

"GETTER SYSTEMS COMPRISING AN ACTIVE PHASE INSERTED IN A
POROUS MATERIAL DISTRIBUTED IN A LOW PERMEABILITY MEANS"

5 The present invention relates to getter systems comprising a phase active in gas sorption inserted in a porous material distributed in a low permeability means.

Getter materials and systems are widely used in industry in all the applications wherein it is necessary to keep the vacuum, to control the composition of the gaseous atmosphere through the sorption of traces of undesired gases or to protect devices being sensitive to particular gaseous contaminants.

10 Getter materials widely used for such purposes are porous materials, such as active carbons, particularly useful for the sorption of organic substances, or zeolites, silica or alumina, useful for the sorption of gaseous molecules having small size. Another class of particularly interesting compounds is comprised of anhydrous chemical desiccants, specific for moisture sorption, such as the oxides of alkaline-earth metals, or
15 some hygroscopic salts such as chlorides (e.g. calcium chloride, CaCl_2), perchlorates (e.g. magnesium perchlorate, $\text{Mg}(\text{ClO}_4)_2$), or sulphates (e.g. calcium sulphate, CaSO_4).

One problem common to many of these materials is that they are generally in the form of powders without a cohesion sufficient to form compact bodies; this is particularly true in the case of desiccants after moisture sorption. This is a relevant
20 problem as in almost all foreseen industrial applications the absence of free particles is required.

The problem is in some cases tackled by inserting the getter materials inside permeable containers (e.g. non-woven fabric envelopes, as shown for instance in patent US 4,668,551 directed to insulating panels).

25 Another possible approach to the problem is to distribute the getter material inside a dispersing matrix, capable of retaining the getter particles in a fixed location while letting the gases pass towards the getter itself. Examples of this second solution are set forth in numerous documents. Japanese patent application JP 60-132274 discloses desiccant materials dispersed in a silicone matrix; patent US 3,704,806 discloses
30 desiccant compositions comprising zeolites dispersed inside a matrix formed of a thermosetting polymer, such as the epoxy resins; patent US 4,081,397 discloses a

desiccant system comprising particles of an oxide of an alkaline-earth metal dispersed in an elastomeric polymer; patent US 5,304,419 discloses desiccant compositions comprising a desiccant material dispersed in a matrix that can be formed of silicone, polyurethanes or similar polymers; patent US 5,591,379 discloses desiccant
5 compositions comprising a desiccant chosen among zeolites, alumina, silica gel, alkaline-earth metal oxides and alkaline metals carbonates, dispersed in a matrix of porous glass or ceramic; patent US 6,226,890 B1 discloses desiccant systems wherein a desiccant material (e.g. an alkaline-earth metal oxide) is dispersed in a polymer, such as silicones, epoxides, polyamides, polymethylmethacrylates or others, which in the patent
10 is said to have the property of not reducing or even increasing the sorption speed of water by the desiccant material; patent US 6,819,042 B2 discloses desiccant systems comprised of a desiccant material dispersed in a resin, e.g. a polyethylene, polypropylene, polybutadiene or polyisoprene resin; finally, patent US 6,833,668 B1 discloses a system to damp the impact of moisture on the sensitive components of
15 organic light emitting displays (OLEDs), which is based on an impermeable resin barrier containing a desiccant powder; the barrier function of such a system is pointed out by the use as a means for sealing OLED cavities.

One limit that is common to many of the systems disclosed in these patents, be these based on dispersing matrixes being permeable to gases or having poor
20 permeability, is that, due to the reaction with the gas to be sorbed, the getter material generally undergoes structural and morphological modifications, e.g. swellings, which, in particular in the case of desiccants, can be considerable; the presence of a matrix surrounding the particle of getter material can hinder these morphological modifications and inhibit or delay the gas sorption reactions.

25 In addition, some industrial applications may pose other requirements to getter systems. For instance, OLEDs of the last generation require a getter system that is transparent and has constant optical properties throughout the whole life of the device, that is, soon after manufacture (when the getter material has not yet sorbed moisture, but for minimum amounts), near the end of the life of the device (when the getter device has
30 already sorbed relatively large amounts of moisture, even up to the saturation of the system) and also at intermediate steps of the OLED life, that is when the various getter

particles dispersed in the matrix have sorbed different amounts of moisture; the different level of moisture absorbed by getter particles during the OLED life can change optical properties of the system, such as its light transmission or refractive index, thus impairing the quality of the display. The problem is discussed, for example, in patent
5 US 6,465,953 disclosing a getter system for OLED, comprised of getter particles in a transparent matrix, wherein the particles have sufficiently small size not to interact with the luminous radiation. Given the importance of this application, in order to illustrate the uses of the getter systems of the invention reference will be particularly made to the use in OLEDs, but the getter systems of the invention are of a general use and may be
10 also used in other applications.

