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(54) FLUIDIZED BED REACTION APPARATUS AND METHODS FOR USING THE SAME

WIRBELBETT-REAKTIONSVORRICHTUNG UND ANWENDUNGSVERFAHREN DAFÜR

APPAREIL DE RÉACTION EN LIT FLUIDISÉ ET SES PROCÉDÉS D’UTILISATION

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Description

[0001] This disclosure relates to apparatuses useful for preparing sol-gel solutions and to sol-gel processes used to form photoreceptor layers. The present disclosure relates specifically to apparatuses for preparing sol-gel solutions and to efficient, scalable methods of making such sol-gel solutions.

[0002] In electrophotography, an electrophotographic substrate containing a photoconductive insulating layer on a conductive layer is imaged by first uniformly electrostatically charging a surface of the substrate. The substrate is then exposed to a pattern of activating electromagnetic radiation, such as, for example, light. The light or other electromagnetic radiation selectively dissipates the charge in illuminated areas of the photoconductive insulating layer while leaving behind an electrostatic latent image in non-illuminated areas of the photoconductive insulating layer. This electrostatic latent image is then developed to form a visible image by depositing finely divided electroscopic marking particles on the surface of the photoconductive insulating layer. The resulting visible image is then transferred from the electrophotographic substrate to a necessary member, such as, for example, an intermediate-transfer member or a print substrate, such as paper. This image-developing process can be repeated as many times as necessary with reusable photoconductive insulating layers.

[0003] Image-forming apparatus such as copiers, printers and facsimiles, including electrophotographic systems for charging, exposure, development, transfer, etc., using electrophotographic photoreceptors have been widely employed. In such image-forming apparatus, there are ever-increasing demands for improving the speed of the image-forming processes, improving image quality, miniaturizing and prolonging the life of the apparatus, reducing production and running costs, etc. Further, with recent advances in computers and communication technology, digital systems and color-image output systems have been applied also to image-forming apparatuses.

[0004] Electrophotographic imaging members or photoreceptors are well known. Photoreceptors having either a flexible belt or a rigid drum configuration are commonly used in electrophotographic processes. Photoreceptors may comprise a photoconductive layer including a single layer or composite layers. These photoreceptors take many different forms. For example, layered photo-responsive imaging members are known in the art. U.S. Patent No. 4,265,990 describes a layered photoreceptor having separate photo-generating and charge-transport layers. The photo-generating layer disclosed in the 990 patent is capable of photo-generating holes and injecting the photo-generated holes into the charge-transport layer. Thus, in the photoreceptors of the 990 patent, the photo-generating material generates electrons and holes when subjected to light.

[0005] More advanced photoconductive photoreceptors containing highly specialized component layers are also known. For example, multi-layered photoreceptors may include one or more of a substrate, an undercoating layer, an intermediate layer, an optional hole- or charge-blocking layer, a charge-generating layer (including a photo-generating material in a binder) over an undercoating layer and/or a blocking layer, and a charge-transport layer (including a charge-transport material in a binder). Additional layers, such as one or more overcoat layer or layers, may be included as well. In view of such a background, improvement in electrophotographic properties and durability, miniaturization, reduction in cost, etc., in photoreceptors have been studied, and photoreceptors using various materials have been proposed.

[0006] Silicon-containing compounds used in photoreceptor layers, such as in photosensitive and protective layers, have been shown to increase the mechanical lifetime of photoreceptors, under charging conditions and scorotron-charging conditions. However, there are shortcomings associated with photoreceptor layers that include silicon-containing compounds, including cross-linked siloxane-containing overcoat layers. For example, sol-gel solutions for making such layers must be prepared at the site at which the layers are prepared, because polymerization of the sol-gel solutions must be carried out during layer formation.

[0007] Sol-gel processes are generally known in the art, and embodiments of this disclosure include apparatuses and methods for preparing sol-gel solutions. In exemplary known processes, compositions formed by sol-gel processes and solutions comprise an organic-inorganic composite structure, generally characterized as an inorganic glassy polymer having an organic material dispersed in or interpenetrated into and/or chemically bonded into the inorganic polymer network.

[0008] The organic-inorganic composite structure includes a glassy polymer, such as an inorganic silica polymer such as a silica glass structure. The glassy polymer is prepared by a solution-gelation (or "sol-gel") process during which hydrolysis, followed by condensation polymerization, of a silicon alkoxide takes place in the presence of water and an alcohol. The general process for forming sol-gels is taught, for example, in C. J. Brinker and G. Scherer, Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing (Academic Press, Boston, 1990). This two-step reaction process, which transforms a miscible one-phase liquid solution into a two-phase material, is called "sol-gel transition". Generally, the silicon alkoxide/water/ alcohol mixture is slow to hydrolyze. The hydrolysis rate is a function of the solution pH and, therefore, may be controlled by the addition of an acid or base as a catalyst. The reaction mixture can further include other materials, such as organic monomers or polymers or other additives, which can become either chemically bound into the glassy polymer network, or entrapped in the glassy polymer structure.

[0009] As is known in the sol-gel art, solution pH may influence the properties of the formed glassy polymer gel.

Polymerization in an alkaline solution generally yields a polymer gel that is relatively porous and translucent, and is characterized by clusters of oxides of, for example, Al, B, Si, Sn, Ti, or Zr such as for example, silica, titania, alumina, zirconia, and aluminum phosphate, that are linked together to form the gel. Polymerization in an acidic solution, on the other hand, generally yields a transparent polymer gel that is characterized by a very fine porosity and by uniform, linear molecules that coalesce during subsequent sintering to form a high-density material at relatively low temperatures (e.g., about 800°C).

[0010] Polymer gels formed by the sol-gel process are two-phase materials, denoted "alcogels," one phase of which contains a solid siloxane skeletal network (i.e., $(\text{-Si-O-Si-})_n$), and an aqueous phase containing water and alcohol in the pores. Once the alcogel is formed, it is dried by slowly heating the gel to vaporize the volatile species, such as alcohol. By properly driving off the volatile species by natural evaporation, the formed polymer gel comprises a two-phase, rigid xerogel (a gel containing an oxide skeleton and micropores). The number and size of the pores found in the final glass product (and, thus, the density of the final glass product) are a function of the rate of heating, the ultimate sintering temperature, and the period of time the xerogel is maintained at the ultimate sintering temperature. In sol-gel processes, an acid catalyst is generally used to speed the sol-gel reactions.

[0011] When used in applications relating to photoreceptor layers, sol-gel reaction components, and any desired additives, are mixed with conventional photoreceptor layer materials. The hydrolysis of the sol-gel reaction components takes place *in situ* in the coating solution. After coating, solvents used in the process evaporate, and a desired thin film forms. The condensation of the sol-gel reaction components takes place *in situ* during thermal drying, and an organic-inorganic interpenetrating network is formed, which unexpectedly provides better wear resistance, deletion control and other benefits.

[0012] However, these sol-gel formulations for preparing siloxane-containing materials, for example, can involve processes in which large volume changes may take place. Such issues make scaling sol-gel procedures beyond a laboratory scale difficult.

[0013] Thus, there remains a need for improved, scalable apparatuses and methods for preparing sol-gel solutions that will produce high yields of the desired sol-gel solutions having the electrical and physical properties on a large scale that are obtained on a laboratory scale.

[0014] US-A-4751203 discloses a method for preparing a sol-gel solution comprising hydrolyzing metal alcoholates in the presence of water and an acid, followed by polycondensation.

[0015] The present invention provides:

(1) an apparatus for preparing sol-gel solutions, comprising
a vessel optionally containing a stirrer;
a pump;
a fluidized bed reaction column; and
multiple fluid lines;
wherein said fluid lines connect the vessel and the pump in a first circulation loop and said fluid lines connect the vessel, the pump and the fluidized bed reaction column in a second circulation loop.

[0016] Embodiments of the invention include:

(2) the apparatus according to (1), wherein said first circulation loop further comprises a heat exchanger;
(3) the apparatus according to (1), wherein said fluidized bed column comprises an upper portion, a body and a lower portion;
(4) the apparatus according to (3), wherein said upper portion and said body are separated by a first fluid permeable membrane;
(5) the apparatus according to (3), wherein said lower portion is connected to said fluid lines by a connector, and said lower portion and said connector are separated by a second fluid permeable membrane;
(6) the apparatus according to (3), wherein said lower portion has a conical shape in which a wider portion of said conical shape is connected to the body and a narrower portion of said conical shape connects to said connector;
(7) the apparatus according to (6), wherein said lower portion has a conical shape in which an angle at a projected vertex of said conical shape is from 1 to 175 degrees;
(8) the apparatus according to (6), wherein said lower portion has a conical shape in which an angle at a projected vertex of said conical shape is from 30 to 90 degrees;
(9) the apparatus according to (6), wherein said lower portion has a conical shape in which an angle at a projected vertex of said conical shape is from 40 to 60 degrees;
(10) the apparatus according to (3), wherein
said upper portion and said body are separated by a first fluid permeable membrane;

said lower portion is connected to said fluid lines by a connector, and said lower portion and said connector are separated by a second fluid permeable membrane; and
said body contains a solid state material that is not permeable through said first fluid permeable membrane or said second fluid permeable membrane;

(11) the apparatus according to (10), wherein said solid state material is chosen from powdered materials and granular materials;
(12) the apparatus according to (10), wherein said solid state material is chosen from solid state acid catalysts.

[0017] The present invention further provides:
(13) a method for preparing a sol-gel solution, comprising:

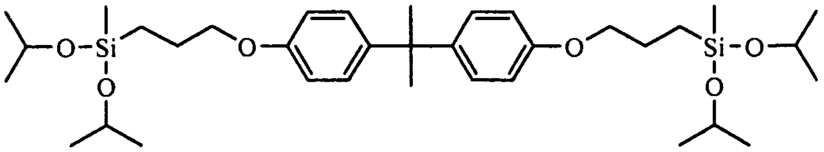
providing an apparatus that comprises:

a vessel optionally containing a stirrer,
a pump,
a fluidized bed reaction column having an upper portion, a body and a lower portion, and
multiple fluid lines,
wherein said fluid lines connect the vessel and the pump in a first circulation loop and said fluid lines connect the vessel, the pump and the fluidized bed reaction column in a second circulation loop, said upper portion and said body are separated by a first fluid permeable membrane; said lower portion is connected to said fluid lines by a connector, and said lower portion and said connector are separated by a second fluid permeable membrane; and said body contains a solid state acid catalyst that is not permeable through said first fluid permeable membrane or said second fluid permeable membrane;

providing sol-gel precursor materials to the vessel;
blending said sol-gel precursor materials, water and methanol with an optional solvent;
circulating said mixture through a first circulation loop; and
reacting said sol-gel precursor materials by circulating said mixture through the second circulation loop and contacting said sol-gel precursor materials with said solid state acid catalyst.

