(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 3 492 551 A1

(12) **EUROPEAN PATENT APPLICATION**
published in accordance with Art. 153(4) EPC

(43) Date of publication:
05.06.2019 Bulletin 2019/23

(21) Application number: **17834168.1**

(22) Date of filing: **20.07.2017**

(51) Int Cl.:
C09K 11/00 *(2006.01)* ***C09K 9/00*** *(2006.01)*
C09K 11/64 *(2006.01)* ***C09K 11/70*** *(2006.01)*
C09K 11/80 *(2006.01)* ***G01T 1/20*** *(2006.01)*
G21K 4/00 *(2006.01)*

(86) International application number:
PCT/JP2017/026373

(87) International publication number:
WO 2018/021160 (01.02.2018 Gazette 2018/05)

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA ME
Designated Validation States:
MA MD

(30) Priority: **29.07.2016 JP 2016149215**

(71) Applicant: **National Institute of Advanced Industrial Science and Technology**
Tokyo 100-8921 (JP)

(72) Inventors:
- **Terasaki Nao**
  Tosu-shi
  Saga 841-0052 (JP)
- **Kikunaga Kazuya**
  Tosu-shi
  Saga 841-0052 (JP)

(74) Representative: **Lichtnecker, Markus Christoph**
Lichtnecker & Lichtnecker
Patent- und Rechtsanwaltspartnerschaft mbB
Im Schloßpark Gern 2
84307 Eggenfelden (DE)

(54) CHARGED PARTICLE DETECTION MATERIAL, AND CHARGED PARTICLE DETECTION FILM AND CHARGED PARTICLE DETECTION LIQUID USING SAME

(57) [Problem]

To provide a charged particle detection material which can detect charged particles due to a discharge phenomenon or the like caused even in a very low voltage which cannot be observed by a prior art, as well as a charged particle detection film and a charged particle detection liquid using the material.

[Solution]

The charged particle detection material and the charged particle detection film according to the present invention contain at least one of a fluorescent substance, a luminescent substance, an electroluminescent substance, a fractoluminescent substance, a photochromic substance, an afterglow substance, a photostimulated luminescent substance and a mechanoluminescent substance and can easily detect emission or incidence of charged particles in real time.

EP 3 492 551 A1

Description

Technical Field

[0001] The present invention relates to a charged particle detection material which can easily detect emission or incidence of charged particles such as electrons and ions from or to a member in real time, and a charged particle detection film and a charged particle detection liquid using the material.

Background Art

[0002] Materials for detecting charged particles such as electrons and ions have been required in the technical fields widely ranging from theoretical physics to applied engineering.

[0003] Examples of such a material for detecting charged particles include a fluorescent material such as cesium iodide used as a scintillator, and a semiconductor such as silicon or germanium used for a semiconductor charged particle detector (see Patent Document 1).

[0004] In addition, other examples of the material include a fluorescent material such as (Zn, Cd)S:Ag used in a fluorescent screen used for reflection high-energy electron diffraction (RHEED) and low-energy electron diffraction (LEED).

Prior Art Documents

Patent Documents

[0005] Patent Document 1: Japanese Patent Application Laid-Open No. 2010-67738

Summary of Invention

Problem to be solved

[0006] However, these charged particle detection materials have such a problem that charged particles cannot be easily detected, e.g. measuring equipment other than the charged particle detection material is required for detecting charged particles. In addition, fluorescent materials used as scintillators, semiconductors used for semiconductor charged particle detectors, and fluorescent materials used for RHEED have such a problem that only charged particles having high energy (100 eV or higher) can be detected. Furthermore, fluorescent materials used for RHEED and LEED have such a problem that it can be used only under a condition of a high degree of vacuum (lower than 10^{-4} Torr) for obtaining a diffraction pattern on a sample surface.

Solution to Problem

[0007] As a result of continuous studies on static electricity, the inventor of the present invention observed that charged particles were emitted from a surface of a member negatively charged at a low voltage (potential difference) in the atmosphere and entered a surface of another member, and for the first time in the world, the inventor discovered a phenomenon that even if a very weak electric field (1 kV/mm or lower) was applied with a gap of 35 mm (distance) in the atmosphere for example, the member emitted light in response to a trace amount of emitted charged particles.

[0008] As described in detail later, a charged particle detection material according to the present invention is applied on a charged particle-emitting part and a surface of the charged particle-emitting part, so that light is emitted from the surface of the charged particle-emitting part which are emitting charged particles, and at the same time, light is emitted also from a surface of a charged particle incident part which the charged particles enter. Thus, the charged particles can be detected in real time by observing these lights. Note that it has been conventionally considered that an aerial discharge phenomenon (spark discharge, corona discharge, glow discharge, arc discharge, etc.) can be caused in air only by applying an electric field on the order of about 1 to 3 kV/mm. In addition, a discharge caused by an electric field much weaker than the above-mentioned electric field is called a dark discharge, and a very weak current due to electrolytic dissociation of gaseous molecules by cosmic rays, radiations resulting from natural radioactivity, and the like is called a dark current. Although the dark discharge/dark current may be generated due to static electricity, they could not have been detected visually or by means of a camera or the like because they are not associated with a luminous phenomenon.

[0009] Furthermore, the positions of the dark discharge/dark current resulting from static electricity can be grasped to a certain extent by detecting electromagnetic waves resulting from the dark discharge/dark current. However, the positions could not have been observed due to influence of noises or the like at a manufacturing site where noises are always

generated, at a place where a plurality of electrostatic discharges are generated, in a case where an energy of electrostatic discharge is low, or the like.

[0010] The discharge phenomenon in such a complicated environment could not have been observed by a conventional observation method known so far, but could be observed only by the present invention. Then, the present inventor named this phenomenon resulting from static electricity was named as static electrical luminescence (SEL).

[0011] As described above, an object of the present invention is to provide a charged particle detection material which can detect charged particles due to a discharge phenomenon or the like caused even in a very weak electric field (low potential difference) which cannot be observed by a prior art, as well as a charged particle detection film and a charged particle detection liquid using the material.

[0012] A first aspect of the present invention for solving the above-described problems consists in a charged particle detection material for detecting emission of charged particles from a charged particle-emitting part or incidence of the charged particles to a charged particle incident part, which characteristically contains at least one of a luminescent substance, an electroluminescent substance, a fractoluminescent substance, a photochromic substance, an afterglow substance, a photostimulated luminescent substance and a mechanoluminescent substance.

[0013] Herein, the term "charged particles" refers to particles, clusters, gases and the like carrying an electrical charge. Examples of the charged particles include electrons, protons, ionized atoms (including atomic nucleus itself), ionized molecules (including complexes), electrolytically-dissociated/ionized gases and the like.

[0014] In addition, the term "luminescent substance" refers to a luminescent substance other than a fluorescent substance described later, which is a substance capable of emitting light by X-ray, ultraviolet ray, visible light or the like, and a substance capable of emitting light by chemical change or biological enzymes. Specific examples of the luminescent substance include: phosphorescent luminescent materials such as iridium complexes (typified by tris (2-phenylpyridinate) iridium (III)) and platinum complexes; chemiluminescent substances typified by luminol, rofin, lucigenin and oxalate; photosensitive luminescent dye such as 9,10-diphenylanthracene, 9,10-bis (phenylethynyl) anthracene, tetracene, 1-chloro-9,10-bis (phenylethynyl) anthracene, 5,12-bis (phenylethynyl) naphthacene, rubrene, Rhodamine 6G and Rhodamine B; bioluminescent substances typified by luminol; and the like.

[0015] The term "electroluminescent substance" refers to a substance that emits light by applying an electric field. Specific examples of the electroluminescent substance include: a low molecular weight substances such as tris (8-quinolinolato) aluminum complex (Alq), bis (benzoquinolinolato) beryllium complex (BeBq), tri (dibenzoylmethyl) phenanthroline europium complex (Eu (DBM) 3 (Phen)), ditoluylvinylbiphenyl (DTVBi) and rubene; π-conjugated polymer substances such as poly (p-phenylenevinylene) and polyalkylthiophene; and the like.

[0016] The term "fractoluminescent substance" refers to a substance that emits light in association with breakage due to mechanical stimulation such as destruction and friction. Specific examples of the fractoluminescent substance include: an inorganic material such as dolomite, muscovite, quartz, trilithionite, pectolite, fluorite and polylithionite; an organic material such as an Eu (TTA) 3 type, a carbazole derivative, an anthranilic acid type and a sugar; and the like.

[0017] The term "photochromic substance" refers to a substance which shows change in physical characteristics such as color by irradiation with X-ray, ultraviolet ray or visible ray. Specific examples of the photochromic substance include: an organic pigment typified by a spiropyran type, a diarylethene type and a fulgide type; an inorganic material typified by barium magnesium silicate ($BaMgSiO_4$); and the like.

[0018] The term "afterglow substance" refers to a substance which accumulates lights (electromagnetic waves) of visible ray, ultraviolet ray and the like with which the substance is irradiated, and emits the lights even when the irradiation is stopped. Specific examples of the afterglow substance include a radium compound, a promethium compound, a zinc sulfide (ZnS type), a strontium aluminate ($SrAl_2O_4$ type) and the like, and a zinc sulfide (ZnS type) and a strontium aluminate ($SrAl_2O_4$ type) to which monovalent to trivalent metal ions such as Dy and Eu are added in an arbitrary proportion are preferable. Herein, the term "add" refers to a concept that includes "co-doping", which means simultaneous addition of two or more substances, and "activation".

[0019] The term "photostimulated luminescent substance" refers to a substance which emits light by excitation of visible or infrared ray after irradiation with a high-energy laser, radiation or the like. Specific examples of the photostimulated luminescent substance include $BaFX:Eu^{2+}$ (X represents Br or I) and the like.

[0020] The term "mechanoluminescent substance" refers to a substance which emits light (including visible ray, ultraviolet ray, near-infrared ray) through deformation caused by a mechanical external force. Examples of the mechanoluminescent substance include: a substance mainly composed of an oxide, a sulfate, a selenide or a telluride which has a spinel structure, a corundum structure, a β-alumina structure, a silicate, a defect-controlling aluminate and a structure with coexistence of a wurtzite type structure and a sphalerite type structure, and the like; and a substance in which at least a part of alkali metal ions and alkali earth metal ions constituting the above-described structure is substituted by at least one metal ion of rare earth metal ions and transition metal ions; and the like.

[0021] The mechanoluminescent substances are classified into an alumina type, a silica type, a phosphoric acid type, a titanium oxide type, a zinc sulfide type and others.

[0022] Specific examples of the alumina type include: $xSrO{\cdot}yAl_2O_3{\cdot}zMO$ (M represents a divalent metal Mg, Ca or

Ba; each of x, y and z represents an integer. Note that M is not limited as long as it is a divalent metal, but Mg, Ca and Ba are preferable. In addition, x, y and z represents an integer equal to or larger than 1.); $Al_2O_3:Tb^{3+}$; $SrAl_2O_4$:M (doped with M = at least one of Eu^{2+}, Dy^{3+}, Ce^{3+} and Ho^{3+}); $ZnAl_2O_4$:M (doped with M = at least one of Eu^{2+}, Mn^{2+}, Dy^{3+}, Ce^{3+} and Ho^{3+}); $SrAl_2O_4:Eu^{2+}$; $SrAl_2O_4:Ce^{3+}$; $SrAl_2O_4:Eu^{2+},Dy^{3+}$; $SrAl_2O_4:Eu^{2+},Ho^{3+}$; $SrAl_2O_4:Ho^{3+},Ce^{3+}$; XAl_2O_4:M (doped with X = one or two of Sr, Ba, Mg, Ca and Zn, and doped with M = at least one of Eu^{2+}, Dy^{3+}, Tb^{3+}, Ho^{3+}); $SrAl_2O_4:Eu^{2+},Cr^{3+},Nd^{3+}$; and the like.