Object of the present invention is to provide a low permeability getter system being capable to sorb the permeating gaseous species.

According to the present invention, this and other objects are obtained with a getter system comprising:

- 15 - a polymeric means poorly permeable to the gases to be sorbed;
- a powder of a porous material distributed in the polymeric means;
- a phase active in the sorption of one or more gases in the pores of the porous material.

The invention will be described in the following with reference to the drawings,
20 wherein:

- Figure 1 shows a getter system of the invention;
- Figure 2 shows one particle of powder of the porous material;
- Figures 3a and 3b schematically show the gas sorption reaction that takes place inside the pores of the particle of Figure 2.

25 The getter systems of the invention differentiate from those of the prior art in that the material being active in the sorption of gases is not directly dispersed in the matrix, but is present inside the pores of a "guest" phase, the latter being in the form of powders dispersed in the matrix; this feature ensures that the physical properties of the system are essentially invariant with respect to gas sorption: for example, although the active
30 material may undergo morphological modifications during gas sorption, these modifications are not transmitted outside the individual porous particle, so that the

interactions between the latter and the environment (the matrix) are not modified.

With respect to the known getter systems, in addition to the above-illustrated difference, the systems of the invention offer a number of advantages. Firstly, if the dispersed porous material has well defined geometric features (e.g. in the case it is a natural or synthetic zeolite, fullerenes or the like), it is capable of transforming a reversible reaction or process into a non-reversible reaction or process due to the steric hindrance of the products and/or due to particularly high chemical forces exerted against the pore walls, such that the reaction products are tightly held in the pores. In addition, the porous material may receive a catalyst in addition to the active phase, thus ensuring mutual proximity, which is a particularly clear advantage if the active phase and the catalyst are solid and thereby they would have a poor mobility if freely distributed in the polymeric means. Finally, in the case where the porous material is a zeolite, the zeolite itself can act as a catalyst (acid or basic according to Lewis and/or Broensted) for a wide class of reactions, thus supporting the reaction of the active phase with the gas to be sorbed as explained.

In Figure 1 a system of the invention is shown, in a generic embodiment thereof: in this case the system 10 is shown in the form of a short parallelepiped in a broken view, but the system could have any other shape, e.g. a ribbon, a drop, or could be directly formed on an internal surface of the device whose atmosphere must be controlled, for example in the form of a thin layer, or occupy recesses of this surface.

The getter system is comprised of a polymeric means 11, characterized by a low permeability to the gas to be sorbed, inside which powders 12 of a porous material are distributed. The means 11 may be formed of any polymeric material being poorly permeable to the gaseous species to be sorbed; preferably, this polymer shows adhesive characteristics, so that it may be fixed onto an internal wall of the final device without using additional adhesives.

The low permeability to gases of the polymeric means 11 also allows this latter to accomplish the function of a barrier to the inlet of impurities into the body of the same means, thereby limiting the amount of impurities that must be sorbed by the active phase, prolonging in time the efficacy of the getter system and consequently the life of the devices in which such system is used. By low permeability it is intended a

permeability not higher than 1×10^{-12} ($m_{(STP)}^3 \cdot m^2 / \text{bar} \cdot m^3 \cdot s$) ($m_{(STP)}^3$ stands for cubic meters of gas measured at standard temperature and pressure).

Porous materials suitable for forming powders 12 useful for the purposes of the invention are for example the natural or synthetic zeolites, silicalites (i.e. substantially
5 zeolites without aluminum), aluminosilicates other than zeolites, fullerenes and metal-organic frameworks (better known in the field as MOF; see for example the article "Metal-organic frameworks: a new class of porous materials", by J. L. C. Roswell and O. M. Yaghi, published on-line in "Microporous and Mesoporous Materials", no. 73, pages 3-14, June 2004).

10 Figure 2 schematically shows an enlarged sectional view of a particle 12: the particle of porous material shows pores 20, 20', ..., inside which one phase active in gas sorption is arranged; the active phase is represented in the form of deposits 21, 21', 21'', ..., in the drawing the most general case is shown, wherein the pores are essentially in the form of channels having a variable section (between different pores and also in
15 different locations inside the same pore) reaching the surface of the particle 12, and the deposits 21, 21', 21'', ..., adhere to the internal walls of the pores; alternatively, for instance in the case of zeolites, the pores have dimensions that are rigidly fixed by the crystalline structure, which, as it is known, may show cavities mutually connected through passages of reduced section, and the active phase could be simply arranged in
20 the cavities, without being bonded to the internal surfaces of the same.

