, Fe₂O₃, and Ta₂O₅.

5. The photocatalytic coating sol composition according to claim 4, wherein the average diameter of the photocatalyst particles is 5 to 50 nm.

6. The photocatalytic coating sol composition according to claim 1, wherein the inorganic adsorbent is silicates compound of magnesium or calcium, talc, diatomite, or zeolite coated with silver and/or copper ion.

7. The photocatalytic coating sol composition according to claim 1, wherein the inorganic binder is an isopropoxide compound or a silane compound.

8. The photocatalytic coating sol composition as according to claim 1, wherein the organic solvent is an alcohol having lower alkyl group.

9. A method for the preparation of a photocatalytic coating sol composition, comprising the steps of:

stirring at 1000 to 1500 rpm at room temperature for 10 to 30 min after mixing 1% to 20% by weight of an inorganic binder, 55% to 95% by weight of an organic solvent and 0.1% to 0.5% by weight of a strong acid or a strong base if necessary; and

treating for 10 to 15 min in an ultrasonic device after adding 0.1% to 20% by weight of a photocatalyst powder and 0.1% to 10% by weight of an inorganic adsorbent to the mixture, and adding 0.1% to 10% by weight of metal a compound to the mixture, if necessary.

10. A substrate prepared by coating the photocatalytic coating sol composition according to claim 1 using a printing method, a spraying method or a dipping method, and followed by drying.

11. The substrate according to claim 10, wherein the substrate is aluminum filter, a polyethylene filter or a polypropylene filter.

12. A substrate prepared by coating the photocatalytic coating sol composition according to claim 2 using a printing method, a spraying method or a dipping method, and followed by drying.

13. A substrate prepared by coating the photocatalytic coating sol composition according to claim 3 using a printing method, a spraying method or a dipping method, and followed by drying.

14. A substrate prepared by coating the photocatalytic coating sol composition according to claim 4 using a printing method, a spraying method or a dipping method, and followed by drying.

15. A substrate prepared by coating the photocatalytic coating sol composition according to claim 5 using a printing method, a spraying method or a dipping method, and followed by drying.

16. A substrate prepared by coating the photocatalytic coating sol composition according to claim 6 using a printing method, a spraying method or a dipping method, and followed by drying.

17. A substrate prepared by coating the photocatalytic coating sol composition according to claim 7 using a printing method, a spraying method or a dipping method, and followed by drying.

18. A substrate prepared by coating the photocatalytic coating sol composition according to claim 8 using a printing method, a spraying method or a dipping method, and followed by drying.

* * * * *