[0018] Embodiments of the invention include:

(14) the method according to (13), wherein said sol-gel precursor materials are chosen from the group consisting of reactive siloxane-containing binder materials, reactive siloxane-containing hole-transport materials and mixtures thereof;
(15) the method according to (14), wherein said reactive siloxane-containing hole-transport materials are chosen from aromatic silicon-containing compounds and mixtures thereof;
(16) the method according to (15), wherein said aromatic silicon-containing compounds are chosen from



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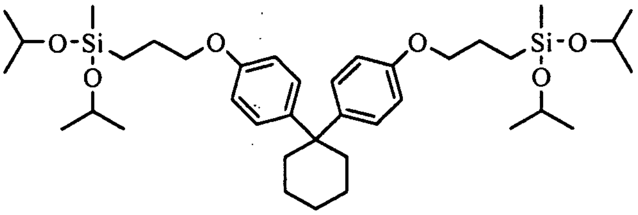

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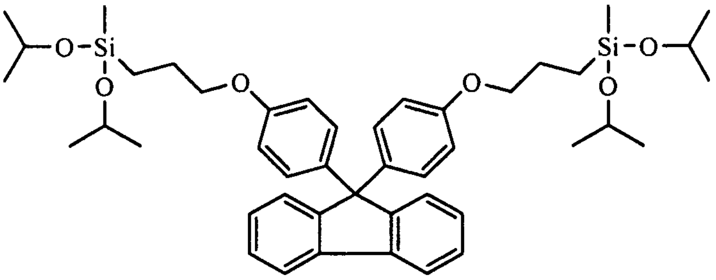
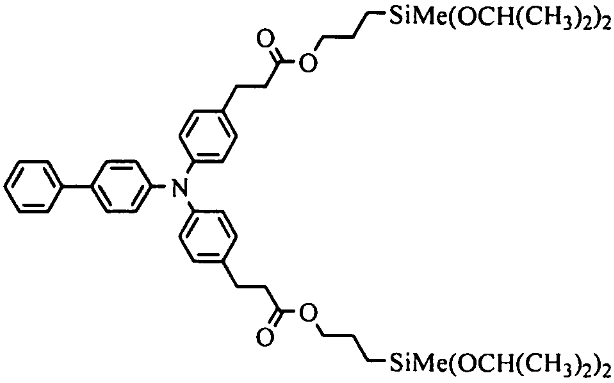


(IV)

and mixtures thereof;

(17) the method according to (14), wherein said reactive siloxane-containing hole-transport materials are chosen from silicon-containing arylamine compounds and mixtures thereof;

(18) the method according to (14), wherein said reactive siloxane-containing hole-transport materials are Compound (VI)



(VI) ;

(19) the method according to (14), wherein said reactive siloxane-containing hole-transport materials may be reacted in amounts from 0.01 to 99 % by weight, based on the total weight of the reactants;

(20) the method according to (13), further comprising incorporating into the reacted mixture one or more of stabilizers, antioxidants, polymeric binder materials and surfactants;

(21) the method according to (20), wherein said stabilizers are chosen from the group consisting of aluminum(III) acetylacetonate ($Al(AcAc)_3$), acetylacetonate (AcAc) and mixtures thereof;

(22) the method according to (20), wherein said antioxidants are chosen from the group consisting of antioxidants having a hindered-phenol, hindered-amine, thioether or phosphite partial structure;

(23) the method according to (20), wherein said polymeric binders are chosen from the group consisting of polyvinyl acetal resins, polyamide resins, cellulose resins and phenol resins and mixtures thereof;

(24) the method according to (20), wherein said surfactants are chosen from the group consisting of FLUOROLINK S-10 in butanol.

[0019] The sol-gel solution prepared by the method of the invention may be used for forming one or more layers of an electrophotographic imaging member comprising a substrate; a charge-generating layer; a charge-transport layer; and optionally an overcoating layer. The electrophotographic imaging member may be used in an electrographic image development device.

FIG. 1 is a schematic cross sectional view showing an embodiment of an electrophotographic photoreceptor.
FIG. 2 is a schematic view showing an embodiment of an image forming apparatus.
FIG. 3 is a schematic view showing another embodiment of an image forming apparatus.
FIG. 4 is a schematic view showing an embodiment of a sol-gel solution preparation system of the disclosure.
FIG. 5 is a schematic view an exemplary fluidized bed reaction apparatus of the disclosure.

[0020] In this specification and the claims that follow, singular forms such as "a," "an," and "the" include plural forms unless the content clearly dictates otherwise. Unless specifically disclaimed, all numerical ranges include the endpoints and all specific values and sub-ranges between the endpoints, as well as those values approximating or equivalent to the specifically mentioned endpoints, values and ranges.

[0021] Reference may be made to a number of terms that shall be defined as follows:

The term "room temperature" refers, for example, to temperatures in a range of from 20°C to 25°C. The terms "high temperature environment" and "high temperature conditions" refer, for example, to an atmosphere in which the temperature is at least 28 or 30°C, and may be as high as 300°C. The terms "high humidity environment" and "high humidity conditions" refer, for example, to an atmosphere in which the relative humidity is at least 75 or 80 %.

[0022] The term "organic molecule" refers, for example, to any molecule that is made up predominantly of carbon and hydrogen, such as, for example, alkanes and arylamines. The term "heteroatom" refers, for example, to any atom other than carbon and hydrogen. Typical heteroatoms included in organic molecules include oxygen, nitrogen, sulfur and the like

[0023] The terms "hydrocarbon" and "alkane" refer, for example, to branched and unbranched molecules having the general formula C_nH_{2n+2}, in which n is a number of 1 or more, such as of from 1 to 60. Exemplary alkanes include methane, ethane, n-propane, isopropane, n-butane, isobutane, tert-butane, octane, decane, tetradecane, hexadecane, eicosane, tetracosane and the like. Alkanes may be substituted by replacing hydrogen atoms with one or more functional groups. The term "aliphatic" refers, for example, to straight-chain molecules, and may be used to describe acyclic, unbranched alkanes. The term "long-chain" refers, for example, to hydrocarbon chains in which n is a number of from 8 to 60, such as from 20 to 45 or from 30 to 40. The term "short-chain" refers, for example, to hydrocarbon chains in which n is a number of from 1 to 7, such as from 2 to 5 or from 3 to 4.

[0024] The term "saturated" refers, for example, to compounds containing only single bonds. The term "unsaturated" refers, for example, to compounds that contain one or more double bonds and/or one or more triple bonds.

[0025] The term "alkyl" refers, for example, to a branched or unbranched saturated hydrocarbon group, derived from an alkane and having the general formula C_nH_{2n+1}, in which n is a number of 1 or more, such as of from 1 to 60. Exemplary alkyl groups include methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, tert-butyl, octyl, decyl, tetradecyl, hexadecyl, eicosyl, tetracosyl and the like. The term "lower alkyl" refers, for example, to an alkyl group of from 1 to 12 carbon atoms. "Halogenated alkyl" refers, for example, to an alkyl group in which at least one hydrogen atom, and optionally all hydrogen atoms, is replaced by a halogen atom.

[0026] The term "alkylene" refers, for example, to a branched or unbranched saturated hydrocarbon group of 1 to 12 carbon atoms and having two bonds to other portions of the molecule. Exemplary alkylene groups have the structure $-(CH_2)_a-$, in which a is an integer in a range of from 1 to 12.

[0027] The term "alkenyl" refers, for example, to a branched or unbranched hydrocarbon chain containing from 2 to 24 carbon atoms and at least one double bond. "Lower alkenyl" refers, for example, to an alkenyl group of 2 to 6 carbon atoms. "Halogenated alkenyl" refers, for example, to an alkenyl group in which at least one hydrogen atom, and optionally all hydrogen atoms, is replaced by halogen atoms.

[0028] The term "alkoxy" refers, for example, to an alkyl group bound through a single, terminal ether linkage; that is, an "alkoxy" group is defined as -OR in which R is an alkyl as defined above. A "lower alkoxy" refers, for example, to an alkoxy group containing 1 to 6 carbon atoms.

[0029] The term "siloxane" refers, for example, to compounds containing silicon atoms bound to oxygen atoms and to organic groups. Exemplary siloxanes have the structure ROSiR'R"R'", in which O represents oxygen, Si represents silicon and R, R', R" and R'" represent independently selected organic groups, such as alkyl, alkenyl, alkynyl, alkoxy and other suitable groups.

[0030] The term "aromatic" refers, for example, to an organic molecule or radical in which some of the bonding electrons are delocalized or shared among several atoms within the molecule and not localized in the vicinity of the atoms involved in the bonding. Aromatic compounds may include heteroatoms in the molecules, and may include one or more cyclic or ring systems that may include one or more fused aromatic rings. Examples of aromatic compounds include, for example, benzene (C_6H_6), naphthalene ($C_{10}H_8$), anthracene ($C_{14}H_{10}$), pyridine (C_5H_5N) and the like. Optionally, these aromatic compounds may be substituted with one or more independently selected substituents, including alkyl, alkenyl, alkoxy, aryl, hydroxyl and nitro groups.

[0031] The term "aryl" refers, for example, to an organic group derived from an aromatic compound and having the same general structure as the aromatic compound. Examples of aromatic compounds include, for example, phenyl (C_6H_5), benzyl (C_7H_7), naphthyl ($C_{10}H_7$), anthracyl ($C_{14}H_9$), pyridinyl (C_5H_4N) and the like. Optionally, these aromatic groups may be substituted with one or more independently selected substituents, including alkyl, alkenyl, alkoxy, aryl, hydroxyl and nitro groups.

[0032] The term "aralkylene" refers, for example, to moieties containing both alkylene and monocyclic species, typically containing less than 12 carbon atoms in the alkylene portion, and wherein the aryl substituent is bonded to the structure of interest through an alkylene linking group. Exemplary aralkylene groups have the structure $-(CH_2)_a-Ar$, in which Ar represents an aryl group and a is an integer in a range of from 1 to 6.

[0033] The term "arylamine" refers, for example, to moieties containing both aryl and amine groups. Exemplary aralkylene groups have the structure Ar-NRR', in which Ar represents an aryl group and R and R' are groups that may be independently selected from hydrogen and substituted and unsubstituted alkyl, alkenyl, aryl and other suitable functional groups. The term "triarylamine" refers, for example, to arylamine compounds having the general structure NArAr'Ar", in which Ar, Ar' and Ar" represent independently selected aryl groups.

[0034] "Alcohol" refers, for example, to an alkyl moiety in which one or more of the hydrogen atoms has been replaced by an -OH group. The term "lower alcohol" refers, for example, to an alkyl group of 1 to 6 carbon atoms in which at least one, and optionally all, of the hydrogen atoms has been replaced by an -OH group. The term "primary alcohol" refers, for example to alcohols in which the -OH group is bonded to a terminal or chain-ending carbon atom, such as in methanol, ethanol, 1-propanol, 1-butanol, 1-hexanol and the like. The term "secondary alcohol" refers, for example to alcohols in which the -OH group is bonded to a carbon atom that is bonded to one hydrogen atom and to two other carbon atoms, such as in 2-propanol (isopropanol), 2-butanol, 2-hexanol and the like. The term "tertiary alcohol" refers, for example to alcohols in which the -OH group is bonded to a carbon atom that is bonded to three other carbon atoms, such as in methylpropanol (tert-butanol) and the like.