Figures 3a and 3b schematically show the operation mechanism of the getter systems of the invention: Figure 3a shows, in a further enlarged view, a detail of particle 12, and in particular a pore 20, inside which deposits 21, 21', ... of the active phase are present, while the molecules of the gaseous species to be sorbed are designated by 30;
25 during their motion the molecules 30 contact the deposits 21, 21', ... and react with them, thus being fixed on or by the deposits, with different mechanisms according to the nature of the components of the specific couple gaseous molecule/active phase; this situation is shown in Figure 3b by the "modified" deposits 31, 31', In the case of zeolites, as previously said, the active phase could be present not in the form of a
30 deposit, but rather in the form of particles being "trapped" in the zeolite cavities, and the product of the reaction with the molecules 30 will be in turn in the form of a species

trapped in the same cavities.

The chemical nature of the active phase depends on the species desired to be sorbed. For instance in the case the species to be sorbed is oxygen, the active phase can be formed of easily oxidable metals such as the alkaline metals, alkaline-earth metals or
5 other metals such as iron, tin and copper; metal oxides having low oxidation state such as manganese or copper oxide; salts with phosphite or phosphonite anion; or easily oxidable organic compounds such as phenols, secondary aromatic amines, thioethers or aldehydes. In the case of carbon monoxide sorption it is possible to use deposits of metals like nickel or iron, which form complexed species with this gas, or alkenes,
10 amines and ketones in the presence of lithium-based organometallic compounds. In the case of carbon dioxide the active phase can be a hydroxide of an alkaline or alkaline-earth metal. In the (unusual) case where it is necessary to sorb nitrogen, inorganic materials can be used such as lithium, barium, or the compound $BaLi_4$, or porphyrins, namely, metallorganic molecules which have the ability of fixing this gas to the central
15 metallic atom of the complex.

The most common and important case is however that of moisture removal. For this purpose, the active species can be chosen from a wide spectrum of materials, which work according to different sorption mechanisms, as summarized in the following list:

- materials adding water: to this group belong epoxides; organic molecules with
20 double or triple bonds (activated); oxides of alkaline metals, of alkaline-earth metals or of pseudo-alkaline-earth metals (i.e. essentially nickel, zinc and cadmium); organic (e.g. phthalic) and inorganic (e.g. boric) anhydrides;
- materials undergoing hydrolysis or nucleophilic substitution: to this group belong for instance some alkoxides (e.g. of aluminum, $Al(OR)_3$), some
25 halides, e.g. $AlCl_3$, acyclic halides (and particularly chlorides) having general formula $RCOX$ (where X is an halogen atom), or compounds forming carbocations;
- materials reacting with water with dissociation thereof and with formation of either an oxide and a hydride or of a solid solution; examples of these
30 materials are iron for what concerns the reaction with water, whereas, for what concerns the hydrogen sorption, yttrium, palladium or mixtures thereof;

- materials being solvated by water, such as magnesium sulphate, or metallic centers present in zeolites in order to compensate the missing charge due to aluminum.

5 In a preferred embodiment, the getter systems of the invention have the further property of being transparent to the visible radiation throughout their life, as previously described; in this mode, the systems of the invention are suitable for the application in the previously cited screens of OLED type.

These preferred getter systems comprise:

- 10 - an amorphous polymeric means having a low permeability to the gases to be sorbed;
- powder of a porous material distributed in the polymeric means, with powder particles having mean size lower than 100 nanometers;
- a phase active in the sorption of one or more gases in the pores of the porous material.

15 In this preferred embodiment, the components of the systems exhibit, as additional characteristics, the fact that the polymeric means is amorphous, whereas the porous material dispersed in the polymeric means is nanosized, being formed of particles having size in the order of about 100 nanometers or less. The reason for the first one of these two additional requirements is that polymers are transparent only if
20 perfectly crystalline or completely amorphous: as it is essentially impossible to obtain perfectly crystalline polymers, especially in the case of the present invention wherein powder must be dispersed in the means, it is necessary to resort to completely amorphous polymers. The second requirement comes from the fact that particles having dimensions of less than half the wavelength of the visible radiation do not cause
25 interactions with the same, and thereby do not alter the transparency of the polymeric means.