[0023] Other specific examples of the alumina type include: general formula $Sr\{1-(2x+3y+3z)/2\}Al_2O_4:xEu^{2+}$, yCr^{3+}, zNd^{3+}(here, each of x, y and z represents 0.25 to 10 mol%, preferably 0.5 to 2 mol%); $Sr_3Al_2O_6:Eu^{2+}$; $CaYAi_3O_7:Eu^{2+}$; $CaYAl_3O_7$:M (doped with M = at least one of Eu^{2+}, Ce^{3+}, Dy^{3+}, Ce^{3+} and Ho^{3+}); $SrMgAl_{10}O_{17}:Ce^{3+}$; and the like.

[0024] Specific examples of the silica type include: $xSrO{\cdot}yAl_2O_3{\cdot}zSiO_2$ (each of x, y and z represents an integer); $Ca_2Al_2Si_2O_7:Ce^{3+}$; $X_2Al_2SiO_7$:M (doped with X = one of Ca and Sr, and doped with M = at least one of Eu^{2+}, Eu^{3+}, Ce^{3+} and Dy^{3+}); $Ca_2MgSi_2O_7;Ce^{3+}$; $XMgSi_2O_7$:M (doped with X = one of Ba_2, Ca_2 and Sr_2 or X = one of SrCa and SrBa, and doped with M = at least one of Eu^{2+}, Dy^{3+} and Ce^{3+}); $CaAl_2Si_2O_8:Eu^{2+}$, $SrCaAl_2Si_2O_8:Eu^{2+}$; $Ca_3Y_2Si_3O_{12}:RE^{3+}$ (doped with RE^{3+} = at least one of Dy^{3+} and Eu^{2+}); $BaSi_2O_2N_2:Eu^{2+}$; and the like.

[0025] Specific examples of the phosphoric acid type include: Li_3PO_4:RE (RE = Dy^{3+}, Tb^{3+}, Ce^{3+} or Eu^{2+}); $LiXPO_4:Eu^{2+}$ (X = one of Sr and Br); $Li_2BaP_2O_7:Eu^{2+}$; $CaZr(PO_4)_2:Eu^{2+}$; and the like.

[0026] Specific examples of the titanium oxide type include: $CaTiO_3:Pr^{3+}$; $BaCaTiO_3:Pr^{3+}$; $BaTiO_3$-$CaTiO_3:Pr^{3+}$; and the like.

[0027] Specific examples of the zinc sulfide type include: ZnS:M (M is not limited as long as it is bivalent metal, but is preferably Mn, Ga, Cu or the like; doped with M = at least one of Mn^{2+}, Ga^{2+}, Te^{2+}, Cu^{2+}, CuCl, Al); XZnOS:M(doped with X = one of Ca and Ba, and M = one of Mn^{2+} and Cu^{2+}); ZnMnTe; and the like.

[0028] Othe specific examples of mechanoluminescent substance include: $CaZrO_3:Eu^{3+}$; $CaNb_2O_n:Pr^{3+}$(n = 6 or 7); (Sr, Ca, Ba)(2)$SnO_4:Sm^{3+},La^{3+}$; $Sr_{n+1}Sn_nO_{3n+1}:Sm^{3+}$(n=1, 2 or more); $Y_2O_3:Eu^{2+}$; ZrO_2:Ti; $XGa_2O_4:Mn^{2+}$ (X= either one of Zr and Mg); and the like.

[0029] In the first aspect, emission of the charged particles from the charged particle-emitting part or incidence of the charged particles to the charged particle incident part can be easily detected in real time.

[0030] A second aspect of the present invention consists in a charged particle detection material for detecting emission of charged particles from a charged particle-emitting part or incidence of the charged particles to a charged particle incident part in a non-vacuum state, which characteristically contains at least one of a fluorescent substance, a luminescent substance, an electroluminescent substance, a fractoluminescent substance, a photochromic substance, an afterglow substance, a photostimulated luminescent substance and a mechanoluminescent substance.

[0031] Herein, the term "non-vacuum" refers to a state under a pressure of 10^{-4} Torr or more. The charged particle detection material according to the present invention is used in a pressure range of preferably 10^{-3} to 10^5 Torr, more preferably 10^{-3} to 10^4 Torr. Note that the gas molecules in the non-vacuum state are not particularly limited, and they may be an inert gas such as Ar, He and N_2, atmospheric air or the like.

[0032] The term "fluorescent substance" refers to a substance which emits light by absorbing energy such as X-ray, ultraviolet ray and visible ray with which the substance is irradiated. Examples of the fluorescent substance include: ZnS:Ag + (Zn, Cd)S:Ag; $Y_2O_2S:Eu + Fe_2O_3$; ZnS:Cu, Al; ZnS:Ag + $CoAl_2O_3$; Zn_2SiO_4:Mn; ZnS:Ag, Cl; ZnS:Zn; (KF, MgF_2):Mn; (Zn, Cd)S:Ag; (Zn, Cd)S:Cu; ZnO:Zn; (Zn, Cd)S:Cu; ZnS:Cu; ZnS:Cu, Ag; MgF_2:Mn; (Zn, Mg)F_2:Mn; Zn_2SiO_4:Mn; ZnS:Ag + (Zn, Cd)S:Cu; $Gd_2O_2S:Tb$; $Y_2O_2S:Tb$; $Y_2O_2S:Tb$; $Y_3Al_5O_{12}:Ce$; $Y_3(Al, Ga)_5O_{12}:Ce$; $Y_2SiO_5:Ce$; $Y_3Al_5O_{12}:Tb$; $Y_3(Al, Ga)_5O_{12}:Tb$; ZnS:Ag, Al; $InBO_3:Tb$; $InBO_3:EU$; ZnS:Ag; ZnS:Cu, Al; ZnS:Cu, Au, Al; $Y_2SiO_5:Tb$; (Zn, Cd)S:Cu; Cl + (Zn, Cd)S:Ag, CL; $InBO_3:Tb$ + $InBO_3:Eu$; ZnS:Ag + ZnS:Cu + $Y_2O_2S:Eu$; $InBO_3:Tb$ + $InBO_3:Eu$ + ZnS:Ag; (Ba, Eu)$Mg_2Al_{16}O_{27}$; (Ce, Tb)$MgAl_{11}O_{19}$; (Y, Eu)$_2O_3$; (Sr, Eu, Ba, Cf)$_5(PO_4)_3CL$; (La, Ce, Tb)PO_4; Y_2O_3:Eu; $LaPO_4$:Ce, Tb; (Sr, Cf; Ba)$_{10}(PO_4)_6CL_2$:Eu; (La, Ce, Tb)PO_4:Ce, Tb; Zn_2SiO_4:Mn; Zn_2SiO_4:Mn; Sb_2O_3; $Ce_{0.67}Tb_{0.33}MgAl_{11}O_{19}$:Ce, Tb; Y_2O_3:Eu(III); $Mg_4(F)GeO_6$:Mn; $Mg_4(F)(Ge, Sn)O_6$:Mn; $CaWO_4$; $CaWO_4$:Pb; (Ba, Ti)$_2P_2O_7$:Ti; $Sr_2P_2O_7$:Sn; $Cf_5F(PO_4)_3$:Sb; $Sr_5F(PO_4)_3$:Sb, Mn; $BaMgAl_{10}O_{17}$:Eu, Mn; $BaMg_2Al_{16}O_{27}$:Eu(II); $BaMg_2Al_{16}O_{27}$:Eu(II), Mn(II); $Sr_5Cl(PO_4)_3$:Eu(II); $Sr_6P_5BO_{20}$:Eu; (Cf, Zn, Mg)$_3(PO_4)_2$:Sn; (Sr, Mg)$_3(PO_4)_2$:Sn; $CaSiO_3$:Pb, Mn; $Cf_5F(PO_4)_3$:Sb, Mn; $Cf_5(F, Cl)(PO_4)_3$:Sb, Mn; (Cf, Sr, Ba)$_3(PO_4)_2Cl_2$:Eu; $3Sr_3(PO_4)_2SrF_2$:Sb, Mn; Y(P, V)O_4:Eu; (Zn, Sr)$_3(PO_4)_2$:Mn; $Y_2O_2S:Eu$; (Sr, Mg)$_3(PO_4)_2$:Sn(II); $3.5MgO_{0.5}MgF_2GeO_2$:Mn; $Cf_3(PO_4)_2CaF_2$:Ce, Mn; $SrAl_2O_7$:Pb; $BaSi_2O_5$:Pb; $SrFB_2O_3$:Eu(II); SrB_4O_7:Eu; $Gd_2O_2S:Tb$; $Gd_2O_2S:Eu$; $Gd_2O_2S:Pr$, $Gd_2O_2S:Pr$, Ce, F; $Y_2O_2S:Tb$; $Y_2O_2S:Tb$; $Y_2O_2S:Tb$; Zn(0.5)Cd(0.4)S:Ag; Zn(0.4)Cd(0.6)S:Ag; $CdWO_4$; $CaWO_4$; $MgWO_4$; $Y_2SiO_5:Ce$; $YAlO_3:Ce$; $Y_3Al_5O_{12}:Ce$; $Y_3(Al, Ga)_5O_{12}:Ce$; CdS; ZnO:Ga; ZnO:Zn; (Zn; Cd)S:Cu, Al; ZnO:Zn; (Zn, Cd)S:Cu, Al; ZnS:Cu, Al; ZnCdS:Ag; ZnS:Ag; Zn_2SiO_4:Mn; ZnS:Cu; CsI:Tl; LiF/ZnS:Ag; LiF/ZnS:Cu, Al, Au; a fluorescein-type substance typified by fluorescein isothiocyanate; porphyrin; a porphyrin-based substance typified by platinum porphyrin; Rhodamine; azobenzene derivatives; an organic dye-type substance typified by anthracene; metal complex-type substance typified by ruthenium tris bipyridyl; poly (1, 4-phenylenevinylene); poly (1, 4-phenylene); a polyfluorene; luminescent polymer-type substance typified by poly(thiophene); other substances such as $Y_2O_2:Eu$; and the like.

[0033] In the second aspect, emission of the charged particles from the charged particle-emitting part or incidence of

the charged particles to the charged particle incident part can be easily detected in real time even in a non-vacuum state.

[0034] The third aspect of the present invention consists in the charged particle detection material according to the first or second aspect, characterized in that the electric field between the charged particle-emitting part and the charged particle incident part is within a range of 1 to 3000 V/mm in air. Note that, in an environment other than air, the range of the electric field between the charged particle-emitting part and the charged particle incident part varies depending on their dielectric constants.

[0035] Herein, the term "in air" refers to a state at 700 to 800 Torr, humidity of 10 to 90% and temperature of 0 to 100°C. The charged particle detection material according to the present invention is preferably used under a condition of 720 to 780 Torr, humidity of 30 to 80% and temperature of 10 to 80°C.

[0036] In the third aspect, low-energy charged particles which have been unobservable by the conventional observation method can be easily detected in real time. Furthermore, the electric field is more preferably within a range of 22 to 1000 V/mm. When the electric field is within this range, low-energy charged particles which have been unobservable by the conventional observation method can be more easily detected in real time.

[0037] The fourth aspect of the present invention consists in the charged particle detection material according to any one of the first to third aspects, characterized in that the charged particles are electrons, and a potential difference between the charged particle-emitting part and the charged particle incident part is lower than a voltage V calculated by Paschen's law.