[0035] "Amine" refers, for example, to an alkyl moiety in which one or more of the hydrogen atoms has been replaced by an $-NH_2$ group. The term "lower amine" refers, for example, to an alkyl group of 1 to 6 carbon atoms in which at least one, and optionally all, of the hydrogen atoms has been replaced by an $-NH_2$ group.

[0036] The term "derivative" refers, for example, to compounds that are derived from another compound and maintain the same general structure as the compound from which they are derived. For example, saturated alcohols and saturated amines are derivatives of alkanes.

[0037] The term "homologous" refers, for example, to any number of series of organic compounds that have similar chemical properties and that differ by a constant relative molecular mass. For example, lower alcohols are a homologous series that includes CH_3OH, CH_3CH_2OH, $CH_3CH_2CH_2OH$, $CH_3(CH_2)_2CH_2OH$, $CH_3(CH_2)_3CH_2OH$ and $CH_3(CH_2)_4CH_2OH$, as well as isomers of these molecules.

[0038] The terms "halogen" or "halogen atom" refer, for example, to atoms of the elements fluorine (F), chlorine (Cl), bromine (Br), iodine (I) and astatine (At). The term "halo" refers, for example, to substitution of a halogen atom for a hydrogen atom in an organic compound. "Haloalkyl" refers, for example, to an alkyl moiety in which one or more of the hydrogen atoms has been replaced by a halogen atom. The term "lower haloalkyl" refers, for example, to an alkyl group of 1 to 6 carbon atoms in which at least one, and optionally all, of the hydrogen atoms has been replaced by a halogen atom. The term "perhalogenated" refers, for example, to a compound in which all of the hydrogen atoms have been replaced by halogen atoms, while the phrase "partially halogenated" refers, for example, to a compound in which less than all of the hydrogen atoms have been replaced by halogen atoms.

[0039] The term "heterogeneous reaction" refers, for example, to a reaction in which there is an interface between the reactants, such as reactions between a gas and a solid, a liquid and a gas, a solid and a liquid, two immiscible liquids, or two different solids.

[0040] "Optional" or "optionally" refer, for example, to instances in which subsequently described circumstance may or may not occur, and include instances in which the circumstance occurs and instances in which the circumstance does not occur.

[0041] The terms "one or more" and "at least one" refer, for example, to instances in which one of the subsequently described circumstances occurs, and to instances in which more than one of the subsequently described circumstances occurs.

[0042] Sol-gel formulations for preparing siloxane-containing materials, for example, are known to involve multi-step processes that can include steps of combining the component materials, including at least one silicon-containing material, exchanging silicon-substituent groups for more reactive substituents, polymerizing the component materials, and stabilizing the reaction system. On a laboratory scale, such processes are conducted in a reaction vessel chosen to accommodate any volume changes that may take place. On larger scales, however, accommodating large volume changes by using very large reaction vessels or by transferring reaction mixtures between vessels can be costly and difficult.

[0043] This disclosure provides scalable apparatuses and systems for the formulation of sol-gel solutions, as well as methods for producing sol-gel solutions using such apparatuses and systems. The apparatuses and processes of embodiments are generally applicable to sol-gel systems; however, for exemplary purposes, the specific embodiments disclosed herein are described with respect to photoreceptor layers and their preparation. In particular, this disclosure relates to novel apparatuses utilizing fluidized bed reaction columns suitable for preparation of any sol-gel solution. Exemplary apparatuses utilizing fluidized bed reaction columns will be described first, followed by descriptions of sol-gel processes utilizing such apparatuses.

[0044] In embodiments, an apparatus comprises a vessel containing a stirring means, a pump, an optional heat exchanger, a fluidized bed reaction column and fluid lines. Exemplary apparatuses, such as the apparatus shown in FIG. 4, may be constructed to allow two or more circulation loops by which fluid and reactants may be circulated through the apparatus. For example, a suitable apparatus **200** may include a vessel **201** that has a stirring means **202** within the vessel. The vessel **201** is connected to a fluid line **203a** that contains a pump **204** and connects to an optional heat exchanger **205.** The heat exchanger **205** in turn connects to another fluid line **203b** that connects to the vessel **201.** This defines a first circulation loop. A second circulation loop of the apparatus **200** includes vessel **201,** fluid line **203a,** pump **204,** optional heat exchanger **205** and fluid line **203b** In addition, the second circulation loop includes fluid line **203c,** which connects to fluid line **203b** and to fluidized bed reaction column **206,** which then connects through fluid line **203d** to fluid line **203b** and vessel **201.**

[0045] In exemplary apparatuses, the fluidized bed reaction column **206,** such as that shown in FIG. 5, may have a body **207** that has a generally cylindrical shape and has a lower portion having a conical shape. This lower portion has a conical shape to allow fluidization of solid state materials within the body **207.** This lower portion may be truncated and may contain a connector **208,** which connects the body **207** to fluid line **203c,** and a screen or membrane between the lower portion and the connector **208.** The body **207** may also contain an upper portion that connects the body **207** to fluid line **203d** and an additional screen or membrane **212** between the body **207** and the upper portion **209.** The body **207** may also include a lower window **210a** and/or an upper window **210b,** through which reaction in and flow through the fluidized bed reaction column **206** may be observed.

[0046] In exemplary apparatuses, lower portion of the body **207** may have portions that are cylindrical and/or conical in shape. The lower portion of the body **207** may have, in embodiments, a truncated conical shape in which an angle at a projected vertex of the conical shape is from 1 to 175 degrees, such as from 30 to 90 degrees or from 40 to 60 degrees.

[0047] In exemplary apparatuses, upper portion **209** of the body **207** may have a conical shape. The conical shape may be, in embodiments, a truncated conical shape in which an angle at a projected vertex of the conical shape is from 1 to 175 degrees, such as from 45 to 160 degrees or from 60 to 115 degrees.

[0048] In exemplary apparatuses, screens or membranes **211** and **212** are permeable to fluids used in the apparatuses; that is, screens or membranes **211** and **212** allow fluids and materials dissolved in the fluids to flow through the screens or membranes **211** and **212.** However, screens or membranes **211** and **212** are not permeable to solid materials and materials that are not dissolved in the fluids; such solid materials and materials that are not dissolved in the fluids cannot pass through screens or membranes **211** and **212.**

[0049] In exemplary apparatuses, the fluidized bed reaction column **206,** may contain one or more solid state materials in body **207.** Such solid state materials cannot pass through screens or membranes **211** and **212.** In embodiments, the solid state materials may be solid state catalysts useful for sol-gel reaction systems.

[0050] In embodiments, the first circulation loop of apparatus **200** may allow for circulation of reactants without exposure to any solid state materials in the fluidized bed reaction column **206.** Thus, reactants may be completely blended and circulated through the first circulation loop without passing through fluidized bed reaction column **206.** The second circulation loop of the apparatus of exemplary embodiments allows reactants to circulate through fluidized bed reaction column **206,** contacting any solid state materials, such as catalysts, that may be contained within the fluidized bed reaction column **206.**

[0051] In embodiments, fluidized bed reaction column **206** may have a geometry such that the solid state material forms a fluidized bed column with an expansion that is variable with fluid flow rate. For example, in embodiments, the solid state material may form fluidized bed column that expands to approximately three times its original volume when fluid flow rate is approximately 3.3 L/min. Embodiments of this disclosure includes variations in the flow rate to produce a "lean" expansion of the solid state material, in which each solid state particle has little or no contact with its nearest neighboring solid state particles, or a "dense" expansion of the solid state material, in which each solid state particle is in direct physical contact with one or more of its nearest neighboring solid state particles. In particular embodiments, the flow rate may be adjusted to produce a "lean" expansion of the solid state material.

[0052] In processes for sol-gel preparation, solid state materials may be provided to fluidized bed reaction column **206.** Suitable solid state materials are fluidizable powder or granular materials, and such solid state materials may be used for preparation of multiple sol-gel formulations.

[0053] In embodiments, the solid state materials may comprise solid state catalysts, such as acid catalysts, basic catalysts, and solid state catalysts that contain chemical elements physically or chemically absorbed onto the surface, so that these chemical elements (which may have acidic or basic properties) affect hydrolysis and condensation of reactive siloxane materials in the presence of water. Such solid state catalysts may be organic catalysts, such as those sold under the AMBERLYST trademark by Rohm & Haas, or inorganic, such as certain clays and/or zeolites that will be identifiable by those of skill in the art. As suitable solid state catalysts, any of the known solid state catalysts can be used. Suitable solid state catalysts include ion exchange resins, such as those commercially available under the trademark AMBERLYST (Rohm & Haas). By changing the amount of catalyst present, one of ordinary skill will be able to adjust the reaction kinetics for reactions in sol-gel processes of embodiments.

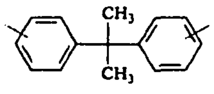
[0054] In processes for sol-gel preparation that may be conducted in apparatuses such as exemplary apparatus **200,** sol-gel precursor materials may be introduced into vessel **201.** As suitable precursor sol-gel materials, any of the known or after-developed desirable materials can be used. Suitable sol-gel precursor materials include reactive siloxane-containing hole-transport materials and reactive siloxane-containing binder materials, and other known compounds that may be used in sol-gel solutions, as well as mixtures thereof. The binder materials may be, in embodiments, reactive siloxane materials and may include between 2 and 4 reactive alkoxide residues around a tetravalent silicon atom, with the remaining valencies containing hydrocarbon residues. In embodiments, the sol-gel precursor materials include one or more reactive siloxane-containing hole-transport materials and one or more reactive siloxane-containing binder materials.