Polymers suitable for manufacturing a low permeability and transparent means are, for example, polyvinylchloride (PVC), polystyrene (PS), polymethyl(meth)acrylate (PMMA), copolymers acrylonitrile-butadiene-styrene (ABS), copolymerized
30 cycloolefins, polysulfones, polyethersulfone (PES) and particularly polyaryleneethersulfone, copolymers with polyvinylidenefluoride, copolymers with

polyhexafluoroisobutylene, copolymers with polyethylene, copolymers with
polyperfluorodimethyldioxole, chlorinated polyamides, polyimides (PI), fluorinated
polyimides (FPI), polycarbonate (PC), polyethyleneterephthalate (PET), acrylic resins,
epoxy resins, polyurethanes (PU), polytetrafluoroethylene (PTFE) and liquid crystal
5 polymers (LCP).

Generally, in order to obtain a low permeability means, the cited polymers and
their manufacturing processes are preferably selected among those allowing to obtain
the minimum free volume of the polymeric means, the minimum order and regularity of
the polymeric chains, the maximum cross-link rate, the maximum packing density and
10 the minimum interactions with the permeating species.

The systems of the invention may contain, in addition to the already cited
components, also additional elements improving some properties or supporting the
achievement of the same.

For example, inside the pores of the porous material catalysts may be present,
15 capable of accelerating the reactions between the species to be sorbed and the active
phase: for example, in the case of the sorption of water by unsaturated organic
molecules by addition to a double or triple bond, the catalyst could be an acid or a base
according to Lewis or Broensted; metals like platinum and palladium can catalyze the
sorption of hydrogen, other metals like nickel, iron, rhodium, ruthenium, copper or
20 silver can also catalyze a variety of reactions involving an organic compound and a gas,
both through the formation of coordination compounds involving the organic compound
and/or the gas, and through redox mechanisms.

Other elements that may be added in order to reduce the permeability of the getter
system are nanosized particles formed of inorganic materials such as silica, alumina,
25 aluminosilicates, tungsten oxide, zinc oxide, tin dioxide, titanium oxide and also
particles commonly known in the art as "platelets" (see, for instance, the article
"Polymer nanocomposites: from fundamental research to specific applications" by H.
Fischer, published in Materials Science and Engineering, vol. C 23 (2003), pages 763–
772); the function of said nanosized particles is to delay the diffusion and improve the
30 uniform distribution of the impurities.

The systems of the invention may be produced by pre-impregnating the active

phase in the porous material, and then forming suspensions of the so impregnated porous material in the polymeric means, if this has sufficiently low viscosity. Alternatively, it is possible to prepare a suspension of particles of the impregnated porous material in a solvent, wherein it is possible to solubilize also the polymer. The
5 suitable solvents depend on the chosen polymer and are well known in organic chemistry; examples of solvents are chloroform, acetone, dimethylformamide and dimethylsulfoxide for polyaryleneethersulfones; nitrobenzene and trichloroacetic acid for PET. Alternatively, it is possible to form a suspension between the porous material pre-impregnated of the active phase and precursors of the polymer (e.g. oligomers or
10 monomers which will form the polymer) and cause the polymer be formed *in-situ*, e.g. by radiating with UV radiation. In order to stabilize the suspensions it is also possible to add suitable surfactants thereto, well known in organic chemistry and not requiring further descriptions. The starting solution (if this contains the polymer or its precursors), or the low viscosity polymer inside which the powders of the porous material are
15 already present, may be poured into suitable molds, or directly in the final housing, for example onto a suitable internal surface of an OLED screen; once the liquid mixture has been poured into the desired housing, it may be made to "solidify" (meaning as "solid", in this case, a material having a very high viscosity, such as to maintain the given shape) by extraction of the solvent, polymerization *in-situ*, or, if the low viscosity was granted
20 by maintaining the polymer in the melted state, by cooling.