[0038] Herein, the term "Paschen's law" refers to an experimental rule regarding a voltage at which discharge occurs (sparking voltage), and is represented by the following Equation.

$$V = \frac{Bpd}{\ln A\, pd + C}$$

(Each of A and B represents a constant shown in the following table 1, p represents a pressure of gas, and d represents a distance between electrodes (a distance between the charged particle-emitting part and the charged particle incident part).)

Gas	A [$Pa^{-1}\cdot m^{-1}$]	B [$V\cdot Pa^{-1}\cdot m^{-1}$]	V_{sm} [V]	pd_{sm} [Pa·m]
H_2	3.8±0.8	98±20	270±54	1.53±0.3
He	2.1±0.4	26±6	156±32	5.3±1.0
N_2	9.3±1.8	257±52	250±50	0.89±0.18
Ar	10.2±3.0	176±96	233±46	1.01±0.20
Air	11.0±2.0	274±54	330±66	0.76±0.16

[0039] In Table 1, V_{sm} represents a minimum sparking voltage, and pd_{sm} represents a pd value at the minimum sparking voltage. In addition, each constant is not particularly limited as long as it is within the range described in Table 1, but a median value of a range of each constant (e.g. when the gas is air, A=1.1, B=274, V_{sm}=330, pd_{sm}=0.76) is particularly preferable.

[0040] Note that C is a constant decided depending on the type of the gas and the electrode material and can be determined by an experiment. Additionally, in a case of a gas not listed in Table 1, the value of each constant can be determined by fitting the resultant value of an experiment in accordance with the least squares method, or the like.

[0041] In the fourth aspect, low-energy electrons can be easily detected in real time at a low voltage range where discharge has not conventionally been accompanied by a luminous phenomenon. Note that the inventor of the present invention succeeded for the first time in the world in detecting discharge resulting from static electricity by means of lights, by using the material (charged particle detection material) on which low energy electrons moved from the charged particle-emitting part to the charged particle incident part to induce light emission even at this voltage range.

[0042] As the detection condition in this aspect, e.g. the voltage is preferably 3 kV or more under a condition of an interelectrode distance of 10 to 55 mm in air, preferably 2 to 3 kV under a condition of an interelectrode distance of 10 to 45 mm in air, and preferably 1 to 3 kV air under a condition of an interelectrode distance of 10 to 35 mm in air.

[0043] The fifth aspect of the present invention consists in the charged particle detection material according to any one of the first to fourth aspects, characterized in that the total weight ratio of the fluorescent substance, the luminescent substance, the electroluminescent substance, the fractoluminescent substance, the photochromic substance, the after-glow substance, the photostimulated luminescent substance and the mechanoluminescent substance is 20 to 80 wt%.

[0044] In the fifth aspect, the charged particle detection material can be easily applied on the surface of the charged particle-emitting part or the charged particle incident part and can emit light with sufficient luminance so as to detect the charged particles can by a general industrial camera or the like, so that the charged particles can be easily detected.

[0045] The sixth aspect of the present invention consists in the charged particle detection material according to any one of the second to fifth aspects, characterized in that the non-vacuum state is under a pressure within a range of 10^{-3} to 10^{5} Torr.

[0046] In the sixth aspect, even under a pressure within the range of 10^{-3} to 10^{5} Torr, emission of the charged particles from the charged particle-emitting part or incidence of the charged particles to the charged particle incident part can be easily detected in real time.

[0047] The seventh aspect of the present invention consists in the charged particle detection material according to any one of the first to sixth aspects, characterized in that the afterglow substance is a substance represented by $SrAl_2O_4$ which is doped with Eu^{2+} and Dy^{3+}, a substance represented by $SrAl_2O_4$ which is doped with Eu^{2+}, Dy^{2+} and M (M = monovalent to trivalent metal ions), or a substance represented by $Zn_3(PO_4)$ which is doped with Mn^{2+} and M (M = monovalent to trivalent metal ions).

[0048] In the seventh aspect, the charged particle detection material can emit light with higher luminance so that the charged particles can be more easily detected.

[0049] The eighth aspect of the present invention consists in the charged particle detection material according to any one of the first to sixth aspects, characterized in that the mechanoluminescent substance is a substance represented by $SrAl_2O_4$ which is doped with Eu^{2+}, a substance represented by $SrAl_2O_4$ which is doped with at least one of Eu^{2+}, Ho^{3+}, Dy^{2+}, M_1, M_2 and M_3 (M_1, M_2, M_3 = monovalent to trivalent metal ions different from each other), or a substance represented by $CaYAl_3O_7$ which is doped with Eu^{2+}.

[0050] In the eighth aspect, the charged particle detection material can emit light with higher luminance so that the charged particles can be more easily detected.

[0051] The ninth aspect of the present invention consists in a charged particle detection film including the charged particle detection material according to any one of the first to eighth aspects.

[0052] Herein, the "charged particle detection film" is not particularly limited as long as it is composed of a material containing at least one of the above-described substances. The charged particle detection film may be prepared by homogenously mixing e.g. an epoxy resin or a urethane resin, a curing agent and a solvent for controlling crosslinking/curing reaction of these resins, the above-described substance, and a dispersant/adjuvant for homogenously dispersing the substance. In addition, the concentration (weight ratio) of the above-described substance contained in the charged particle detection film is not particularly limited, but a range of 20 to 80 wt% is preferable because light emission can be visually confirmed, and a range of 50 to 70 wt% is more preferable because light emission can be visually confirmed more obviously. In addition, the thickness of the charged particle detection film is not particularly limited, but a thickness range of 1 μm to 1 mm is preferable from the viewpoints of light emission intensity and ease of handling, and a thickness range of 10 to 500 μm is more preferable from the viewpoints of light emission intensity and ease of handling.

[0053] Note that the charged particle detection film may be directly formed (applied as a solution/cured) on a surface of a measurement object, or alternatively may be formed on the surface of the measurement object by sticking the preformed "charged particle detection film" onto the surface of the measurement object.

[0054] In the ninth aspect, the charged particle detection film can be easily formed or stuck without being influenced by the shape of the measurement object. As a result, even if the measurement object has a complex three-dimensional shape such as a curved surface, charged particles entering the surface can be easily detected.

[0055] The tenth aspect of the present invention consists in a charged particle detection liquid including the charged particle detection material according to any one of the first to eighth aspects.

[0056] Herein, components other than the charged particle detection material constituting the charged particle detection liquid are not particularly limited as long as they can disperse the charged particle detection material, and they may be e.g. water, a transparent/translucent resin, or the like.

[0057] In the tenth aspect, the charged particle detection material can be poured (placed) even to surfaces of a measurement object having a complicated shape and a measurement object having a narrow portion or the like incapable of forming a charged particle detection film, so that the charged particles entering the measurement object having such a complicated shape can be easily detected. In addition, the charged particle detection material is three-dimensionally dispersed in the liquid so that the trajectory of the charged particles moving in the liquid can be visualized.

[0058] Each of the "fluorescent substance", "luminescent substance", "electroluminescent substance", "fractoluminescent substance", "photochromic substance", "afterglow substance", "photostimulated luminescent substance" and "mechanoluminescent substance" may have not only the property of each substance itself but also the properties of other substances. For example, the "mechanoluminescent substance" may have the property of the "fluorescent substance". In this case, this substance is a "mechanoluminescent substance" and is also a "fluorescent substance".

[0059] Also, the charged particle detection material may contain substances other than the above-mentioned sub-

stances. Note that the substances other than the above-mentioned substances are not particularly limited.

Brief Description of Drawings

[0060]

Figure 1 shows a schematic drawing of a charged particle detection system according to Embodiment 1.
Figure 2 shows a photograph of a luminescent part P2 formed on a surface of a charged particle incident part in Example 1.
Figure 3 shows a schematic drawing of the charged particle detection system at the time that a charged member is inserted between a charged particle-emitting part and the charged particle incident part in Example 1.
Figure 4 shows a photograph of a luminescent part P3 before the charged member is inserted between the charged particle-emitting part and the charged particle incident part in Example 1.
Figure 5 shows a photograph of the luminescent part P3 at the time that the charged member is inserted between the charged particle-emitting part and the charged particle incident part in Example 1.
Figure 6 shows a photograph of the luminescent part P3 at the time that the charged member inserted between the charged particle-emitting part and the charged particle incident part is pulled out in Example 1.
Figure 7 shows a photograph of a test result when using $SrAl_2O_4:Ho^{3+}$, Ce^{3+} as the mechanoluminescent substance.
Figure 8 shows a photograph of a test result when using $CaYAl_3O_7:Eu^{2+}$ as the mechanoluminescent substance.
Figure 9 shows a photograph of a test result when using $SrAl_2O_4:Eu^{2+}$, Cr^{3+}, Nd^{3+} as the mechanoluminescent substance.
Figure 10 shows a photograph of a test result when changing the polarity of the electrode in Example 1.
Figure 11 shows a photograph at the time that a human hand is moved while applying a voltage to a rod on which a charged particle detection film is formed in Example 2.
Figure 12 shows a photograph of a luminescent part formed on the surface of the charged particle incident part at the time that a voltage is applied on an electrode needle and the charged particles are made to enter the charged particle detection film in Example 3.
Figure 13 shows a photograph of the luminescent part formed on the surface of the charged particle incident part at the time that a voltage is applied to the electrode needle and the charged particles are made to enter the charged particle detection film in Example 4.
Figure 14 shows a photograph of the luminescent part formed on the surface of the charged particle incident part at the time that a voltage is applied to the electrode needle and the charged particles are made to enter the charged particle detection film in Example 5.
Figure 15 shows a photograph of the luminescent part formed on the surface of the charged particle incident part at the time that a voltage is applied to the electrode needle and the charged particles are made to enter the charged particle detection film in Example 6.
Figure 16 shows a photograph of the luminescent part formed on the surface of the charged particle incident part at the time that a voltage is applied to the electrode needle and the charged particles are made to enter the charged particle detection film in Example 7 ($SrAl_2O_4:Eu^{2+}$, Dy^{3+}).
Figure 17 shows a photograph of the luminescent part formed on the surface of the charged particle incident part at the time that a voltage is applied to the electrode needle and the charged particles are made to enter the charged particle detection film in Example 7 (β-$Zn_3(PO_4)_2:Mn^{2+}$, Ga^{3+}).
Figure 18 shows a photograph at the time that the charged particles are detected using a $SrAl_2O_4:Eu^{2+}$ powder.
Figure 19 shows a photograph at the time that the charged particles are detected using a luminescent sheet in which a $SrAl_2O_4:Eu^{2+}$ powder is dispersed.
Figure 20 shows a photograph at the time that the charged particle detection film containing $SrAl_2O_4:Eu^{2+}$ is formed on an aluminum foil, to which the charged particles are made to enter.
Figure 21 shows a photograph at the time that the charged particles are made to enter a paper nonwoven fabric in which the charged particle detection material is dispersed.
Figure 22 shows a photograph at the time that the charged particles are made to enter a liquid mixture of $SrAl_2O_4:Eu^{2+}$ and photocurable acryl.
Figure 23 shows a photograph at the time that a surface of the liquid mixture of $SrAl_2O_4:Eu^{2+}$ and photocurable acryl is cured, and then the charged particles are made to enter the surface.

Description of Embodiments

[0061] A charged particle detection material according to the present invention detects emission of charged particles from a charged particle-emitting part or incidence of charged particles to a charged particle incident part.