[0055] Suitable reactive siloxane-containing binder materials for use in embodiments include aromatic silicon-containing compounds, such as aromatic silane compounds, i.e., a compound having one or more silane groups separated by a linking group that is or contains one or more aromatic groups. For example, the aromatic silicon-containing compound can generally be represented by the following formula (1):

$$Ar\text{-}[X\text{-}L\text{-}SiR_n(OR')_{3-n}]_m \qquad (I).$$

[0056] In formula (I), Ar represents an aromatic group, which can have one or more phenyl groups. Suitable examples of Ar include the following structures (II-1) to (II-44):

II-1



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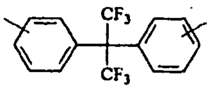

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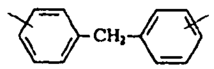

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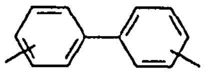

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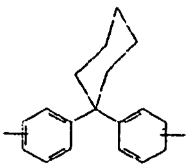

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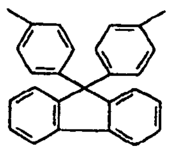

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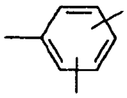

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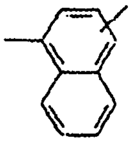

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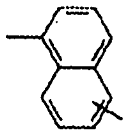

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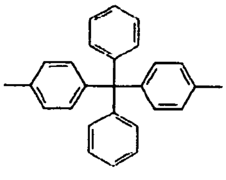

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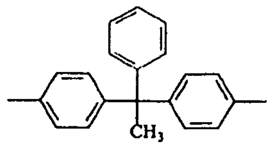

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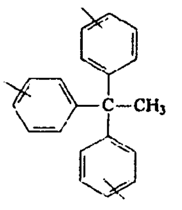

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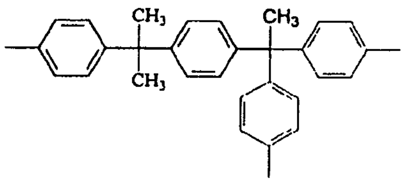

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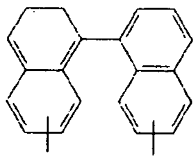

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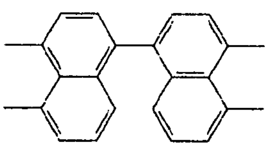

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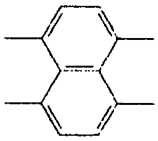

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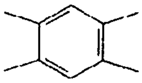

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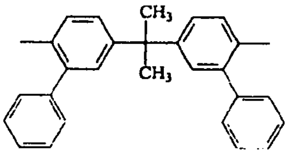

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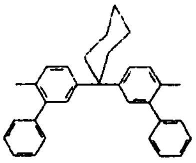

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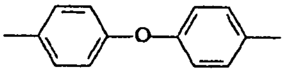

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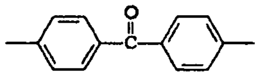

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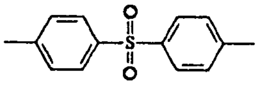

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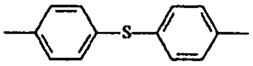

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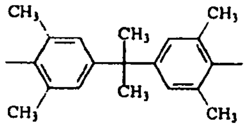

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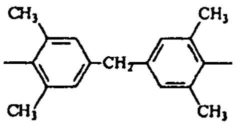

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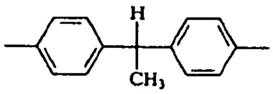

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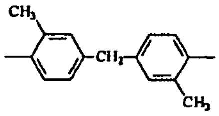

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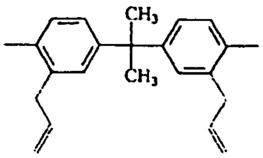

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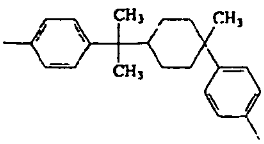

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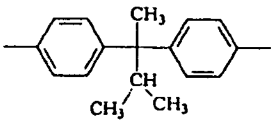

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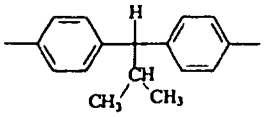

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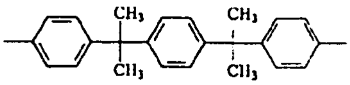

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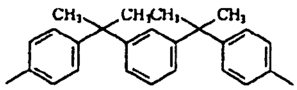

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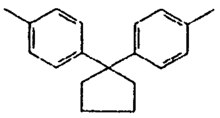

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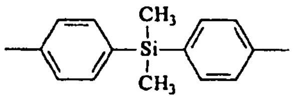

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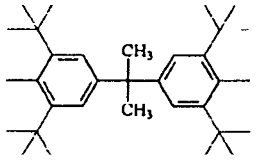

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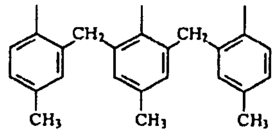

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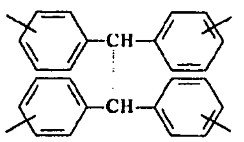

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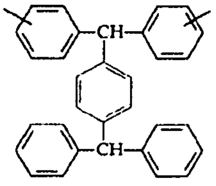

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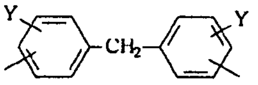
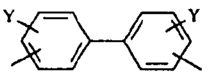


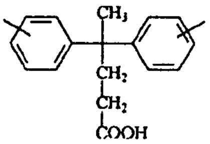
(Y is F, Cl, Br, NO_2),

II-42



(Y is F, Cl, Br, NO_2),

II-43



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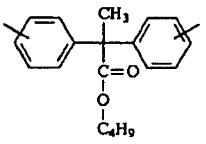
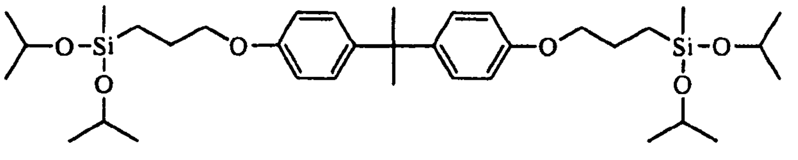
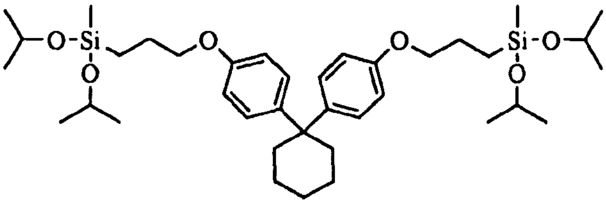


[0057] In formula (I), X represents a divalent/trivalent group. Suitable examples of X include; an oxy group (-0-), a thio group (-S-), an oxycarbonyl group (-COO-), a thiocarbonyl group (-COS-), a carbamate group (-OCO-NH-), an imide group (-CO-NH-OC-), an amide group (-CO-NH-), a carbonate group (-OCOO-) and the like, or a divalent group in which two or more of them are combined. L represents a divalent linking group. Suitable examples of L include: a divalent hydrocarbon group represented by $-C_mH_{2m}-$, $-C_mH_{2m-2}-$, $-C_mH_{2m-4}-$(m is an integer of 1 to 15, such as from 2 to 10), $-CH_2-C_6H_4-$ or $-C_6H_4-C_6H_4-$, or a divalent group in which two or more of them are combined. The divalent group L may also optionally have a substituent group such as an alkyl group, a phenyl group, an alkoxyl group or an amino group on its side chain. R represents a hydrogen atom, a lower alkyl group or an aryl group. R' represents a lower alkyl group. In addition, n is an integer, which can be 0, 1 or 2, and m is an integer, which can be from 1 to 10, such as from 1 to 5.

[0058] Typical examples of the reactive siloxane-containing compounds include compounds such as Compounds III-V:



(III)



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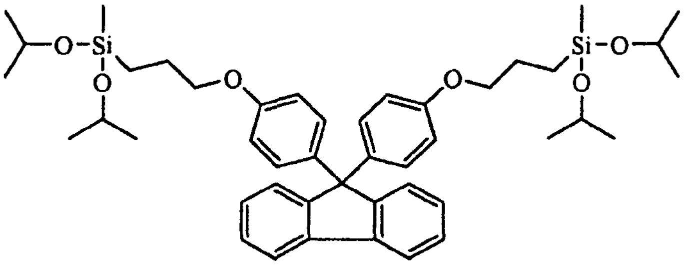
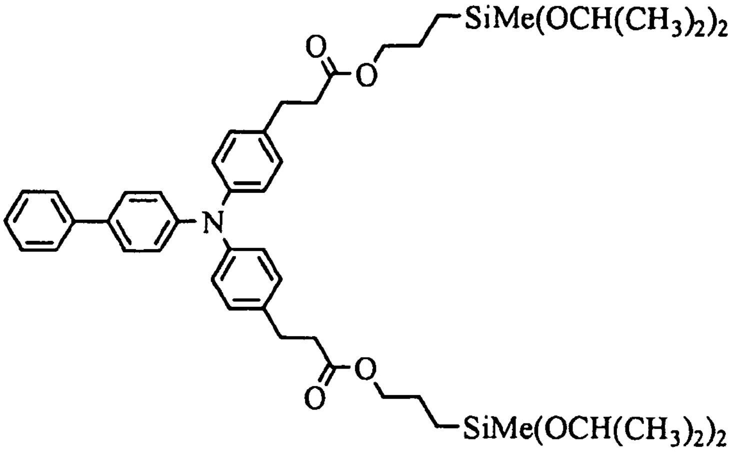


(IV)

[0059] In embodiments, the reactive siloxane-containing binder materials may be reacted in amounts from 0.01 to 99 % by weight, or from 5 to 20 % by weight, based on the total weight of the reactants. It should be noted, however, that the amounts of reactive siloxane-containing binder materials can vary widely because the apparatus of embodiments may be used to prepare very dilute solutions of sol-gel materials or very concentrated or neat mixtures of siloxane materials.

[0060] Suitable reactive siloxane-containing hole-transport molecules for use in embodiments include silicon-containing arylamine compounds, such as, for example, Compound (VI), and the like.



(VI)

[0061] In embodiments, the reactive siloxane-containing hole-transport molecules may be reacted in amounts from 5 to 50 % by weight, or from 10 to 15 % by weight, based on the total weight of the reactants.

[0062] In addition, additional sol-gel precursor materials may include known compounds comprising alkoxysilyl or hydroxysilyl groups suitable for use embodiments include: alkyltrialkoxysilanes, such as, phenyltrimethoxysilane, methyltrimethoxysilane, methyltriethoxysilane, 3-glycidoxypropyltrimethoxysilane, 3 -trifluoropropyltrimethoxysilane, methacryloxypropyltriethoxysilane, triethoxy-silylisobutyl-POSS (POSS is polyhedral oligomeric silsesquioxane), octa(trichloro-silylethyl)-POSS, and the like, tetraalkoxysilanes, such as, tetramethoxysilane ("TMOS"), tetraethoxysilane ("TEOS") and oligomeric condensates of TEOS such as ethylsilicate 40, tetraisopropoxysilane, tetrapropoxysilane, tetraisobutoxysilane, tetrabutoxysilane, and the like. Other siloxane compounds include bis(triethoxysilyl)methane, 1,9-bis(triethoxysilyl)nonane, diethoxydichlorosilane, triethoxychloro-silane, and the like. Other suitable precursor sol-gel materials include titanium (IV) isopropoxide, titanium (IV) methoxide, diisopropoxybisethylacetoacetato titanate, triethanolamine titanate, triethanolamine zirconate, aluminum sec-butoxide, and the like.

[0063] In embodiments, additional sol-gel precursor materials may be reacted in amounts from 0.01 to 100 % by weight, or from 5 to 20 % by weight, based on the total weight of the reactants.

