

“COMPOSITION AND DEVICES FOR GAS SORPTION AND
PROCESS FOR THEIR MANUFACTURING”

The present invention relates to a composition for gas sorption, as well as to
5 devices formed with the composition; the invention also refers to processes for
obtaining the composition.

In particular, the invention refers to compositions and devices for sorption
of traces of gases, both residual gases in evacuated chambers and impurities in
inert gases, in applications in which the space available for the sorbing device is
10 reduced.

An example of systems requiring the control of the internal atmosphere, but
having only limited room for the gas sorbing device are the flat panel displays,
both field emission displays (also known as FEDs, generally requiring an inner
vacuum atmosphere) and plasma displays (also known as PDPs, inside which
15 there's an atmosphere of a given composition). Another particularly important
application is represented by the OLED screens (from the definition “Organic
Light Emitting Display”), in which sorption of moisture from the screen inner
space is essential, but it can be necessary also sorbing other gases such as oxygen
or carbon dioxide. Due to the relevance of this application, in the following of the
20 description reference will be made to these screens, but it is intended that
compositions and sorbing devices of the invention can be used in a wide range
applications needing gas sorption, particularly when the thickness available for
housing the sorbing device is reduced little.

OLED screens are used as displays for mobile phones, for Hi-Fi
25 equipments, for car dashboards and the like; this kind of screens and the problems
related to water entering inside them are disclosed e.g. in US patent No.
5,882,761.

The search publication RD 430061 and the International Patent Application
Publication WO-A-02/27812 in the applicant's name disclose moisture sorbing
30 systems which are specific for OLEDs. These systems are formed of a part with a
central cavity filled with drying material, welded at the edges to a water-

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permeable membrane.

Patents US 4,985,296 and US 5,078,909 and International Patent Application Publication WO-A-01/88041 disclose sorbing systems based on an alternative approach to the problem: in this case powders of the material active in
5 gas sorption are incorporated in a resin or in a polymeric material, having gas permeability enough to allow gases to reach the particles of sorbing material.

A problem common to all the known sorbing systems is nevertheless that these, once manufactured, must be kept under inert atmosphere throughout storage time and during transportation, to avoid in these steps any contact with reactive
10 gases and hence their loss of functionality.

Object of the present invention is to provide a composition and sorbing devices obtained using this composition which avoid said problem.

Said object is achieved according to the present invention by means of a composition comprising a gas sorbing component A dispersed in a component B,
15 this latter being in the form of a cross-linked and porous matrix, said composition being obtainable by means of a process in which:

- at least one material A', that can be converted through a thermal treatment into said sorbing component A, is mixed with said component B or a precursor thereof, B', wherein B is chosen for mixing with A' if B
20 is capable of resisting essentially unaltered the thermal treatment for changing A' into A, while B' is chosen for mixing with A' if B' is able to transform into B after said thermal treatment; and
- the so obtained mixture is subjected to a thermal treatment under vacuum or under an atmosphere of a gas inert as regards component A,
25 in conditions such as to cause the conversion of material A' into sorbing component A.

As used here above with reference to component B, "essentially unaltered" means that this component either resists unchanged the thermal treatment, or, if it undergoes modifications during the treatment, these are such that characteristics
30 indicated for B, namely porosity and cross-linking, are retained.

The invention will be disclosed later on with reference to the only Figure,

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which graphically shows the result of a moisture sorption test from a device made from a composition of the invention.

The invention differs from all of known systems because the active component, A, is not added as such to a matrix (e.g. polymeric) during the first steps of system manufacturing, but it is mixed into the matrix (or a precursor thereof) in the form of a precursor thereof, A', which is only subsequently converted into active component A, for example just before using in the device of final destination; in this way the composition of the invention is inactive for gas sorbing throughout storage and transportation steps, and consequently in these steps particular precautions, such as storage in containers sealed under vacuum or under inert atmosphere, are not needed.

Material A', sorbing component precursor in the composition of the invention, can be selected among any materials that may be converted into a component A capable of gas sorption by means of a treatment at not too high temperature, or in not too onerous conditions. Said treatment conditions are fixed by component B (or material B'), and by the support onto which the composition is laid; in general, these conditions must be such not to destroy the cross-linked structure of B or close its pores, and not to destroy the support.