[0062] Herein, the charged particle-emitting part and the charged particle incident part are not particularly limited as long as the charged particles can be emitted from or can enter a surface, respectively, when applying an electric field between the charged particle-emitting part and the charged particle incident part by applying voltages to them. Typical examples of substances constituting the charged particle-emitting part and the charged particle incident part include, but are not limited to: a conductor like a metal having a high electric conductivity such as tungsten, stainless steel, gold, silver and copper; a semiconductor such as silicon; and an insulator such as ceramics, polymer and resin. For example, when the charged particles are electrons, the charged particle-emitting part can be exemplified by aluminum or the like, and the charged particle incident part can be exemplified by vinyl chloride or the like.

[0063] Embodiments of ad charged particle detection system using a charged particle detection material according to the present invention will be explained below with reference to the accompanying drawings. Note that the present invention is not limited to the following embodiments.

(Embodiment 1)

[0064] A configuration will be explained, in which a charged particle detection film including a charged particle detection material containing at least one of a fluorescent substance, a luminescent substance, an electroluminescent substance, a fractoluminescent substance, a photochromic substance, a afterglow substance, a photostimulated luminescent substance and a mechanoluminescent substance is formed on surfaces of a charged particle-emitting part and a charged particle incident part, and when an electric field is applied between the charged particle-emitting part and the charged particle incident part, charged particles (e.g. N^+, N^-, electrons, etc.) caused by ionizing a gas around the electrode are emitted from the charged particle-emitting part and enter the charged particle incident part.

[0065] Figure 1 shows a schematic drawing of a charged particle detection system according to this embodiment. As shown in this figure, the charged particle detection system 1 according to the present embodiment is composed of a cylindrical charged particle-emitting part 10 having a lower end formed in a hemispherical shape, a rectangular plate-shaped charged particle incident part 20 disposed below the charged particle-emitting portion 10, and DC high-voltage generators (not shown in figure) respectively connected to the charged particle-emitting part 10 and the charged particle incident part 20. Note that the charged particle-emitting part 10 and the charged particle incident part 20 are fixed by jigs not shown in figure. In addition, the shape of the charged particle-emitting part 10 is not particularly limited, and its end may be spherical, needle-shaped or planar.

[0066] A charged particle detection film 21 including a charged particle detection material containing a substance such as the above-described fluorescent substance is provided on the upper surface of the charged particle incident part 20 disposed below the charged particle-emitting part 10.

[0067] Herein, the charged particle detection film 21 provided on the surface of the charged particle incident part 20 is not particularly limited as long as it includes the charged particle detection material containing at least one of the above-described substances. The charged particle detection film 21 may be prepared by homogeneously mixing e.g. an epoxy resin or an urethane resin, a curing agent and a solvent for controlling crosslinking/curing reaction of these resins, the above-described substances, and a dispersant/adjuvant for homogeneously dispersing the substances, and applying/curing this mixture on the surface of the charged particle incident part 20. The concentration (weight ratio) of the above-described substances contained in the charged particle detection film 21 is not particularly limited, but a range of 20 to 80 wt% is preferable because light emission can be visually confirmed, and a range of 50 to 70 wt% is more preferable because light emission can be visually confirmed more obviously.

[0068] The DC high-voltage generator is not particularly limited as long as it can apply a predetermined electric field (generate a potential difference) between the charged particle-emitting part 10 and the charged particle incident part 20, and a commercial product may be used. The intensity of the electric field between the charged particle-emitting part 10 and the charged particle incident part 20 is also not particularly limited, but a range of 1 to 3000 V/mm is preferable because low-energy charged particles which have been unobservable by the conventional observation method can be easily detected in real time, and a range of 22 to 1000 V/mm is more preferable because the low-energy charged particles can be more easily detected.

(Example 1)

[0069] Stainless steel was used as the charged particle-emitting part 10, an aluminum foil was used as the charged particle incident part 20, and a mixture of a mechanoluminescent substance $SrAl_2O_4:Eu^{2+}$ and photocurable acrylic resin (made by MICROJET Corporation) (weight ratio of $SrAl_2O_4:Eu^{2+}$ is 70%) was applied and cured to use it as a charged particle detection film 21 (about 100 μm in thickness) formed on the surface of the charged particle incident part 20. The DC high-voltage generator was operated in air at 1 atm, humidity of 30% and temperature of 10°C so as to apply an electric field (100 to 800 V/mm) between the charged particle-emitting part 10 and the charged particle incident part 20 (10 mm). The result is shown in a figure.

[0070] As shown in Figure 2, when the electric field is applied between the charged particle-emitting part 10 and the charged particle incident part 20, a substantially circular luminescent part P2 with a center O beneath the charged particle-emitting part 10 is formed on the upper surface of the charged particle incident part 20. For the luminescent part P2, the center O emits light at first, and when continuing to inject the charged particles into the charged particle incident part 20, the luminescent part spreads outwardly from the center O over time, and the luminance around the center O is decreased. That is, although the center O emits light at first, the luminescent part P2 becomes ring-shaped over time, and the diameter of the ring shape seems to increase. In Figure 2, the luminance is highest at the outermost portion and gradually decreases toward the center O. In addition, a radius of the luminescent part P2 is small at first when activating the DC high-voltage generator, but increases over time.

[0071] It was confirmed that the same experiment in air at 1 atm, 80% humidity and 80°C resulted in light emission in a similar manner. Furthermore, it was confirmed that the same experiment in a state where the pressure inside the container housing the charged particle-emitting part 10 and the charged particle incident part 20 was reduced to 10^{-3} Torr by a rotary pump resulted in light emission in a similar manner.

[0072] Next, as shown in Figure 3, a charged member 30 composed of a rod-shaped aluminum foil in a floating state was inserted between the charged particle-emitting part 10 and the charged particle incident part 20. The result is shown in a figure.

[0073] It was found that a luminescent part P3 was located under the aluminum foil before inserting the charged member 30 as shown in Figure 4, but the luminescent part P3 moved toward the charged member 30 (upward) after inserting the charged member 30 as shown in Figure 5. In addition, an ammeter was provided between the charged particle-emitting part 10 and the charged particle incident part 20, a current therebetween was measured at this time, and as a result, it was found that the current flowed from the charged particle incident part 20 to the charged particle-emitting part 10.

[0074] Note that it was found that when the charged member 30 was pulled from between the charged particle-emitting part 10 and the charged particle incident part 20, the luminescent part P3 returned to the position before inserting the charged member 30 as shown in Figure 6.

[0075] From the above, it was found that the negatively-charged particles moved from the charged particle-emitting part 10 toward the charged particle incident part 20. Herein, the movement of the charged particles is considered to include not only a phenomenon that specific charged particles such as N^- and electrons directly move from the charged particle-emitting part 10 to the charged particle incident part 20, but also a phenomenon that some charged particles continuously push other charged particles like a chain-reaction collision, and as a result, the charged particles seem to move from the charged particle-emitting part 10 to the charged particle incident part 20. Furthermore, it is considered that the movement also includes a phenomenon that the gas molecules around the charged particle-emitting part 10 are ionized and move to the charged particle incident part 20 so that the charged particles seem to move from the charged particle-emitting part 10 to the charged particle incident part 20, is also included.

[0076] Charged particle detection films respectively containing similar mechanoluminescent substances $SrAl_2O_4:Ho^{3+}$, Ce^{3+}; $CaYAl_3O_7:Eu^{2+}$; or $SrAl_2O_4:Eu^{2+}$, Cr^{3+}, Nd^{3+} instead of $SrAl_2O_4:Eu^{2+}$ were prepared, and subjected to the same test. The test results are shown in Figures 7 to 9. As can be seen from these figures, when the charged particles are made to enter the film, the luminescent part P was formed on each charged particle detection film. Therefore it was found that the charged particles could be detected also when using the charged particle detection films including these charged particle detection materials.

[0077] Furthermore, a test result when changing the polarity of the electrode in Example 1 is shown in Figure 10. As shown in Figure 10, it was found that the charged particles could be detected even when changing the polarity of the electrode (i.e., even when charged particles with different polarities entered the film).

(Example 2)

[0078] In Example 1, the charged particle detection film including the charged particle detection material was formed on the surface of the charged particle incident part, but the present invention is not limited thereto. In this example, the same charged particle detection film (about 100 μm in thickness) as the charged particle detection film used in Example 1 was formed on a surface of a cylindrical rod made of stainless steel. Then, a human hand was moved while a voltage was applied to the rod so as to apply an electric field between the rod and the human hand. The result is shown in a figure.

[0079] Figure 11 shows a photograph at the time that the human hand was moved in a direction I while applying a voltage to the rod on which the charged particle detection film was formed. As shown in Figure 11, it was found that the luminescent part moved along a moving direction of the human hand.

[0080] Herein, since the potential of the human hand was lower than the potential (voltage) applied to the rod, it was found that the charged particles were emitted from the rod (charged particle-emitting part) toward the human hand (charged particle incident part).

(Example 3)

[0081] Examples 1 and 2 were explained using the charged particle detection film containing the mechanoluminescent substance as the charged particle detection material, but the charged particle detection material according to the present invention is not limited thereto. In this example, a charged particle detection film (about 100 μm in thickness) containing $SrAl_2O_4:Eu^{2+}$, Dy^{3+} as an afterglow substance instead of the mechanoluminescent substance $SrAl_2O_4:Eu^{2+}$ was used. Then, an electric field (100 to 800 V/mm) was applied between the charged particle-emitting part 10 and the charged particle incident part 20 (gap distance: 10 mm) by activating the DC high-voltage generator in the same manner as in Example 1. The result is shown in a figure.

[0082] As shown in Figure 12, it was found when an electric field (100 to 800 V/mm) was applied between the charged particle-emitting part and the charged particle incident part, a substantially circular luminescent part with a center beneath the charged particle-emitting part was formed on the surface of the charged particle detection film of the charged particle incident part similarly to Example 1.

[0083] As described above, it was found that emission of the charged particles or incidence of the charged particles could be easily detected in real time similarly to Examples 1 and 2 by using the charged particle detection material containing the afterglow substance and the charged particle detection film including the material. In addition, it was found that even charged particles which were generated by a discharge phenomenon caused in an extremely weak electric field (low potential difference, low energy) and had been unobservable by the prior art could be easily detected in real time by using the charged particle detection material according to the present embodiment.

(Example 4)

[0084] In this example, a charged particle detection film (about 50 μm in thickness) containing $Y_2O_2S:Tb^{3+}$ as a fluorescent substance instead of the mechanoluminescent substance $SrAl_2O_4:Eu^{2+}$ in Example 1 was used. Then, a voltage (7 kV) was applied between the charged particle-emitting part and the charged particle incident part (gap distance: 10 mm) by activating the DC high-voltage generator in the same manner as in Example 1. The result is shown in Figure 13.

[0085] As shown in Figure 13, it was found when a voltage (7 kV) was applied between the charged particle-emitting part and the charged particle incident part (gap distance: 10 mm), a substantially circular luminescent part with a center beneath the charged particle-emitting part was formed on the surface of the charged particle detection film of the charged particle incident part similarly to Example 1.

[0086] As described above, it was found that emission of the charged particles or incidence of the charged particles could be easily detected in real time similarly to above-described Example 1 by using the charged particle detection material containing the fluorescent substance and the charged particle detection film including the material. In addition, it was found that even charged particles which were generated by a discharge phenomenon caused in an extremely weak electric field (low potential difference, low energy) and had been unobservable by the prior art could be easily detected in real time by using the charged particle detection material according to the present embodiment.

(Example 5)

[0087] In this example, a charged particle detection film (about 50 μm in thickness) containing methyl salicylate as a fractoluminescent substance instead of the mechanoluminescent substance $SrAl_2O_4:Eu^{2+}$ in Example 1 was used. Then, the result of a test under similar conditions to those in Example 1 is shown in Figure 14.