[0064] The sol-gel precursor materials may be stirred together to ensure complete mixing. Complete mixing of the sol-gel precursor materials may be carried out in any suitable solvent or mixture of solvents. Suitable solvents include, for example, the solvents include alcohols, such as methanol, ethanol, isopropanol and the like; alkanes, such as hexane, decane and the like; ethers, such as diethyl ether, tetrahydrofuran, dimethoxyethane and the like; aromatic solvents, such as toluene, xylene, benzene and the like; and mixtures thereof. The choice of specific solvent or mixture of solvents can be decided based on the solubility of the starting materials and final products, and will be readily apparent or within routine experimentation to those skilled in the art.

[0065] After the sol-gel precursor mixture of embodiments are completely blended, water and methanol or other additional solvents may be added to vessel 201 In embodiments, the proportions of water and of methanol or other cosolvents may be determined based on the desired solution viscosity and desired degree of polymerization, respectively. Experimental methods for determining of these amounts will be obvious to those skilled in the art.

[0066] The sol-gel precursor mixture, water and methanol may be stirred together in vessel **201** by stirring means **202** and circulated through the first circulation loop to ensure complete mixing. After the reaction mixture has been blended completely, the circulation pattern may be changed to allow the reaction mixture to circulate through the second circulation loop. By allowing the reaction mixture to flow through the second circulation loop, the sol-gel precursor materials, methanol and water are brought into contact with the solid state catalyst in the fluidized bed reaction column **206.**

[0067] Temperature may affect catalytic reaction in embodiments. Suitable reaction temperatures may be chosen based on the desired degree of polymerization. It will be obvious to those skilled in the art that the higher the temperature the higher degree of polymerization in combination and consideration of the amount of water present. Experimental methods for the determination of the desired degree of polymerization will also be obvious to those skilled in the art.

[0068] In embodiments, the reaction mixture is allowed to circulate through the second reaction loop until a desired oligomerization ratio is obtained. The oligomerization ratio is determined by comparing the amount of monomer-like sol-gel precursor components present with the amount of oligomer-like components present, based on gas phase chromatography of samples taken from the reaction system. In embodiments, the reaction mixture is allowed to circulate through the second circulation loop and the reaction is allowed to continue until an oligomerization ratio of monomer-like components:oligomer-like components of about 1:1 is obtained. This ratio may be measured by standard experimental techniques, such as gel permeation chromatography. It will be obvious to those skilled in the art that this apparatus can be used to produce sol-gel materials of any desired oligomer ratio and that the oligomer ratio will depend on amount of water, time in the apparatus and the temperature of the apparatus and the desired ratio will depend on a number of factor including desired solution viscosity of the produced solution.

[0069] After the oligomerization ratio is obtained, the circulation pattern is again changed and the reaction mixture is returned to vessel **201.** At this time, additional sol-gel layer components may be added. The additional sol-gel layer components may include stabilizers, antioxidants, polymeric binder materials and surfactants.

[0070] In embodiments, one or more stabilizers may be added. Suitable stabilizers include, for example, aluminum(III) acetylacetonate ($Al(AcAc)_3$), acetylacetonate (AcAc) and mixtures thereof, although other known and later discovered stabilizers may be used in embodiments.

[0071] In embodiments, one or more antioxidants may be added. Suitable antioxidants may include antioxidants having a hindered-phenol, hindered-amine, thioether or phosphite partial structure. This is effective for improvement of potential stability and image quality in environmental variation. The antioxidants include an antioxidant having a hindered-phenol, hindered-amine, thioether or phosphite partial structure. This is effective for improvement of potential stability and image quality in environmental variation. For example, the hindered-phenol antioxidants include SUMILIZER BHT-R, SUMILIZER MDP-S, SUMILIZER BBM-S, SUMILIZER WX-R, SUMILIZER NW, SUMILIZER BP-76, SUMILIZER BP-101, SUMILIZER GA-80, SUMILIZER GM and SUMILIZER GS (the above are manufactured by Sumitomo Chemical Co., Ltd.), IRGANOX 1010, IRGANOX 1035, IRGANOX 1076, IRGANOX 1098, IRGANOX 1135, IRGANOX 1141, IRGANOX 1222, IRGANOX 1330, IRGANOX 1425WLj, IRGANOX 1520Lj, IRGANOX 245, IRGANOX 259, IRGANOX 3114, IRGANOX 3790, IRGANOX 5057 and IRGANOX 565 (the above are manufactured by Ciba Specialty Chemicals), and ADECASTAB AO-20, ADECASTAB AO-30, ADECASTAB AO-40, ADECASTAB AO-50, ADECASTAB AO-60, ADECASTAB AO-70, ADECASTAB AO-80 and ADECASTAB AO-330i (the above are manufactured by Asahi Denka Co., Ltd.). The hindered-amine antioxidants include SANOL LS2626, SANOL LS765, SANOL LS770, SANOL LS744, TINUVIN 144, TINUVIN 622LD, MARK LA57, MARK LA67, MARK LA62, MARK LA68, MARK LA63 and SUMILIZER TPS, and the phosphite antioxidants include MARK 2112, MARK PEP·8, MARK PEP·24G, MARK PEP·36, MARK 329K and MARK HP·10. Of these, hindered-phenol and hindered-amine antioxidants may be particularly suitable, in embodiments.

[0072] In embodiments, the polymeric binder may be a resin soluble in a liquid component in a coating solution used for formation of a silicon-containing layer. Such a resin soluble in the liquid component may be selected based upon the kind of liquid component. For example, if the coating solution contains an alcoholic solvent, a polyvinyl acetal resin such as a polyvinyl butyral resin, a polyvinyl formal resin or a partially acetalized polyvinyl acetal resin in which butyral is partially modified with formal or acetoacetal, a polyamide resin, a cellulose resin such as ethyl cellulose and a phenol resin may be suitably chosen as the alcohol-soluble resins. These resins may be used either alone or as a combination of two or more resins. Of the above-mentioned resins, the polyvinyl acetal resin is particularly suitable in embodiments in terms of electric characteristics.

[0073] In embodiments, the weight-average molecular weight of the polymeric binder component may be from 2,000 to 1,000,000, such as from 5,000 to 50,000. When the weight-average molecular weight is less than 2,000, enhancing discharge-gas resistance, mechanical strength, scratch resistance, particle dispersibility, etc., tend to become insufficient. However, when the weight-average molecular weight exceeds 1,000,000, the resin solubility in the coating solution decreases, and the amount of resin added to the coating solution may be limited and poor film formation may result.

[0074] Further, the amount of the polymeric binder may be, in embodiments, from 0.1 to 15% by weight, or from 0.5 to 10% by weight, based on the total amount of the coating solution. When the amount added is less than 0.1% by weight, enhancing discharge-gas resistance, mechanical strength, scratch resistance, particle dispersibility, etc. tend to become insufficient. However, if the amount of the polymeric binder exceeds 15% by weight, there is a tendency for formation of indistinct images when the electrophotographic photoreceptor of the disclosure is used at high temperature and high humidity.

[0075] In embodiments, one or more surfactant may be added. Suitable surfactants include, for example, polyethylene glycol surfactants, polydimethylsiloxane surfactants that are grafted with polyethylene glycol groups, and perfluoropolyethylene glycol surfactants having terminal reactive aminopropylsiloxane residues, such as the surfactant commercially available as FLUOROLINK S-10, although other known surfactants may be used in embodiments.

[0076] Once the oligomerized reaction mixture and any additional components have been combined, the polymer gel formed by the sol-gel process may be applied to a desired substrate and dried by slowly heating to vaporize the volatile species, such as alcohol. Drying of the alcogel should occur slowly, because rapid drying may result in non-uniform gel shrinkage, which may then cause cracking.

[0077] The sol-gel solutions and layers produced by the apparatuses and processes of embodiments can be used for any known sol-gel application, including the production of photoreceptor layers. An exemplary electrostatographic imaging member will now be described in greater detail.

[0078] In electrophotographic photoreceptors of embodiments, the photoreceptors can include various layers such as undercoating layers, charge-generating layers, charge-transport layers, overcoat layers, and the like. The overcoating layers of embodiments can be a silicon compound-containing layer, which can be a layer formed by the sol-gel process described above.

[0079] Various fine particles can also be added to the silicon compound-containing layer, for example, to further improve the stain adhesion resistance and lubricity of embodiments of the electrophotographic photoreceptor. The fine particles may be used either alone or as a combination of two or more such fine particles. Non-limiting examples of the fine particles include fine particles containing silicon, such as fine particles containing silicon as a constituent element, and specifically include colloidal silica and fine silicone particles. The content of the fine silicone particles in the silicon-containing layer of embodiments may be within the range of 0.1 to 20% by weight, or within the range of 0.5 to 10% by weight, based on the total solid content of the silicon-containing layer.

[0080] Colloidal silica used in embodiments as the fine particles containing silicon in the disclosure is selected from an acidic or alkaline aqueous dispersion of the fine particles having an average particle size of 1 to 100 nm, or 10 to 30 nm, and a dispersion of the fine particles in an organic solvent, such as an alcohol, a ketone or an ester, and generally, commercially available particles can be used.

[0081] There is no particular limitation on the solid content of colloidal silica in a top-surface layer of the electrophotographic photoreceptor of embodiments. However, in embodiments, colloidal silica may be included in amounts of from 1 to 50% by weight, such as from 5 to 30% by weight, based on the total solid content of the top surface layer, in terms of film forming properties, electric characteristics and strength.

[0082] The fine silicone particles used as the fine particles containing silicon in the disclosure may be selected from silicone resin particles, silicone rubber particles and silica particles surface-treated with silicone, which are spherical and have an average particle size of from 1 to 500 nm, such as from 10 to 100 nm, and generally, commercially available particles can be used in embodiments.

[0083] In embodiments, the fine silicone particles are small-sized particles that are chemically inactive and excellent in dispersibility in a resin, and further are low in content as may be necessary for obtaining sufficient characteristics. Accordingly, the surface properties of the electrophotographic photoreceptor can be improved without inhibition of the cross-linking reaction. That is to say, fine silicone particles improve the lubricity and water repellency electrophotographic photoreceptor surfaces where incorporated into strong cross-linked structures, which may then be able to maintain good wear resistance and stain-adhesion resistance for a long period of time. The content of the fine silicone particles in the silicon compound-containing layer of embodiments may be from 0.1 to 20% by weight, such as from 0.5 to 10% by weight, based on the total solid content of the silicon compound-containing layer.

[0084] Other fine particles that may be used in embodiments include fine fluorine-based particles such as ethylene tetrafluoride, ethylene trifluoride, propylene hexafluoride, vinyl fluoride and vinylidene fluoride, and semiconductive metal oxides such as ZnO-Al_2O_3, SnO_2-Sb_2O_3, In_2O_3-SnO_2, ZnO-TiO_2, MgO-Al_2O_3, FeO-TiO_2, TiO_2, SnO_2, In_2O_3, ZnO and MgO.