In case component A is a moisture sorber, this could be an alkaline-earth metal oxide, in particular selected among calcium oxide, CaO, strontium oxide, SrO, and barium oxide, BaO; in this case, preferred precursor materials A' are the related hydroxides, Ca(OH)₂, Sr(OH)₂ and Ba(OH)₂ respectively, that can be dehydrated to yield the oxides by treatments at temperatures from about 300 to 650 °C in times of few hours, under vacuum or under inert atmosphere (the dehydration of Ca(OH)₂ can be carried out under gas, while Sr(OH)₂ and Ba(OH)₂ require vacuum); if dehydration is performed under an inert gas, this is preferably flowing. Among these oxides, BaO presents the best features in moisture sorption, but the use of CaO is preferred owing to low price of its precursor and because, unlike BaO, it does not present toxicity problems; transformation of Ca(OH)₂ into CaO occurs successfully, in about 2 hours, at a temperature of about 300 °C under vacuum; the decrease of treatment times is also possible by increasing

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temperature, for example up to about 500 °C. Calcium oxide has the additional advantage that upon moisture sorption is changed into the hydroxide (reaction $A \rightarrow A'$), that has the capability of sorbing carbon dioxide, CO_2 : some producers of OLEDs have indicated that the proper functioning of these devices also requires the sorption of this gas. Another possible moisture sorber is boron oxide, B_2O_3 , obtainable in a particularly active form from boric acid, H_3BO_3 , according to the procedures disclosed in US patent 6,304,367 (treatment at temperatures lower than 200 °C, preferably at low pressure).

When the gas to be sorbed is oxygen, component A can be for example a transition metal oxide in which the metal has a low oxidation state and is easily further oxidable. An oxide of this type is for example manganese (II) oxide, MnO , that easily sorbs oxygen changing into Mn_2O_3 ; a precursor A' suited for obtaining MnO is manganese carbonate, $MnCO_3$, that is quickly converted into the oxide by means of a thermal treatment at about 300 °C under vacuum. Other useful components A for the sorption of oxygen are FeO and Ni in finely dispersed form, that can be obtained through thermal decomposition under vacuum of the corresponding oxalates, respectively FeC_2O_4 and NiC_2O_4 , at temperatures in the range 350-400 °C. In case A is a metal such as Ni , the dispersion may be favoured by the fact that decomposition takes place in the matrix B or while this is formed, so the metal forms "islands" that deposit on the internal surfaces of the matrix, or small metallic aggregates that are trapped by the same matrix.

The above cited components A are all chemical sorbers, namely, they sorb moisture through a chemical reaction that transforms A into another compound; however, the invention is not limited to chemical gas sorbers, and A can also be a physical sorber, namely, a material that fixes gas molecules at its surface by means of adsorption. In this case too, carrying out the thermal conversion of A into A' in a matrix helps in obtaining material A in a finely divided form, that ensures good sorption properties. An example of possible physical sorber (component A) is γ -alumina, that can be obtained by thermal decomposition under vacuum at around 300 °C of norstrandite, a form of aluminum hydroxide, $Al(OH)_3$, or by thermal decomposition under vacuum at around 250 °C of

boehmite, a form of aluminum oxo-hydroxide, AlOOH .

Obviously, compositions of the invention can comprise several A-type components, and therefore be obtained from mixtures comprising several A'-type materials; for example, in the OLED application, besides moisture, a damaging
5 effect due to oxygen seems to be present, and in this case a composition obtained from a mixture comprising Ca(OH)_2 and MnCO_3 can be used. In these cases, the thermal treatment conditions to which the mixture has to be subjected, must be chosen in order to ensure effective conversion of all materials A' into related sorbing components A.

10 In the starting mixture materials A' are generally used in the form of powders; these have preferably particle sizes lower than about $100\text{ }\mu\text{m}$, and more preferably lower than $50\text{ }\mu\text{m}$ and even more preferably lower than $30\text{ }\mu\text{m}$. During thermal treatment for converting A' into A, powders obviously also undergo a morphologic transformation, and it is observed that granules size slightly
15 decrease, while essentially keeping the same order of magnitude: accordingly, materials A' must be used as fine powders to easily ensure first of all their homogeneous dispersion in final composition and high surface area of component A (decisive for obtaining good properties in gas sorption), and moreover to allow achievement of devices having thin thickness from these compositions.

20 Component B and material B' are such that, during thermal treatment for converting A' into A, respectively either retain cross-linked structure and porosity or transform into a B-type component. B component has inner cohesion and is capable to retain particles of A. The preferred component B or material B' are certain silicone resins resistant to high temperature treatments, for example used
25 as carriers of heat-resistant paints for mufflers, boilers or similar applications. Phenyl-methyl-polysiloxane resins supplied by Tego Chemie Service Italia of Pandino (CR) as Silikophen[®] (registered name by Goldschmidt AG, DE) are an example. These resins resist in continuous, by themselves, at temperatures up to $350\text{ }^\circ\text{C}$, and up to about $650\text{ }^\circ\text{C}$ when filled with inorganic materials. Determining
30 chemical composition or structure of these resins is extremely complicated, especially after thermal treatment; however IR analyses showed that, after thermal

treatments necessary for converting A' into A, these resins lose only partially their organic components and undergo partial vitrification. In these treatments, resins used in compositions of the invention keep cross-linking, as shown by particles retention even after treatment, and keep adhesion to the substrate even if wrapped
5 around objects with circular section having diameter of about 1 cm.