[0088] As shown in Figure 14, it was found that a luminescent part was formed on the surface of the charged particle detection film of the charged particle incident part. From the above, it was found that the same effect as that of above-described Example could be obtained by using the charged particle detection material containing the fractoluminescent substance and the charged particle detection film including the material.

(Example 6)

[0089] In this example, a fractoluminescent substance $Eu(TTA)_3phen$ ([1,10-phenanthroline) tris [4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedionato] europium(III)]) was used as a charged particle detection material instead of the mechanoluminescent substance $SrAl_2O_4:Eu^{2+}$ in Example 1. Then, the result of a test under similar conditions to those in Example 1 is shown in Figure 15.

[0090] As shown in Figure 15, it was found that a luminescent part was formed on the surface of the charged particle detection film of the charged particle incident part. From the above, it was found that the same effect as that of above-described Example could be obtained by using the charged particle detection material containing the fractoluminescent substance and the charged particle detection film including the material similarly to Example 5.

(Example 7)

[0091] In this example, a charged particle detection films (about 50 μm in thickness; weight ratio of the afterglow substance: 70%) respectively containing $SrAl_2O_4:Eu^{2+}$, Dy^{3+} and β-$Zn_3(PO4)_2:Mn^{2+}$, Ga^{3+} as the fluorescent substances instead of the mechanoluminescent substance $SrAl_2O_4:Eu^{2+}$ in Example 1 was used. Then, a voltage (10 kV) was applied between the charged particle-emitting part and the charged particle incident part (gap distance: 10 mm). The result is shown in Figure 16 ($SrAl_2O_4:Eu^{2+}$, Dy^{3+}) and Figure 17 (β-$Zn_3(PO4)_2:Mn^{2+}$, Ga^{3+}).

[0092] As shown in Figures 16 and 17, it was found that a luminescent part was formed on the surface of the charged particle detection film of the charged particle incident part. From the above, it was found that the same effect as that of above-described Example could be obtained by using the charged particle detection film including the charged particle detection material containing the afterglow substance.

(Embodiment 2)

[0093] Although Embodiment 1 was intended to detect the charged particles by forming the charged particle detection film including the charged particle detection material on the surface of the charged particle-emitting part 10 or the charged particle incident part 20, the present invention is not limited to this embodiment.

[0094] For example, the charged particle detection material can be configured using a transparent/translucent material like glass or acrylic resin containing at least one of a fluorescent substance, a luminescent substance, an electroluminescent substance, a fractoluminescent substance, a photochromic substance, an afterglow substance, a photostimulated luminescent substance and a mechanoluminescent substance.

[0095] When the charged particles are made to enter the charged particle detection material, the surface or the inside of the glass or the like emits light, and it is also possible to detect the depth of incidence of the charged particles inside of the glass or the like.

(Embodiment 3)

[0096] Although the above-described embodiment was intended to detect the charged particle by forming the charged particle detection film including the charged particle detection material containing the mechanoluminescent substance and the like, the present invention is not limited to this embodiment. For example, a mechanoluminescent substance (powder) may be used as it is as the charged particle detection material.

[0097] Figure 18 shows a photograph at the time that charged particles were detected using a mechanoluminescent substance (powder) $SrAl_2O_4:Eu^{2+}$ powder as a charged particle detection material. It was found that the charged particles could be detected in the same manner as the above-described embodiment even when using the charged particle detection material in such a form (powder).

[0098] In addition, a luminescent sheet prepared using the charged particle detection material may be used instead of the mechanoluminescent substance (powder), in which a fine particle made of the mechanoluminescent substance and the like is dispersed.

[0099] Figure 19 shows a photograph at the time that charged particles were detected using a luminescent sheet prepared by curing a charged particle detection material in which a mechanoluminescent substance $SrAl_2O_4:Eu^{2+}$ was dispersed in a photocurable acrylic resin (made by MICROJET Corporation). It was found that the charged particles could be detected in the same manner as the above-described embodiment even when using the charged particle detection material in such a form.

(Embodiment 4)

[0100] In the above-described embodiment, the charged particle detection film including the charged particle detection material was formed on the charged particle-emitting part or the charged particle incident part having a certain thickness, but the present invention is not limited to this embodiment. For example, the same charged particle detection film as used in Example 1 may be formed on an aluminum foil. Figure 20 shows a photograph at the time that a charged particle detection film composed of a photocurable acrylic resin (made by MICROJET Corporation) in which a charged particle detection material ($SrAl_2O_4:Eu^{2+}$ (made by Sakai Chemical Industry Co., Ltd.)) was dispersed was formed on an aluminum foil, to which charged particles were made to enter. As shown in Figure 20, it was found that charged particles could be detected in the same manner as the above-described embodiment even when a charged particle detection film made of a charged particle detection material was formed on a thin film.

[0101] In addition, the charged particle detection material may be dispersed in e.g. a nonwoven fabric or the like. Figure 21 shows a photograph at the time that the charged particle detection material was dispersed in and made to adhere to a paper nonwoven fabric, to which the charged particles were made to enter. As shown in Figure 21, it was

found that charged particles could be detected in the same manner as the above-described embodiment even when using a nonwoven fabric or the like in which the charged particle detection material was dispersed.

(Embodiment 5)

[0102] Although the above-described embodiment was intended to detect the charged particles using the charged particle detection film or the charged particle detection material, the present invention is not limited to this embodiment. For example, the charged particles may be detected by using a charged particle detection liquid prepared by dispersing a charged particle detection material in a liquid.

[0103] Charged particles entering a measurement object having a complicated shape can be easily visualized by using the charged particle detection liquid. In addition, the charged particle detection material is three-dimensionally dispersed in the charged particle detection liquid so that the trajectory of the charged particles moving in the liquid can be visualized.

(Example 8)

[0104] A charged particle detection liquid was prepared, in which a mechanoluminescent substance $SrAl_2O_4:Eu^{2+}$ (made by Sakai Chemical Industry Co., Ltd.) was dispersed in a transparent photocurable acrylic resin (VisiJet CR-CL, made by 3D Systems Corporation) (weight ratio of $SrAl_2O_4:Eu^{2+}$: 70%). Then this charged particle detection liquid was dropped onto the stainless steel plate to form a puddle, to which the charged particles were made to enter from above in the same manner as in Example 1. The result is shown in Figure 22. At this time, a rod-shaped member was brought into contact with the surface of the charged particle detection liquid for confirming that the photocurable acrylic resin was not cured, and the charged particles were made to enter the liquid thereafter.

[0105] As a result, as shown in Figure 22, it was found that the inside of the charged particle detection liquid emitted light. From this, it was found that the charged particle detection liquid could detect charged particles similarly to the charged particle detection film.

[0106] Next, this liquid mixture was irradiated with ultraviolet ray at 365 nm (0.7 mW/cm^2) for 10 minutes to cure only the surface of the charged particle detection liquid and then the charged particles were made to enter the surface similarly to the above. The result is shown in Figure 23. As shown in Figure 23, it was found that the cured portion (surface) emitted stronger light compared to before curing.

(Other Embodiments)

[0107] If the charged particle detection material can be three-dimensionally dispersed in a gas such as air similarly to the above-described charged particle detection liquid, the trajectory of the charged particles moving in the gas can be detected.

[0108] It should be noted that this application claims priority based on Japanese Patent Application No. 2016-149215 filed on July 29, 2016, and the content of this application is incorporated herein as a reference.

Reference Numerals

[0109]

1	charged particle detection system
10	charged particle-emitting part
20	charged particle incident part
21	charged particle detection film
30	charged member
P, P2, P3	luminescent part

Claims

1. A charged particle detection material for detecting emission of charged particles from a charged particle-emitting part or incidence of the charged particles to a charged particle incident part, **characterized in that** the charged particle detection material contains at least one of a luminescent substance, an electroluminescent substance, a fractoluminescent substance, a photochromic substance, an afterglow substance, a photostimulated luminescent substance and a mechanoluminescent substance.

2. A charged particle detection material for detecting emission of charged particles from a charged particle-emitting part or incidence of the charged particles to a charged particle incident part in a non-vacuum state, **characterized in that** the charged particle detection material contains at least one of a fluorescent substance, a luminescent substance, an electroluminescent substance, a fractoluminescent substance, a photochromic substance, an afterglow substance, a photostimulated luminescent substance and a mechanoluminescent substance.

3. The charged particle detection material according to claim 1 or 2, **characterized in that** an electric field between the charged particle-emitting part and the charged particle incident part is within a range of 1 to 3000 V/mm in air.

4. The charged particle detection material according to any one of claims 1 to 3, **characterized in that**:

the charged particles are electrons; and
a potential difference between the charged particle-emitting part and the charged particle incident part is lower than a voltage calculated by Paschen's law.

5. The charged particle detection material according to any one of claims 1 to 4, **characterized in that** a total weight ratio of the fluorescent substance, the luminescent substance, the electroluminescent substance, the fractoluminescent substance, the photochromic substance, the afterglow substance, the photostimulated luminescent substance and the mechanoluminescent substance is 20 to 80 wt%.

6. The charged particle detection material according to any one of claims 2 to 5, **characterized in that** the non-vacuum state is under a pressure within a range of 10^{-3} to 10^{5} Torr.

7. The charged particle detection material according to any one of claims 1 to 6, **characterized in that** the afterglow substance is a substance represented by $SrAl_2O_4$ which is doped with Eu^{2+} and Dy^{3+}, a substance represented by $SrAl_2O_4$ which is doped with Eu^{2+}, Dy^{2+} and M (M = monovalent to trivalent metal ions), or a substance represented by $Zn_3(PO_4)$ which is doped with Mn^{2+} and M (M = monovalent to trivalent metal ions).

8. The charged particle detection material according to any one of claims 1 to 6, **characterized in that** the mechanoluminescent substance is a substance represented by $SrAl_2O_4$ which is doped with Eu^{2+}, a substance represented by $SrAl_2O_4$ which is doped with at least one of Eu^{2+}, Ho^{3+}, Dy^{2+}, M_1, M_2 and M_3 (M_1, M_2, M_3 = monovalent to trivalent metal ions different from each other), or a substance represented by $CaYAl_3O_7$ which is doped with Eu^{2+}.

9. A charged particle detection film including the charged particle detection material according to any one of claims 1 to 8.

10. A charged particle detection liquid including the charged particle detection material according to any one of claims 1 to 8.