[0085] In conventional electrophotographic photoreceptors, when the above-mentioned fine particles are contained in the photosensitive layer, the compatibility of the fine particles with a charge-transport substance or a binding resin may become insufficient, which causes layer separation in the photosensitive layer, and thus the formation of an opaque film. As a result, the electric characteristics have deteriorated in some cases. In contrast, the silicon compound-containing layer of embodiments may contain the resin soluble in the liquid component in the coating solution used for formation of this layer and the silicon compound, thereby improving the dispersibility of the fine particles in the silicon compound-containing layer. Accordingly, the pot life of the coating solution may be sufficiently prolonged, and deterioration of the electric characteristics may be prevented.

[0086] Further, an additive such as a plasticizer, a surface modifier, an antioxidant, or an agent for preventing deterioration by light can also be used in the silicon compound-containing layer of embodiments. Non-limiting examples of plasticizers that may be used in embodiments include, for example, biphenyl, biphenyl chloride, terphenyl, dibutyl phthalate, diethylene glycol phthalate, dioctyl phthalate, triphenylphosphoric acid, methylnaphthalene, benzophenone, chlorinated paraffin, polypropylene, polystyrene and various fluorohydrocarbons.

[0087] There is no particular limitation on the thickness of the silicon-containing layer, however, in embodiments, the silicon-containing layer may be from 2 to 5 μm in thickness, such as from 2.7 to 3.2 μm in thickness.

[0088] The electrophotographic photoreceptor of embodiments may be either a function-separation-type photoreceptor, in which a layer containing a charge-generation substance (charge-generation layer) and a layer containing a charge-transport substance (charge-transport layer) are separately provided, or a monolayer-type photoreceptor, in which both the charge-generation layer and the charge-transport layer are contained in the same layer, as long as the electrophotographic photoreceptor of the particular embodiment has the photosensitive layer provided with the above-mentioned silicon compound-containing layer. The electrophotographic photoreceptor will be described in greater detail below, taking the function-separation-type photoreceptor as an example.

[0089] FIG. 1 is a cross-sectional view schematically showing an embodiment of an electrophotographic photoreceptor, not included in the invention. The electrophotographic photoreceptor **1** shown in FIG. 1 is a function-separation-type photoreceptor in which a charge-generation layer **13** and a charge-transport layer **14** are separately provided. That is, an underlayer **12,** the charge-generation layer **13,** the charge transport layer **14** and a protective layer **15** are laminated onto a conductive support **11** to form a photosensitive layer **16.** The protective layer **15** contains a resin soluble in the liquid component contained in the coating solution used for formation of this layer and the silicon compound. The various layers of the photoreceptor shown in FIG. 1 are generally known, and are described in detail in the above-mentioned commonly owned and co-pending applications.

[0090] The electrophotographic photoreceptor of embodiments should not be construed as being limited to the above-mentioned constitution. For example, the electrophotographic photoreceptor shown in FIG. 1 is provided with the protective layer **15.** However, when the charge-transport layer **14** contains the resin soluble in the liquid component in the coating solution used for formation of this layer and the silicon compound, the charge-transport layer **14** may be used as a top surface layer (a layer on the side farthest apart from the support **11**) without using the protective layer **15.** In this case, the charge-transport substance contained in the charge-transport layer **14** is desirably soluble in the liquid component in the coating solution used for formation of the charge-transport layer **14.** For example, when the coating solution used for formation of the charge-transport layer **14** contains an alcohol solvent, the silicon compounds described above, including arylamine derivatives prepared by processes that include selective hydrogenation by catalytic transfer, can be used as the charge-transport substances.

[0091] FIG. 2 is a schematic view showing an embodiment of an image forming apparatus or xerographic machine. In the apparatus shown in FIG. 2, an electrophotographic photoreceptor 1 is supported by a support 9, and rotatable at a specified rotational speed in the direction indicated by the arrow, centered on the support 9. A charging device 2, an exposure device 3, a developing device 4, a transfer device 5 and a cleaning unit 7 are arranged in this order along the rotational direction of the electrophotographic photoreceptor 1. Further, this exemplary apparatus is equipped with an image fixing device 6, and a medium P to which a toner image is to be transferred is conveyed to the image fixing device 6 through the transfer device 5.

[0092] FIG. 3 is a cross-sectional view showing another exemplary embodiment of an image-forming apparatus The image-forming apparatus **220** shown in FIG. 3 is an image-forming apparatus of an intermediate-transfer system, and four electrophotographic photoreceptors **401a** to **401d** are arranged in parallel with each other along an intermediate-transfer belt **409** in a housing **400.**

[0093] Here, the electrophotographic photoreceptors **401a** to **401d** carried by the image-forming apparatus **220** are each the electrophotographic photoreceptors. Each of the electrophotographic photoreceptors **401a** to **401d** may rotate in a predetermined direction (counterclockwise on the sheet of FIG. 3), and charging rolls **402a** to **402d,** developing device **404a** to **404d,** primary transfer rolls **410a** to **410d** and cleaning blades **415a** to **415d** are each arranged along the rotational direction thereof. In each of the developing device **404a** to **404d,** four-color toners of yellow (Y), magenta (M), cyan (C) and black (B) contained in toner cartridges **405a** to **405d** can be supplied, and the primary transfer rolls **410a** to **410d** are each brought into abutting contact with the electrophotographic photoreceptors **401a** to **401d** through an intermediate-transfer belt **409.**

[0094] Further, a laser-light source (exposure unit) **403** is arranged at a specified position in the housing **400,** and it is possible to irradiate surfaces of the electrophotographic photoreceptors **401a** to **401d** after charging with laser light emitted from the laser-light source **403.** This performs the respective steps of charging, exposure, development, primary transfer and cleaning in turn in the rotation step of the electrophotographic photoreceptors **401a** to **401d,** and toner images of the respective colors are transferred onto the intermediate-transfer belt **409,** one over the other.

[0095] The intermediate-transfer belt **409** is supported with a driving roll **406,** a backup roll **408** and a tension roll **407** at a specified tension, and rotatable by the rotation of these rolls without the occurrence of deflection. Further, a secondary transfer roll **413** is arranged so that it is brought into abutting contact with the backup roll **408** through the intermediate-transfer belt **409.** The intermediate-transfer belt **409,** which has passed between the backup roll **408** and the secondary transfer roll **413,** is cleaned up by a cleaning blade **416,** and then repeatedly subjected to the subsequent image-formation process.

[0096] Further, a tray (tray for a medium to which a toner image is to be transferred) **411** is provided at a specified position in the housing **400.** The medium to which the toner image is to be transferred (such as paper) in the tray **411** is conveyed in turn between the intermediate-transfer belt **409** and the secondary transfer roll **413,** and further between two fixing rolls **414** brought into abutting contact with each other, with a conveying roll **412,** and then delivered out of the housing **400.**

[0097] According to the exemplary image-forming apparatus **220** shown in FIG. 3, the use of electrophotographic photoreceptors of embodiments as electrophotographic photoreceptors **401a** to **401d** may achieve discharge gas resistance, mechanical strength, scratch resistance, etc. on a sufficiently high level in the image-formation process of each of the electrophotographic photoreceptors **401a** to **401d.** Accordingly, even when the photoreceptors are used together with the contact-charging devices or the cleaning blades, or further with the spherical toner obtained by chemical polymerization, good image quality can be obtained without the occurrence of image defects such as fogging. Therefore, also according to the image-forming apparatus for color-image formation using the intermediate-transfer body, such as this embodiment, the image-forming apparatus, which can stably provide good image quality for a long period of time, is realized.

[0098] The disclosure should not be construed as being limited to the above-mentioned embodiments. For example, each apparatus shown in FIG. 2 or 3 may be equipped with a process cartridge comprising the electrophotographic photoreceptor **1** (or the electrophotographic photoreceptors **401a** to **401d**) and charging device **2** (or the charging devices **402a** to **402d**). The use of such a process cartridge allows maintenance to be performed more simply and easily.

[0099] Further, in embodiments, when a charging device of the non-contact charging system such as a corotron charger is used in place of the contact-charging device **2** (or the contact-charging devices **402a** to **402d**), sufficiently good image quality can be obtained.

[0100] Specific examples are described in detail below. All parts and percentages are by weight unless otherwise indicated.

EXAMPLES

Examples 1-4

Preparation of Sol-Gel Solutions in a 1 L System

[0101] An apparatus was provided including a 1 L vessel containing a stirring means, a pump, a heat exchanger, a fluidized bed reaction column having a 0.33 L capacity and fluid lines connecting the vessel pump, heat exchanger and a fluidized bed reaction column in two circulation loops. The first circulation loop of the apparatus includes the vessel, a fluid line to the pump, a fluid line to the heat exchanger and a fluid line connecting back to the vessel. A second circulation loop of the apparatus includes the vessel, a fluid line to the pump, a fluid line to the heat exchanger, a fluid line connecting to the fluidized bed reaction column and another fluid line connecting to the vessel. The fluidized bed reaction column includes 7.22 grams of a solid state acid catalyst, AMBERLYST H-15.

Example 1 - Sol-Gel Solution including Compound III

[0102] The vessel is charged with 84.48 grams of Compound III, 72.24 grams of methanol, 265.31 grams of n-butanol and 32.31 grams of water. This solution was mixed completely, and allowed to circulate through the first circulation loop. The reaction mixture was then allowed to circulate through the second circulation loop and contact with the catalyst at a flow rate of 300 mL/min and a temperature of about 22.5°C. After 4 to 6 hours, the circulation path was changed to return the reaction mixture to the vessel; 1.182 grams of aluminum (III) acetylacetonate, 1.182 grams of 2,4-pentandione, 13.135 grams of polyvinylbutyrol, 1.182 grams of 2,6-di-tert-butyl-4-methylphenol, 1.714 grams of IRGANOX-259 antioxidant and 0.09 grams of FLUOROLINK S-10 were added; and the resulting mixture was stirred to homogenize.

Example 2 - Sol-Gel Solutions including Compound IV

[0103] Sol-gel solutions were prepared according to Example 1, except that 84.48 grams of Compound IV was substituted for Compound III.

Example 3 - Sol-Gel Solutions including Compound V

[0104] Sol-gel solutions were prepared according to Example 1, except that 84.48 grams of Compound V was substituted for Compound III.

Example 4 - Sol-Gel Solutions including Compound IV and Compound VI

[0105] Sol-gel solutions were prepared according to Example 1, except that a mixture, which included 80.04 grams of Compound VI and 43.66 grams of Compound IV, was substituted for Compound III.

Examples 5-8

Preparation of Sol-Gel Solutions in a 6L System

[0106] An apparatus was provided including a 12 L vessel containing a stirring means, a pump, a heat exchanger, a fluidized bed reaction column having a 2 L capacity and fluid lines connecting the vessel pump, heat exchanger and a fluidized bed reaction column in two circulation loops. The first circulation loop of the apparatus includes the vessel, a fluid line to the pump, a fluid line to the heat exchanger and a fluid line connecting back to the vessel. A second circulation loop of the apparatus includes the vessel, a fluid line to the pump, a fluid line to the heat exchanger, a fluid line connecting to the fluidized bed reaction column and another fluid line connecting to the vessel. The fluidized bed reaction column includes 80.03 grams of a solid state acid catalyst, AMBERLYST H-15.