In the mixtures used to manufacture compositions of the invention, weight percent of A can vary within wide limits, depending on specific weight of A'; in case of mixtures of $\text{Ca}(\text{OH})_2$ in Silikophen[®], initial filling up to about 50% can be reached, obtaining after thermal treatment a homogenous sorbing composition, as
10 experimentally proved.

Adding other components to the mixture comprising A' and B (or B') is also possible. For example, it is possible to add a solvent, such as alcohols, glycols, polyethers and esters, useful for controlling mixture viscosity and consequently the possibility of obtaining a homogenous deposit; otherwise a dispersing surface-
15 active additive, useful for allowing a homogenous distribution of particles of A' in the mixture.

The compositions of the invention are generally used in form of films onto a support. The support may be a wall of the device in which vacuum must be maintained (or in which the inner gas composition must be controlled). For
20 instance, in the case of OLEDs, the support may be the inner surface of the rear side (referred to in the field as the backplate), that may be made of glass or metal; similarly, in the case of FEDs or PDPs, it may be possible to deposit the mixture of A' and B (or B') onto a surface of one of the two glass plates making up the display, preferably the rear one, and treat the assembly at the temperature needed
25 for the conversion $\text{A}' \rightarrow \text{A}$; if B or B' is a silicone resin, this keeps good adhesion to the glass surface. Alternatively, it is possible manufacturing discrete sorbing devices, depositing the precursors mixture on a additional support and then adhering this onto an available wall of the final destination device (for example, on the internal surface of the backplate of an OLED). In case of use of an
30 additional support, again this may be made of glass or be a metallic sheet, for example steel or Nichrofer (an alloy of nickel, chromium and iron), having

thickness for example of about 50 μm or less. In the case of the additional support, it is either possible to manufacture sorbing devices one by one, or to manufacture large-sized supports (foils, sheets, plates, or tapes) coated with the precursors mixture, and then to cut these in desired size.

5 Precursors mixtures can be deposited on the desired support in several ways, for example through brush work or spraying; preferred is the use of screen-printing, well known in the printing field, allowing greater control of the deposit thickness (by means of control of screen thickness, through which mixture is forced to pass for reaching the support).

10 In any case, thermal treatment for converting A' into A can be carried out at the most suited moment, for example immediately before introducing the sorbing device into the final system. In the specific case of CaO, it is also possible to "reactivate" the composition, in case that during storing, transporting and handling, the oxide has undergone partial or total transformation into the
15 hydroxide upon water sorption (due to poor control of the process, or to an exposures to air that is either unavoidable or preferred to lower the process complexity and costs). In this case, the ease of transformation of the hydroxide back to the oxide allows this change to be carried out more than one time before the sealing of the device of final destination of the composition of the invention.

20 The compositions of the invention can be used to produce deposits having thickness values in a wide range. The low end of this range is determined by technical needs only, in particular by the need of having component A in an amount enough for the application; in the various tests carried out by the inventors, the lowest limit achieved for thickness of final composition is about 20
25 μm . Compositions and devices of the invention therefore also provide the additional advantage of an easy manufacturing in particularly thin films, of thickness lower than a tenth of millimetre, not obtainable by systems at present known constituted of particles dispersed in a matrix. Thick deposits can be obtained essentially with any desired thickness, but during testing the inventors
30 have noted that thicknesses higher than about 150 μm gave problems of internal cohesion, forming fractures in the deposit; as a consequence, higher deposits can

be formed and used if the cracking of the deposit is not a problem in the foreseen application.

The invention will be further illustrated from the following examples. These non-limiting examples show some embodiments intended to teach to those skilled in the art the manufacturing of the invention and to represent the best way to carry out the invention.

EXAMPLE 1

43.3 g of $\text{Ca}(\text{OH})_2$, 10.3 g of dipropylene glycolmethylether as viscosity regulator, 1 g of Dispers 630 (a dispersing surface-active agent), 1 g of Airex 935 as mixture deaerator and 44.4 g of Silikophen[®] P 80/MPA resin (Dispers, Airex, and Silikophen are supplied by Tego Chemie Service Italia) are mixed under stirring. The mixture so obtained is deposited using screen-printing on a Nichrofer sheet having thickness of 50 μm . From this sheet, some strips of 3 x 6 cm are cut. Three of these strips are introduced in a chamber provided with a gastight valve; this chamber, with the valve open, is introduced into an oven and the strips are subjected to the following thermal treatment under vacuum:

- heating from room temperature to 420 °C in one hour;
- keeping at 420 °C for one hour;
- cooling under vacuum down to 250 °C and subsequently under argon flow down to room temperature.