CLAIMS

1. A getter system (10) for the sorption of one or more gases, comprising:
 - a polymeric means (11) poorly permeable to the gases to be sorbed;
 - 5 - a powder of a porous material (12) distributed in the polymeric means;
 - a phase (21, 21', 21'', ...) active in the sorption of one or more gasescharacterized in that said phase is dispersed in the pores (20, 20', ...) of the porous material, and
said poorly permeable polymeric means shows a value of permeability not higher than
10 $1 \times 10^{-12} \text{ m}^3(\text{STP})\text{m}^{-3}\text{bar}^{-1}\text{s}^{-1}$.
2. A getter system according to claim 1, wherein the porous material is chosen among natural or synthetic zeolites, silicalites, aluminosilicates, fullerenes and metal-organic frameworks.
3. A getter system according to claim 1, wherein when the gas to be sorbed is
15 oxygen, the active phase is chosen among easily oxidable metals, metal oxides having low oxidation state, salts with phosphite or phosphonite anion and easily oxidable organic compounds.
4. A getter system according to claim 3, wherein said easily oxidable metals are chosen among alkaline metals, alkaline-earth metals or other metals such as iron, tin
20 and copper.
5. A getter system according to claim 3, wherein said metal oxides having low oxidation state are chosen between manganese and copper oxides.
6. A getter system according to claim 3, wherein said easily oxidable organic compounds are chosen among phenols, secondary aromatic amines, thioethers and
25 aldehydes.
7. A getter system according to claim 1, wherein when the gas to be sorbed is carbon monoxide, the active phase is chosen among nickel, iron, alkenes, amines and ketones in the presence of lithium-based organometallic compounds.
8. A getter system according to claim 1, wherein when the gas to be sorbed is
30 carbon dioxide the active phase is a hydroxide of an alkaline or alkaline-earth metal.
9. A getter system according to claim 1, wherein when the gas to be sorbed is

nitrogen the active phase is chosen among lithium, barium, the compound $BaLi_4$ and porphyrins.

10. A getter system according to claim 1, wherein, when the gas to be sorbed is water, the active phase is chosen among: epoxides, organic molecules with double or triple bonds, alkaline metal oxides, alkaline-earth metal oxides or oxides of nickel, zinc and cadmium, and organic or inorganic anhydrides and compounds forming carbocations; alkoxides, hydrolysable inorganic halides and acylic halides; mixtures between iron and yttrium or palladium; and magnesium sulphate.

11. A getter system according to claim 1, capable of maintaining the transparency on variations of the sorbed gas amount, comprising:

- an amorphous polymeric means being poorly permeable to the gases to be sorbed; and
- a powder of a porous material distributed in the polymeric means, characterized in that said powder particles have a mean size of less than 100 nanometers and a phase active in the sorption of one or more gases in the pores of the porous material.

12. A getter system according to claim 11, wherein said polymeric means is chosen among polyvinylchloride (PVC), polystyrene (PS), polymethyl(meth)acrylate (PMMA), copolymers acrylonitrile-butadiene-styrene (ABS), copolymerized cycloolefins, polysulfones, polyethersulfone (PES), copolymers with polyvinylidene fluoride, copolymers with polyhexafluoroisobutylene, copolymers with polyethylene, copolymers with polyperfluorodimethyldioxole, chlorinated polyamides, polyimides (PI), fluorinated polyimides (FPI), polycarbonate (PC), polyethylenterephthalate (PET), polysiloxanes and liquid crystal polymers (LCP).

13. A getter system according to one of claims 1 or 11, further containing, inside said pores, catalysts capable of accelerating the reactions between the gases to be sorbed and the active phase.

14. A getter system according to one of claims 1 or 11, comprising a load of inorganic material for reducing the gas permeability of said polymeric means.

15. A getter system according to claim 14, wherein said load is placed in the polymeric means in nanosized form.

16. A getter system according to claim 13, wherein said catalyst is chosen among platinum, palladium, nickel, iron, rhodium, ruthenium, copper and silver.

17. A getter system according to claim 13, wherein said catalyst is an acid or a base according to Lewis or Broensted.

5 18. A process for the preparation of the getter systems of claims 1 or 11, comprising the steps of: pre-impregnating the active phase in the porous material; and forming suspensions of the so impregnated porous material directly in the polymeric means.

10 19. A process for the preparation of the getter systems of claims 1 or 11, comprising the steps of: pre-impregnating the active phase in the porous material; forming a suspension of the so impregnated porous material in a liquid being a solvent of the polymeric means; dissolving in the suspension the polymer with which it is intended to form the polymeric means; and removing the solvent.

15 20. A process according to claim 19, wherein said solvent is chosen among: dimethylformamide and dimethylsulfoxide when the polymer is a polyaryleneethersulfone; nitrobenzene and trichloroacetic acid when the polymer is PET.

20 21. A process for the preparation of the getter systems of claims 1 or 11, comprising the steps of: pre-impregnating the active phase in the porous material; forming a suspension of the so impregnated porous material in a liquid being a solvent for the precursors of the polymer with which it is intended to form the polymeric means; dissolving said precursors in said suspension; causing the polymerization of said precursors to take place in the suspension; and removing the solvent.

25 22. A process according to one of claims 19 or 21, wherein said suspensions are stabilized by adding surfactants.