Example 5 - Sol-Gel Solution including Compound III

[0107] The vessel is charged with 934.60 grams of Compound III, 751.85 grams of methanol, 2761.33 grams of n-butanol and 336.28 grams of water. This solution was mixed completely, and allowed to circulate through the first circulation loop. The reaction mixture was then allowed to circulate through the second circulation loop and contact with the catalyst at a flow rate of 2 l/min and a temperature of about 22.5°C. After 4 to 6 hours, the circulation path was changed to return the reaction mixture to the vessel; 12.30 grams of aluminum (III) acetylacetonate, 12.30 grams of 2,4-pentandione, 136.70 grams of polyvinylbutyrol, 12.30 grams of 2,6-di-tert-butyl-4-methylphenol, 17.84 grams of IRGANOX-259 antioxidant and 0.94 grams of FLUOROLINK S-10 were added; and the resulting mixture was stirred to homogenize.

Example 6 - Sol-Gel Solutions including Compound IV

[0108] Sol-gel solutions were prepared according to Example 4, except that 934.60 grams of Compound IV was substituted for Compound III.

Example 7 - Sol-Gel Solutions including Compound V

[0109] Sol-gel solutions were prepared according to Example 4, except that 934.60 grams of Compound V was substituted for Compound III.

Example 8 - Sol-Gel Solutions including Compound IV and Compound VI

[0110] Sol-gel solutions were prepared according to Example 4, except that a mixture, which included 800.36 grams of Compound VI and 436.56 grams of Compound IV, was substituted for Compound III.

Claims

1. An apparatus for preparing sol-gel solutions, comprising
a vessel optionally containing a stirrer;
a pump;
a fluidized bed reaction column; and
multiple fluid lines;
wherein said fluid lines connect the vessel and the pump in a first circulation loop and said fluid lines connect the vessel, the pump and the fluidized bed reaction column in a second circulation loop.

2. The apparatus according to claim 1, wherein said first circulation loop further comprises a heat exchanger.

3. The apparatus according to claim 1, wherein said fluidized bed column comprises an upper portion, a body and a lower portion.

4. The apparatus according to claim 3, wherein said upper portion and said body are separated by a first fluid permeable membrane.

5. The apparatus according to claim 3, wherein said lower portion is connected to said fluid lines by a connector, and said lower portion and said connector are separated by a second fluid permeable membrane.

6. The apparatus according to claim 3, wherein said lower portion has a conical shape in which a wider portion of said conical shape is connected to the body and a narrower portion of said conical shape connects to said connector.

7. The apparatus according to claim 6, wherein said lower portion has a conical shape in which an angle at a projected vertex of said conical shape is from 1 to 175 degrees.

8. A method for preparing a sol-gel solution, comprising:

   providing an apparatus that comprises:

      a vessel optionally containing a stirrer,
      a pump,
      a fluidized bed reaction column having an upper portion, a body and a lower portion, and
      multiple fluid lines,

   wherein said fluid lines connect the vessel and the pump in a first circulation loop and said fluid lines connect the vessel, the pump and the fluidized bed reaction column in a second circulation loop, said upper portion and said body are separated by a first fluid permeable membrane; said lower portion is connected to said fluid lines by a connector, and said lower portion and said connector are separated by a second fluid permeable membrane; and said body contains a solid state acid catalyst that is not permeable through said first fluid permeable membrane or said second fluid permeable membrane;
   providing sol-gel precursor materials to the vessel;
   blending said sol-gel precursor materials, water and methanol with an optional solvent;
   circulating said mixture through a first circulation loop; and
   reacting said sol-gel precursor materials by circulating said mixture through the second circulation loop and contacting said sol-gel precursor materials with said solid state acid catalyst.

Patentansprüche

1. Vorrichtung zum Zubereiten von Sol-Gel-Lösungen, umfassend
   einen Behälter, der wahlweise einen Rührer enthält,
   eine Pumpe,
   eine Wirbelbett-Reaktionssäule und
   mehrere Fluidleitungen,
   wobei die Fluidleitungen den Behälter und die Pumpe in einer ersten Zirkulationsschleife verbinden und die Fluidleitungen den Behälter, die Pumpe und die Wirbelbett-Reaktionssäule in einer zweiten Zirkulationsschleife verbinden.

2. Vorrichtung gemäß Anspruch 1, wobei die erste Zirkulationsschleife weiter einen Wärmetauscher umfasst.

3. Vorrichtung gemäß Anspruch 1, wobei die Wirbelbettsäule einen oberen Teil, einen Körper und einen unteren Teil umfasst.

4. Vorrichtung gemäß Anspruch 3, wobei der obere Teil und der Körper durch eine erste fluiddurchlässige Membran getrennt sind.

5. Vorrichtung gemäß Anspruch 3, wobei der untere Teil durch ein Verbindungsstück mit den Fluidleitungen verbunden

ist und der untere Teil und das Verbindungsstück durch eine zweite fluiddurchlässige Membran getrennt sind.

6. Vorrichtung gemäß Anspruch 3, wobei der untere Teil eine konische Form hat, bei der ein breiterer Teil der konischen Form mit dem Körper verbunden ist und ein engerer Teil der konischen Form mit dem Verbindungsstück verbindet.

7. Vorrichtung gemäß Anspruch 6, wobei der untere Teil eine konische Form hat, bei der ein Winkel an einem projizierten Scheitelpunkt der konischen Form von 1 bis 175 Grad beträgt.

8. Verfahren zum Zubereiten einer Sol-Gel-Lösung, umfassend Bereitstellen einer Vorrichtung, welche umfasst:

einen Behälter, der wahlweise einen Rührer enthält,
eine Pumpe,
eine Wirbelbett-Reaktionssäule mit einem oberen Teil, einen Körper und einem unteren Teil und
mehrere Fluidleitungen,
wobei die Fluidleitungen den Behälter und die Pumpe in einer ersten Zirkulationsschleife verbinden und die Fluidleitungen den Behälter, die Pumpe und die Wirbelbett-Reaktionssäule in einer zweiten Zirkulationsschleife verbinden, wobei der obere Teil und der Körper durch eine erste fluiddurchlässige Membran getrennt sind, wobei der untere Teil durch ein Verbindungsstück mit den Fluidleitungen verbunden ist und wobei der untere Teil und das Verbindungsstück durch eine zweite fluiddurchlässige Membran getrennt sind und wobei der Körper einen in einem festen Zustand befindlichen Säurekatalysator enthält, welcher nicht durch die erste fluiddurchlässige Membran oder die zweite fluiddurchlässige Membran durchlässig ist,
Bereitstellen von Sol-Gel-Vorläufermaterialien für den Behälter,
Mischen der Sol-Gel-Vorläufermaterialien, Wasser und Methanol mit einem optionalen Lösungsmittel,
Zirkulieren der Mischung durch eine erste Zirkulationsschleife und
Umsetzen der Sol-Gel-Vorläufermaterialien durch Zirkulieren der Mischung durch die zweite Zirkulationsschleife und In-Kontakt-Bringen der Sol-Gel-Vorläufermaterialien mit dem in einem festen Zustand befindlichen Säurekatalysator.

Revendications

1. Dispositif pour préparer des solutions sol-gel, comprenant
un récipient contenant éventuellement un agitateur ;
une pompe ;
une colonne de réaction à lit fluidisé ; et
de multiples conduites de fluide ;
dans lequel lesdites conduites de fluide connectent le récipient et la pompe dans une première boucle de circulation et lesdites conduites de fluide connectent le récipient, la pompe et la colonne de réaction à lit fluidisé dans une deuxième boucle de circulation.

2. Dispositif selon la revendication 1, dans lequel ladite première boucle de circulation comprend en outre un échangeur de chaleur.

3. Dispositif selon la revendication 1, dans lequel ladite colonne à lit fluidisé comprend une partie supérieure, un corps et une partie inférieure.

4. Dispositif selon la revendication 3, dans lequel ladite partie supérieure et ledit corps sont séparés par une première membrane perméable aux fluides.

5. Dispositif selon la revendication 3, dans lequel ladite partie inférieure est connectée auxdites conduites de fluide par un connecteur, et ladite partie inférieure et ledit connecteur sont séparés par une deuxième membrane perméable aux fluides.

6. Dispositif selon la revendication 3, dans lequel ladite partie inférieure a une forme conique dans laquelle une partie plus large de ladite forme conique est connectée au corps et une partie plus étroite de ladite forme conique se connecte audit connecteur.

7. Dispositif selon la revendication 6, dans lequel ladite partie inférieure a une forme conique dans laquelle l'angle à un sommet projeté de ladite forme conique est de 1 à 175 degrés.

8. Procédé pour préparer une solution sol-gel, comprenant :

l'obtention d'un dispositif qui comprend :

- un récipient contenant éventuellement un agitateur ;
- une pompe ;
- une colonne de réaction à lit fluidisé ayant une partie supérieure, un corps et une partie inférieure, et
- de multiples conduites de fluide,

dans lequel lesdites conduites de fluide connectent le récipient et la pompe dans une première boucle de circulation et lesdites conduites de fluide connectent le récipient, la pompe et la colonne de réaction à lit fluidisé dans une deuxième boucle de circulation, ladite partie supérieure et ledit corps sont séparés par une première membrane perméable aux fluides ; ladite partie inférieure est connectée auxdites conduites de fluide par un connecteur, et ladite partie inférieure et ledit connecteur sont séparés par une deuxième membrane perméable aux fluides ; et ledit corps contient un catalyseur acide à l'état solide qui n'est pas perméable à travers ladite première membrane perméable aux fluides ou ladite deuxième membrane perméable aux fluides ;
la fourniture de matériaux précurseurs de sol-gel au récipient ;
le mélange desdits matériaux précurseurs de sol-gel, d'eau et de méthanol avec un solvant optionnel ;
la circulation dudit mélange dans une première boucle de circulation ; et
la réaction desdits matériaux précurseurs de sol-gel par circulation dudit mélange dans la deuxième boucle de circulation et la mise en contact desdits matériaux précurseurs de sol-gel avec ledit catalyseur acide à l'état solide.