Fig. 1

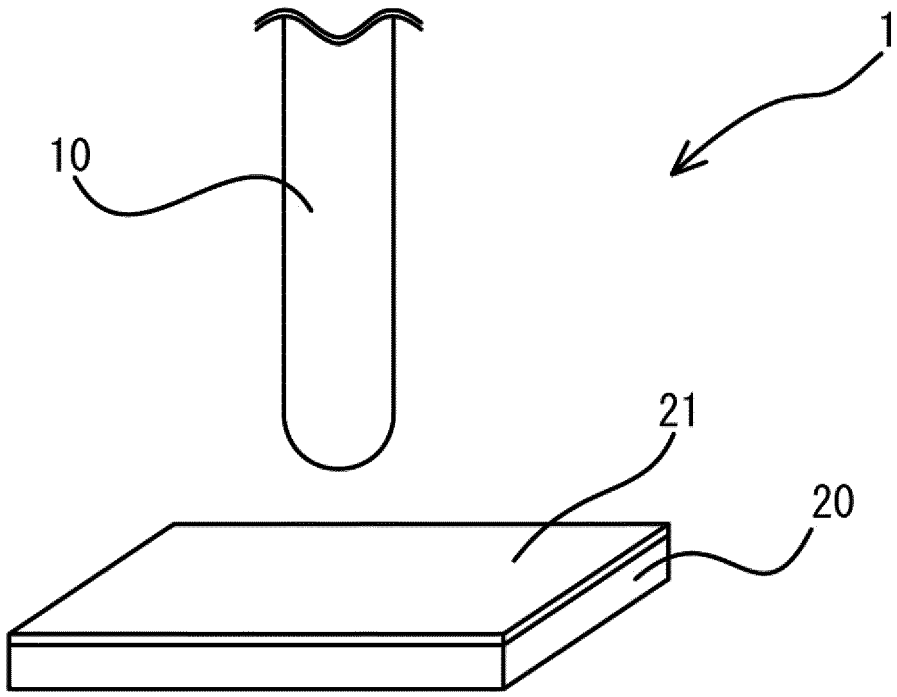


Fig. 2

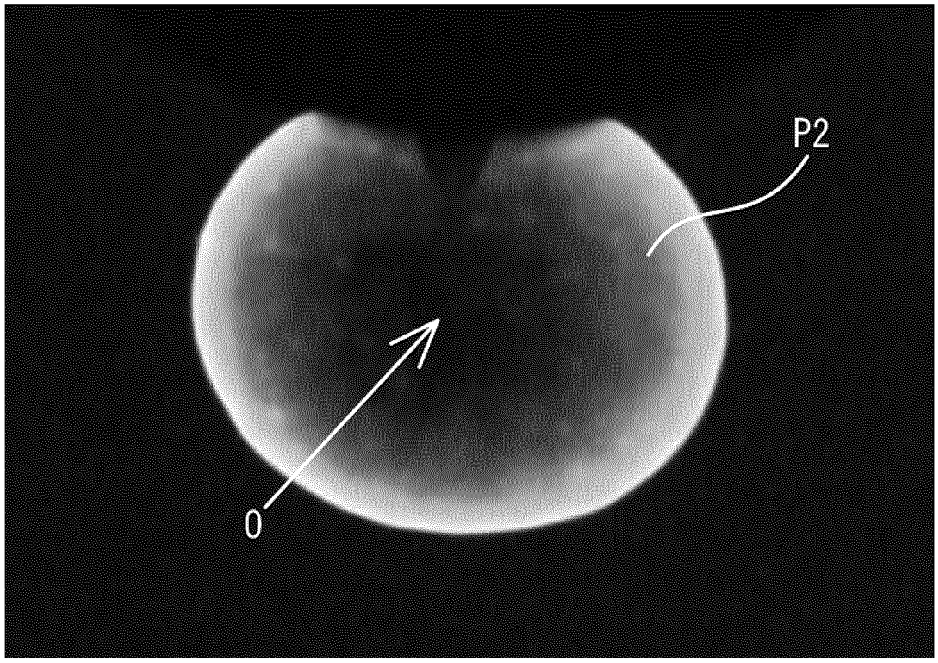


Fig. 3

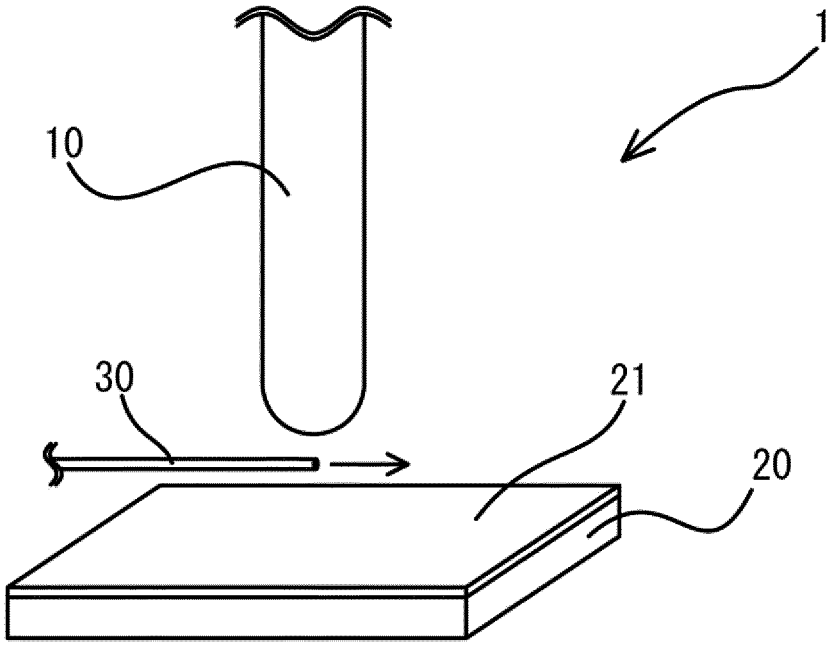


Fig. 4

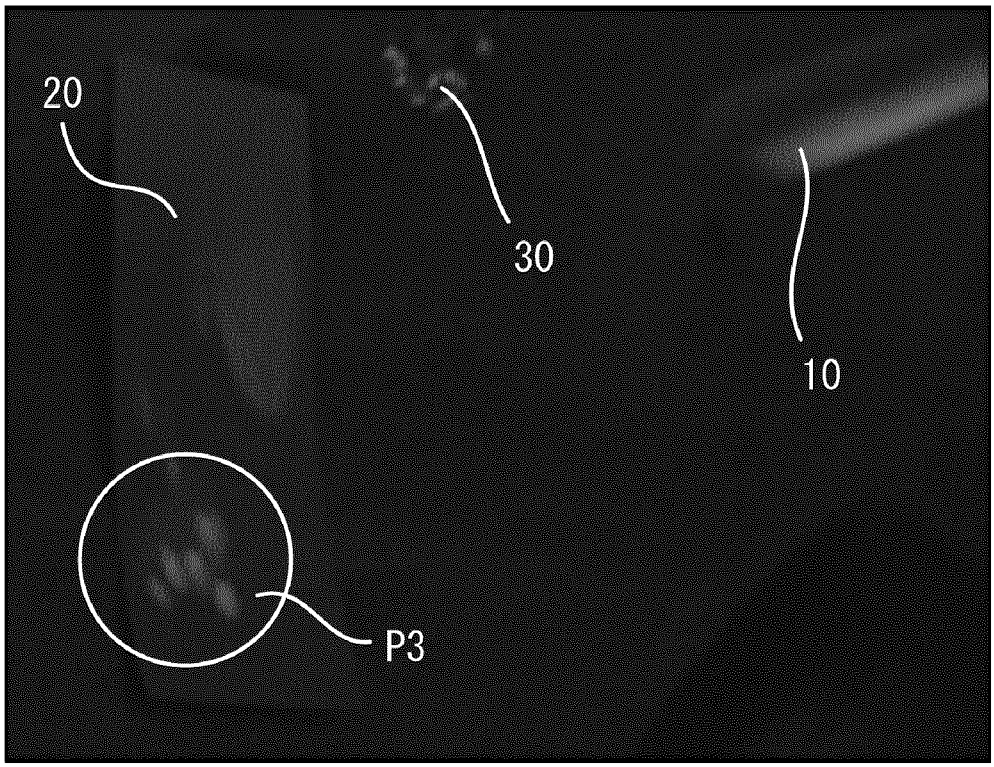


Fig. 5

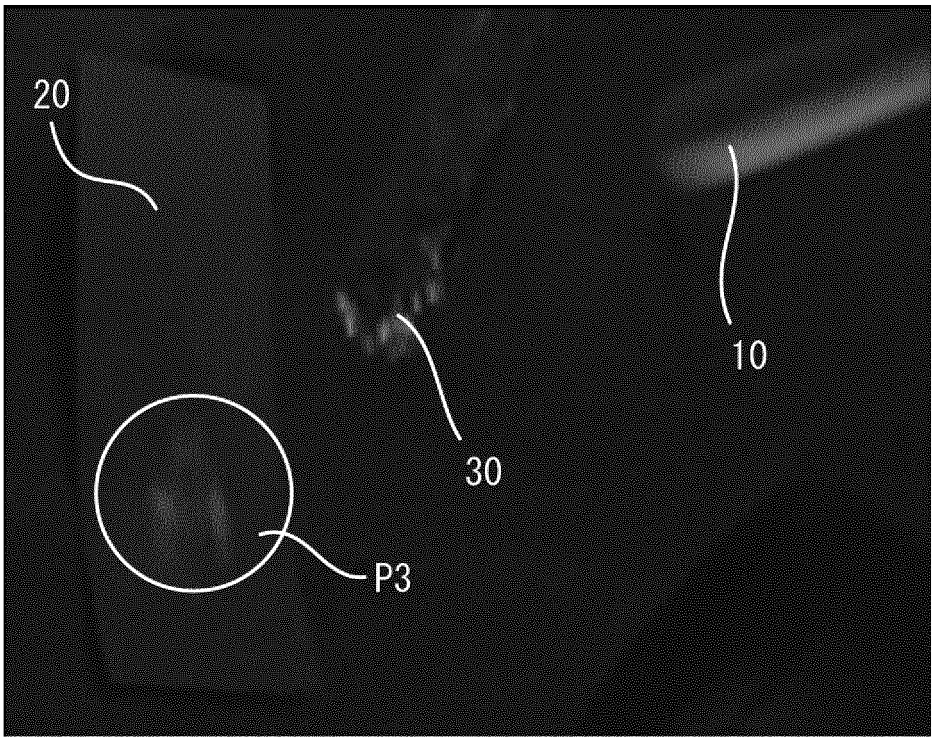


Fig. 6

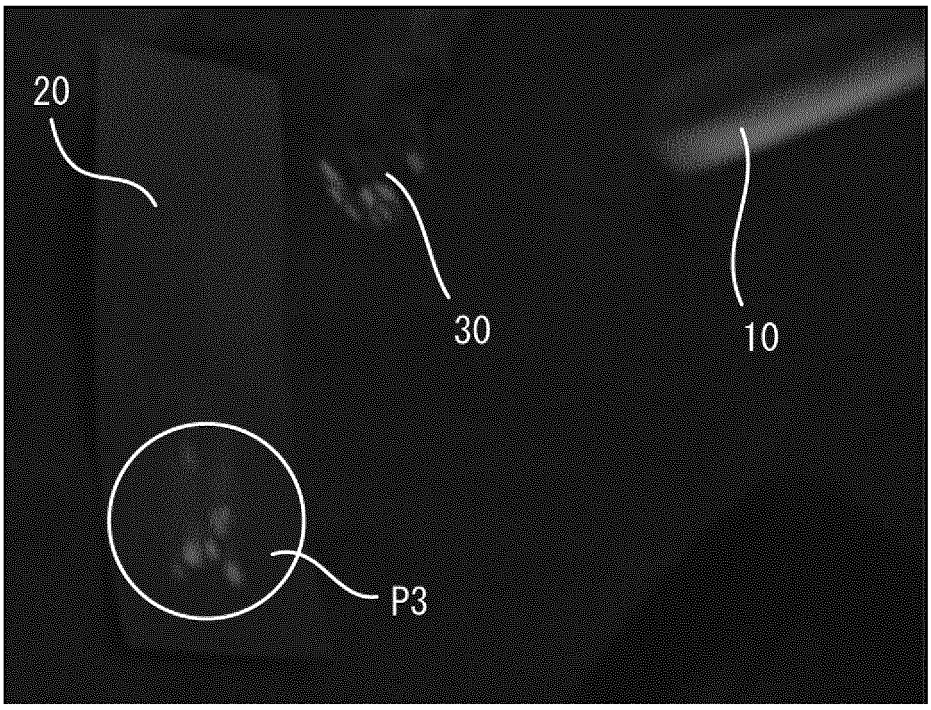


Fig. 7

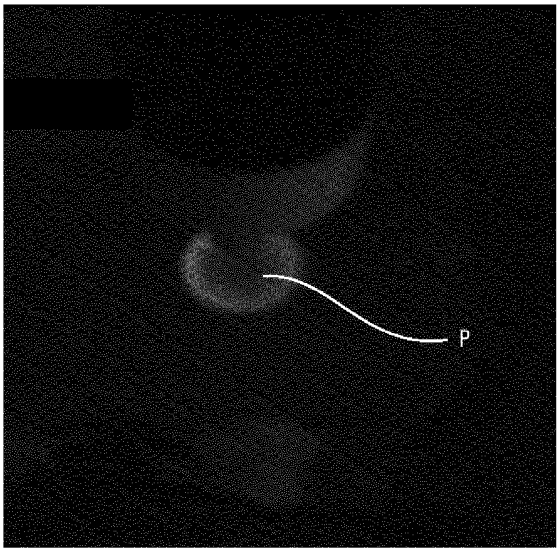


Fig. 8

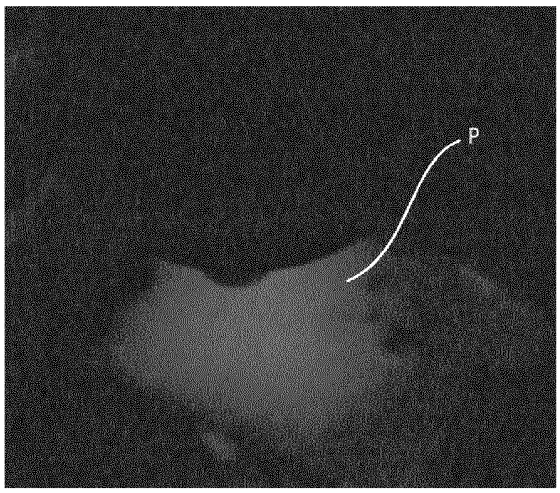


Fig. 9

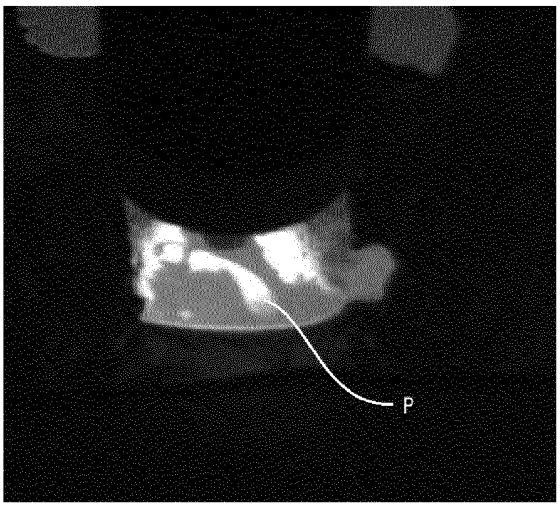


Fig. 10

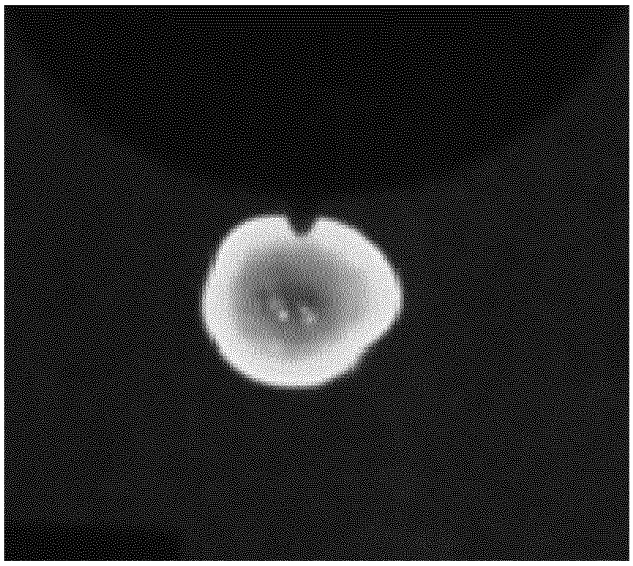


Fig. 11

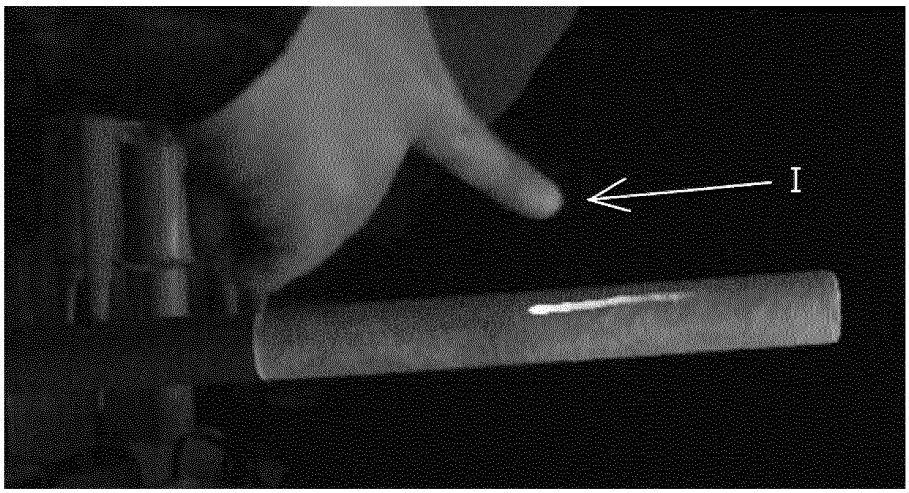


Fig. 12

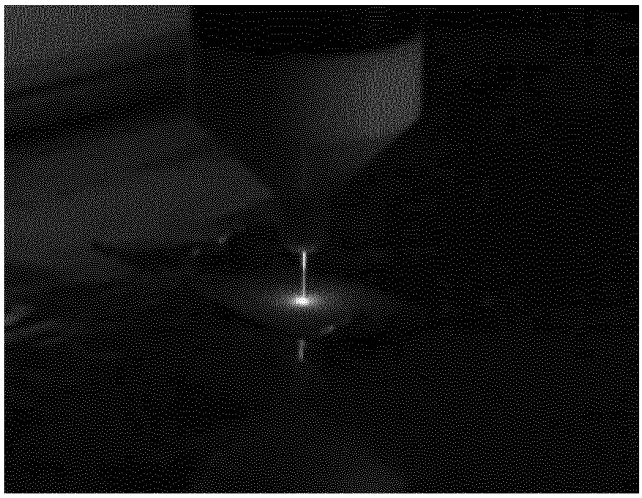


Fig. 13

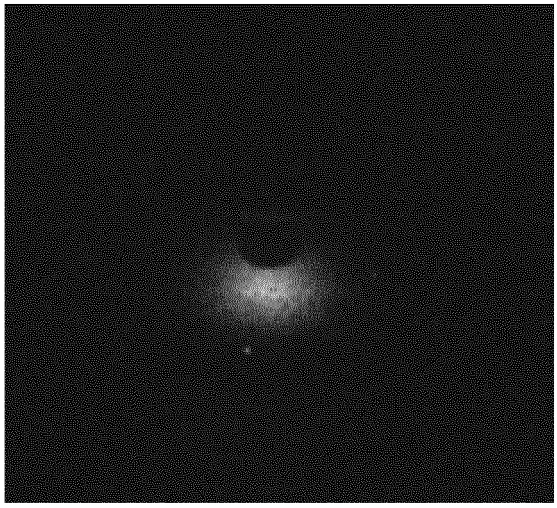


Fig. 14

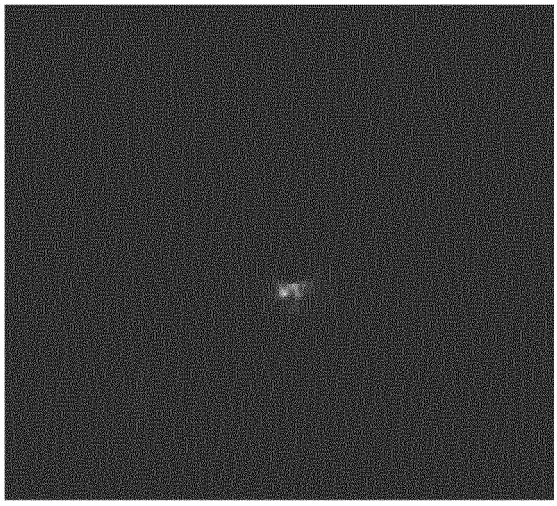


Fig. 15

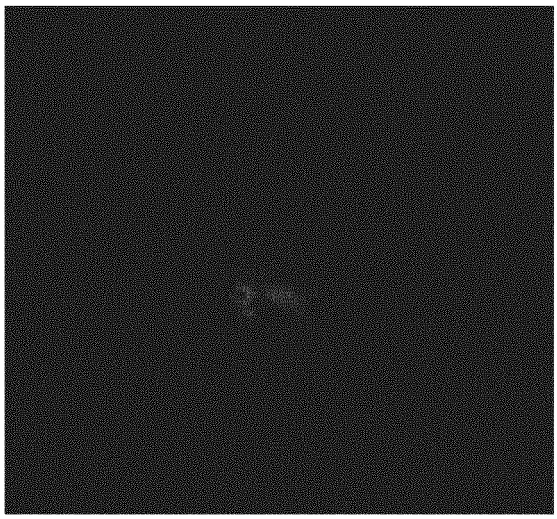


Fig. 16

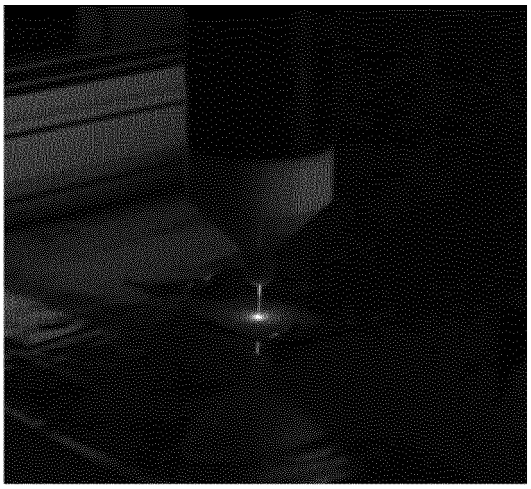


Fig. 17

Fig. 18

Fig. 19

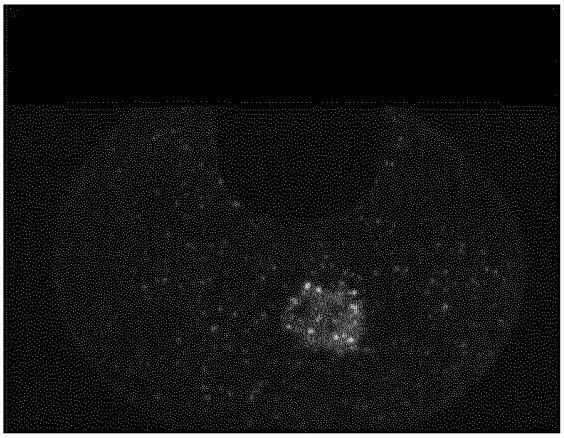


Fig. 20

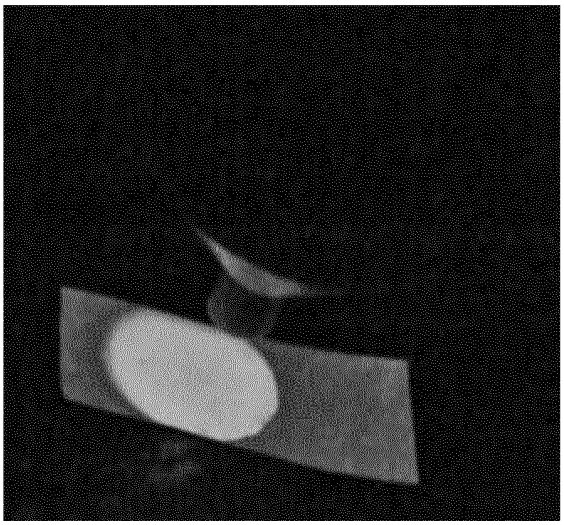


Fig. 21

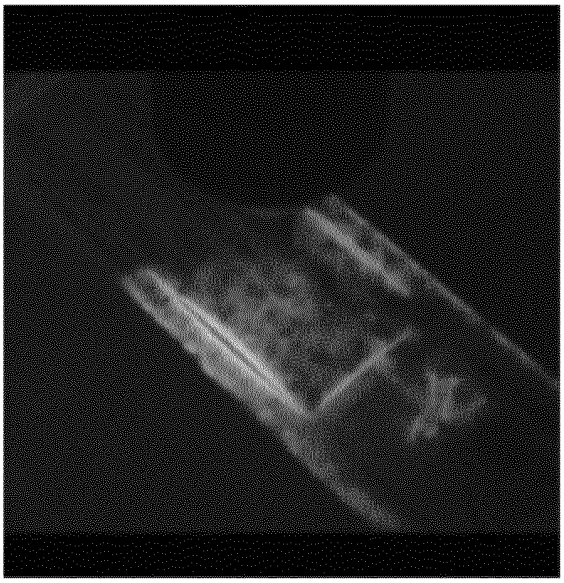


Fig. 22

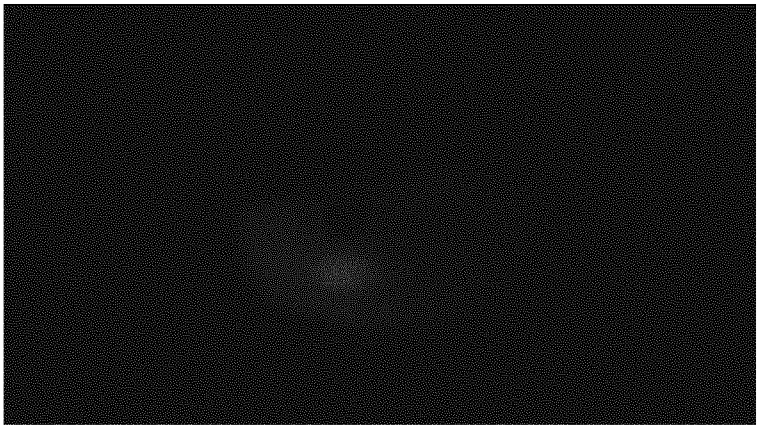
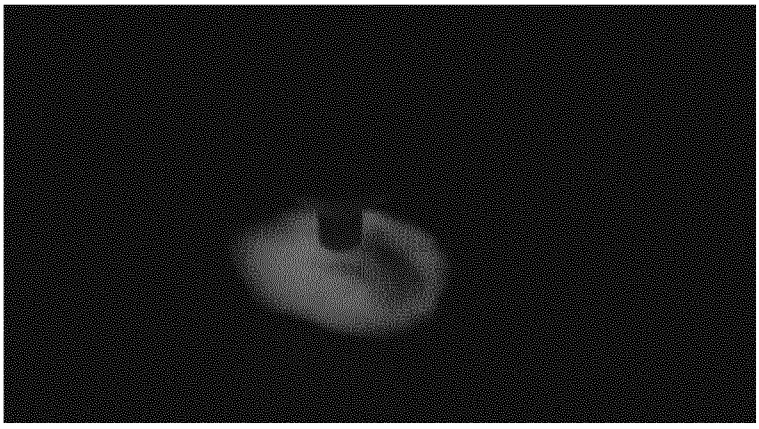


Fig. 23



INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2017/026373

A. CLASSIFICATION OF SUBJECT MATTER
C09K11/00(2006.01)i, *C09K9/00*(2006.01)i, *C09K11/64*(2006.01)i, *C09K11/70*(2006.01)i, *C09K11/80*(2006.01)i, *G01T1/20*(2006.01)i, *G21K4/00*(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C09K11/00, C09K9/00, C09K11/64, C09K11/70, C09K11/80, G01T1/20, G21K4/00

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

Jitsuyo Shinan Koho	1922-1996	Jitsuyo Shinan Toroku Koho	1996-2017
Kokai Jitsuyo Shinan Koho	1971-2017	Toroku Jitsuyo Shinan Koho	1994-2017

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
JSTPlus/JMEDPlus/JST7580(JDreamIII), CAplus/REGISTRY(STN)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	KOWATARI Munehiko et.al., The temperature dependence of luminescence from a long-lasting phosphor exposed to ionizing radiation, NUCLEAR INSTRUMENTS & METHODS IN PHYSICS RESEARCH SECTION A, 2002, 480, pp.431-439, entire text, particularly, Introduction	1,5,7,8 2-4,6,9-10
X Y	KOWATARI Munehiko et.al., The Luminescence from a Long Lasting Phosphor Exposed to Alpha,Beta, and Gamma Rays, Journal of NUCLEAR SCIENCE and TECHNOLOGY, 2002.12, Vol.39,No.12, pp.1251-1259, entire text, particularly, Introduction, Experimental	1,5,7,8,9 2-4,6,9-10