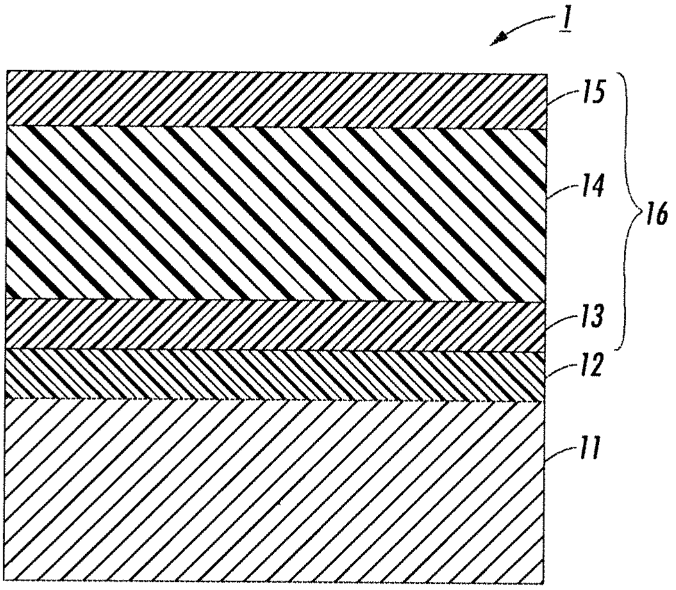


FIG. 1

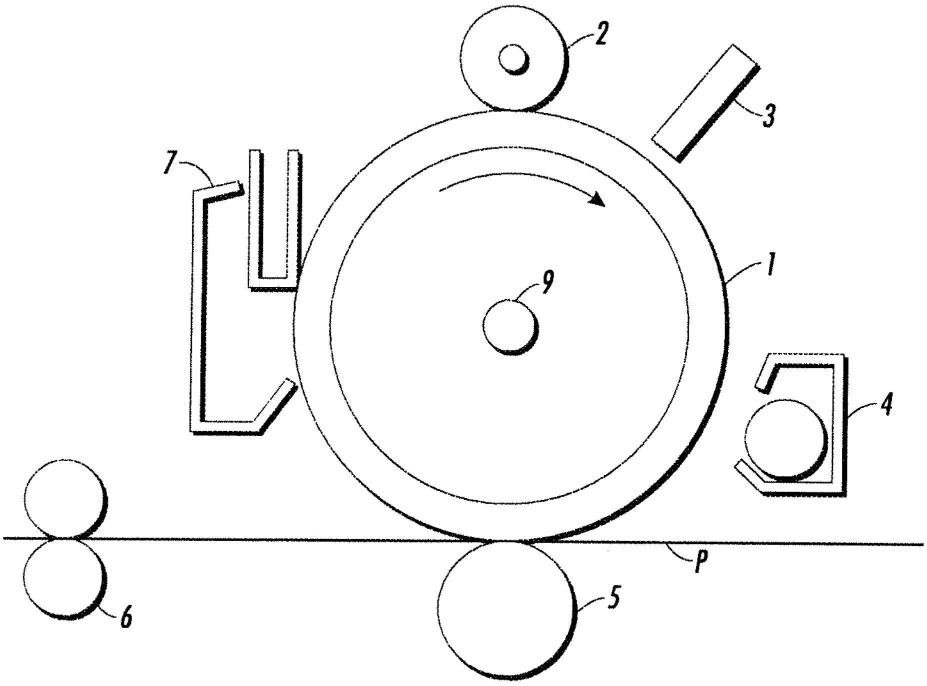
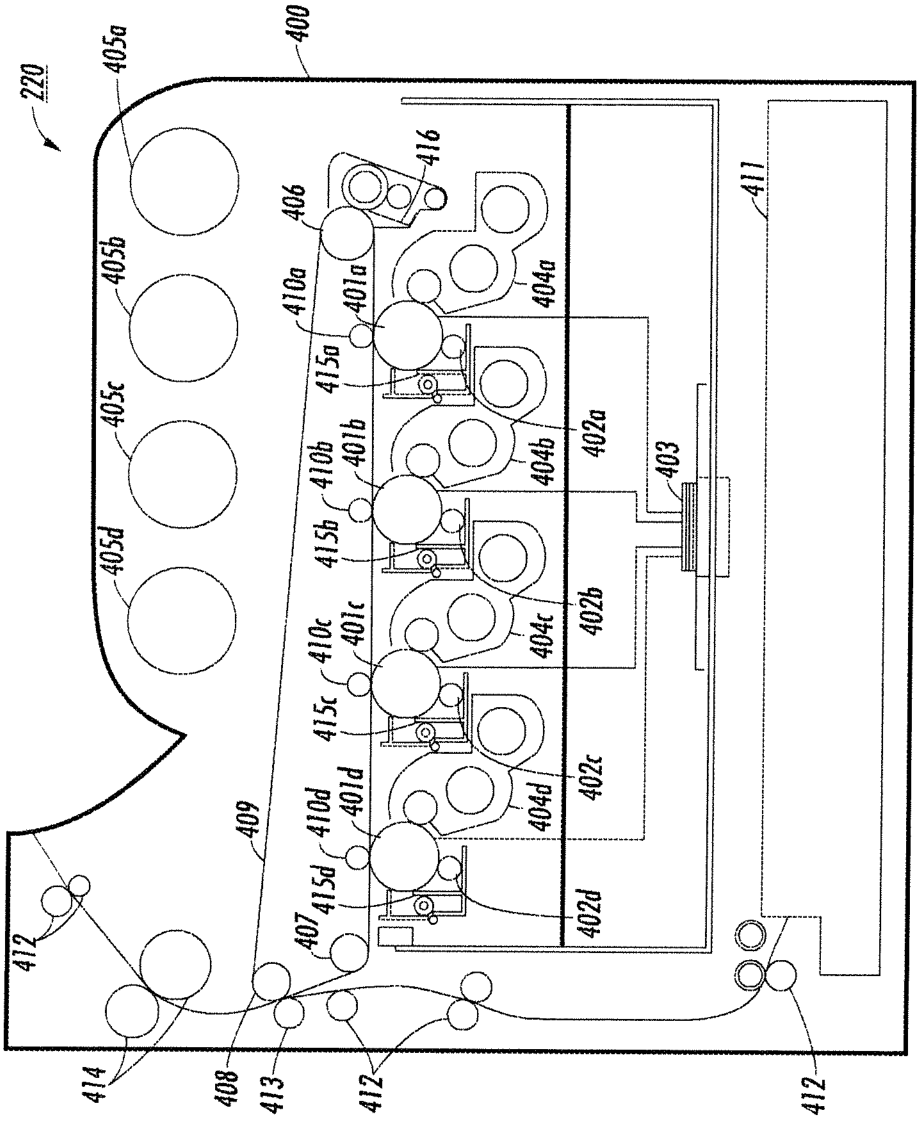


FIG. 2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410c
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415c
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FIG. 3

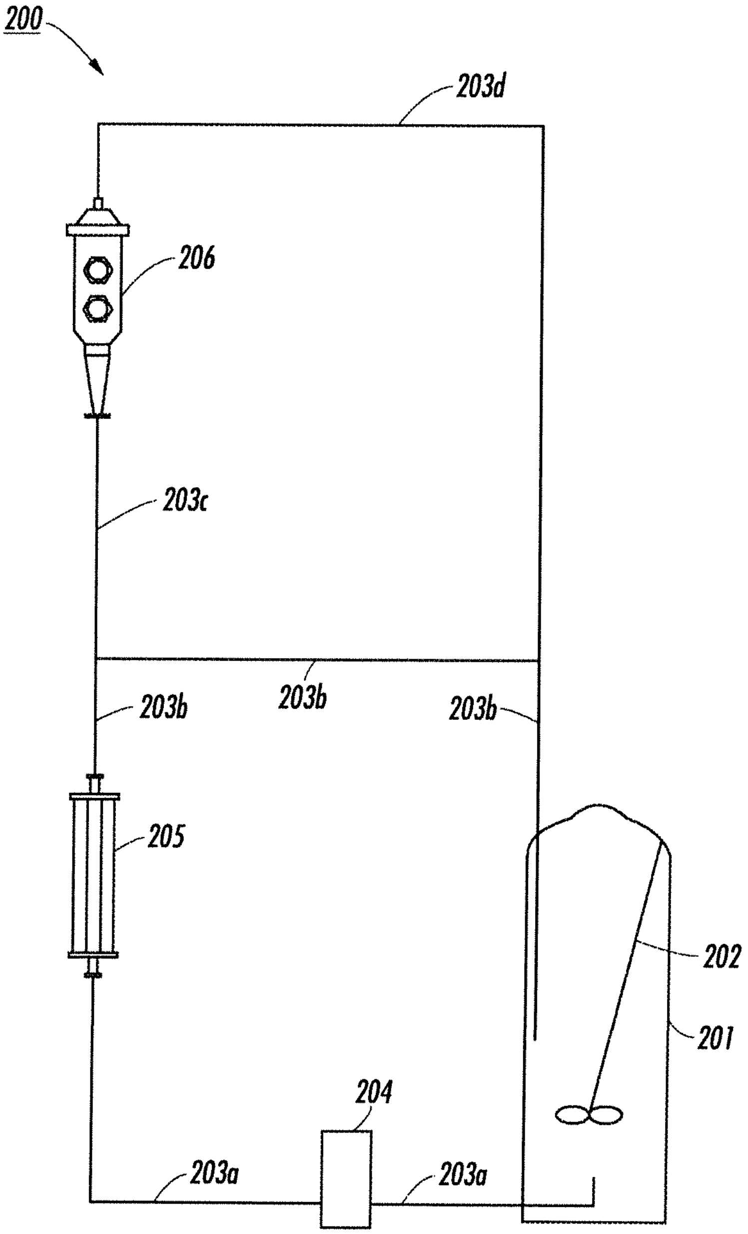

FIG. 4

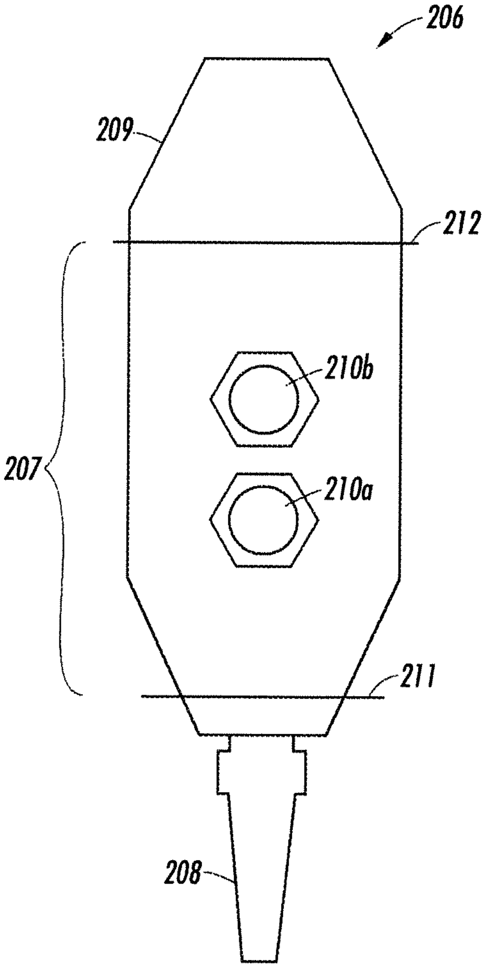

FIG. 5

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- US 4265990 A **[0004]**
- US 4751203 A **[0014]**

Non-patent literature cited in the description

- **C. J. BRINKER ; G. SCHERER.** Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing. Academic Press, 1990 **[0008]**