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
01 September 2017 (01.09.17)	12 September 2017 (12.09.17)

Name and mailing address of the ISA/	Authorized officer
Japan Patent Office 3-4-3,Kasumigaseki,Chiyoda-ku, Tokyo 100-8915,Japan	Telephone No.

Form PCT/ISA/210 (second sheet) (January 2015)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2017/026373

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	JP 2011-132429 A (Asahi Kasei Chemicals Corp.), 07 July 2011 (07.07.2011), paragraphs [0115] to [0135] (Family: none)	1,5,7,8 2-4,6,9-10
X Y	ABBRUSCATO Victor, Optical and Electrical Properties of SrAl2O4:Eu2+, J.Electrochem. Soc.:SOLID STATE SCIENCE, 1971.06, Vol.118, No.6, pp.930-932, entire text, particularly, ABSTRACT	1,5,8 2-4,6,9-10
X Y	JP 63-047688 A (Masaru TAKAGI et al.), 29 February 1988 (29.02.1988), claims; page 5, upper right column, lines 1 to 8 (Family: none)	1 2-4,6,9-10
X Y	ZUNIGA-RIVERA,N.J. et.al., Persistent luminescence,TL and OSL characterization of beta irradiated SrAl2O4:Eu2+,Dy3+ combustion synthesized phosphor, NUCLEAR INSTRUMENTS AND METHODS IN PHYSICS RESEARCH.SECTION B. BEAM INTERACTIONS WITH MATERIALS AND ATOMS, 326, 2014, pp.99-102, entire text, particularly, ABSTRACT, Experimental	1,5,7,8 2-4,6,9-10
A	JP 2015-166423 A (Panasonic Corp.), 24 September 2015 (24.09.2015), (Family: none)	1-10
A	JP 2003-286481 A (Fuji Photo Film Co., Ltd.), 10 October 2003 (10.10.2003), & US 2003/0066973 A1 & EP 1271558 A2	1-10
A	JP 2009-133759 A (Toshiba Corp.), 18 June 2009 (18.06.2009), (Family: none)	1-10
A	WO 2007/145167 A1 (Nemoto & Co., Ltd.), 21 December 2007 (21.12.2007), (Family: none)	1-10

Form PCT/ISA/210 (continuation of second sheet) (January 2015)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2017/026373

Claim 1 involves any charged-particle detection material which detects the emission of charged particles from a charged-particle emission part or the incidence of charged particles onto a charged-particle incidence part, the material being characterized by comprising at least one of luminescent substances, electroluminescent substances, triboluminescent substances, photochromic substances, afterglow substances, simulated luminescent substances, and stress-induced luminescent substances. However, among the substances involved in luminescent substances, electroluminescent substances, triboluminescent substances, photochromic substances, afterglow substances, simulated luminescent substances, and stress-induced luminescent substances, only limited substances are disclosed in the description in the meaning of PCT Article 5 as luminescent substances or the like capable of detecting charged particles due to a discharge phenomenon occurring in an extremely weak electric filed, such charged particles being unable to be observed with conventional techniques. The disclosed substances include $SrAl_2O_4:Eu^{2+}$, $SrAl_2O_4:Ho^{3+},Ce^{3+}$, $CaYAl_3O_7:Eu^{2+}$, $SrAl_2O_4:Eu^{2+},Cr^{3+},Ne^{3+}$, $Y_2O_2S:Tb^{3+}$, Eu(TTA)$_3$phen, and β-$Zn_3(PO_4)_2:Mn^{2+},Ga^{3+}$, etc. The charged-particle detection material which includes any of the other fluorescent substances, luminescent substances, electroluminescent substances, triboluminescent substances, photochromic substances, afterglow substances, simulated luminescent substances, and stress-induced luminescent substances lacks a support in the meaning of PCT Article 6.

The above-said opinion may be also applied to claims 2-10.

Therefore, a search was made only for the range supported by and disclosed in the description, that is, for the charged-particle detection material which includes any of the compounds specifically shown in the description, such as $SrAl_2O_4:Eu^{2+}$, $SrAl_2O_4:Ho^{3+},Ce^{3+}$, $CaYAl_3O_7:Eu^{2+}$, $SrAl_2O_4:Eu^{2+},Cr^{3+},Ne^{3+}$, $Y_2O_2S:Tb^{3+}$, Eu(TTA)$_3$phen, and β-$Zn_3(PO_4)_2:Mn^{2+},Ga^{3+}$.

Form PCT/ISA/210 (extra sheet) (January 2015)

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- JP 2010067738 A **[0005]**
- JP 2016149215 A **[0108]**

专利名称(译)	带电粒子检测材料，带电粒子检测膜和使用其的带电粒子检测液		
公开(公告)号	EP3492551A1	公开(公告)日	2019-06-05
申请号	EP2017834168	申请日	2017-07-20
申请(专利权)人(译)	国立先进工业科技THE		
当前申请(专利权)人(译)	国立先进工业科技THE		
[标]发明人	TERASAKI NAO KIKUNAGA KAZUYA		
发明人	TERASAKI NAO KIKUNAGA KAZUYA		
IPC分类号	C09K11/00 C09K9/00 C09K11/64 C09K11/70 C09K11/80 G01T1/20 G21K4/00		
CPC分类号	C09K11/06 C09K11/70 C09K11/7734 C09K11/7771 C09K11/7774 C09K11/7792 F21K2/04 G21K4/00 G01T1/20 C09K9/00 C09K11/00 C09K11/64 G21K2004/06		
优先权	2016149215 2016-07-29 JP		
其他公开文献	EP3492551A4		
外部链接	Espacenet		

摘要(译)

[问题]提供一种带电粒子检测材料，其能够检测由于现有技术无法观察到的极低电压引起的放电现象等引起的带电粒子，以及带电粒子检测膜和带电粒子检测材料。颗粒检测液体使用该材料。 [解决方案]根据本发明的带电粒子检测材料和带电粒子检测膜含有荧光物质，发光物质，电致发光物质，发光物质，光致变色物质，余辉物质，光刺激中的至少一种发光物质和机械发光物质，可以很容易地实时检测带电粒子的发射或入射。

$$V = \frac{Bpd}{\ln A pd + C}$$