The valve of chamber containing the strips is closed, the chamber is extracted from the oven, introduced in a glove box, opened and then the strips are withdrawn. Inside the glove box, the deposit thickness is measured using a comparator and it results equal to $60 \pm 10 \mu\text{m}$.

Still inside glove box, a strip is punched obtaining rectangular-shaped pieces of 10 x 18 mm. Two of these pieces are inserted into a glass bulb provided with insulating valves, used to carry pieces to the system for measuring moisture sorption properties.

EXAMPLE 2

The bulb with pieces prepared as described in Example 1 is assembled on a bench for sorption tests, allowing to dose known amounts of water vapour. The

bulb valve is opened, the system is evacuated to remove argon, and the pieces are connected to the system of water dosing in order to keep a constant water pressure of 1 Pa on the pieces and measuring the pieces weight increase Δp in time (normalized as regards the deposit surface). The result of test is represented in

5 Figure 1, showing that samples of the invention rapidly sorb moisture from the surrounding environment.

Thanks to the fact that the compositions of the invention can be manufactured in extremely reduced thickness, while retaining good sorption capabilities, these are suited for using in OLED screens, in which the available

10 thickness for the gas sorber is always limited. In particular, compositions of the invention can be useful especially for manufacturing OLED screens as disclosed in Japanese Patent No. 3,293,527, in the name of Fuji Electric, which, unlike previous OLED screens, do not have a dedicated housing for the sorbing device, in the form e.g. of a recess or hollow on the rear support of the screen, whereby

15 the thickness available for the sorbing material is further reduced. In these conditions, the possibility offered by the present invention to form sorbing layers having thicknesses even of few tens of μm results particularly useful and advantageous.

CLAIMS

1. A composition for gas sorption comprising a gas sorbing component A dispersed in a component B, this latter being in the form of a cross-linked and porous matrix, said composition being obtainable by means of a process in which:
 - at least one material A', that can be converted through a thermal treatment into said sorbing component A, is mixed with said component B or a precursor thereof, B', wherein B is chosen for mixing with A' if B is capable of resisting essentially unaltered the thermal treatment for changing A' into A, while B' is chosen for mixing with A' if B' is able to transform into B after said thermal treatment; and
 - the so obtained mixture is subjected to a thermal treatment under vacuum or under an atmosphere of a gas inert as regards component A, in conditions such as to cause the conversion of material A' into sorbing component A.
2. A composition according to claim 1 wherein said component A is a moisture sorber.
3. A composition according to claim 2 wherein said component A is an oxide selected among calcium oxide, strontium oxide, barium oxide and magnesium oxide, and said material A' is the respective hydroxide.
4. A composition according to claim 2 wherein said component A is boron oxide and said material A' is boric acid.
5. A composition according to claim 1 wherein said component A is an oxygen getter.
6. A composition according to claim 5 wherein said component A is manganese (II) oxide, MnO, and said material A' is manganese (II) carbonate, MnCO₃.
7. A composition according to claim 5 wherein said component A is iron (II) oxide, FeO, and said material A' is iron (II) oxalate, FeC₂O₄.

8. A composition according to claim 5 wherein said component A is metallic nickel, and said material A' is nickel (II) oxalate, NiC_2O_4 .
9. A composition according to claim 1 wherein said component A is a physical gas sorber.
- 5 10. A composition according to claim 9 wherein said physical gas sorber is a moisture sorber.
11. A composition according to claim 10 wherein said moisture sorber is γ -alumina, and the A' material is either the aluminum hydroxide norstrandite or the aluminum oxo-hydroxide boehmite.
- 10 12. A composition according to claim 1 wherein said material B' or component B is a phenyl-methyl-polysiloxane resin.
13. A process for obtaining a composition according to any of claims 1 to 12, comprising the steps of:
 - mixing at least a material A' precursor of component A and either a
 - 15 component B or a material B' precursor of component B;
 - subjecting the thus obtained mixture to a thermal treatment under vacuum or under an atmosphere inert as regards component A, in conditions such to cause conversion of all materials A' into related sorbing components A.
- 20 14. A process according to claim 13 wherein said step of thermal treatment is carried out immediately before introducing the composition into the final destination device.
15. A process according to claim 13 wherein said material A' is an alkaline-earth metal hydroxide and said thermal treatment is carried out at
- 25 temperature from about 300 to 600 °C.
16. A process according to claim 13 wherein said material A' is boric acid and said thermal treatment is carried out at a temperature lower than 200 °C.
17. A process according to claim 13 wherein said material A' is manganese carbonate, and said thermal treatment is carried out at a temperature of
- 30 about 300 °C.
18. A process according to claim 13 wherein said material A' is an oxalate of

iron or nickel, and said thermal treatment is carried out at a temperature in the range between about 300 and 400 °C.

19. A process according to claim 13 wherein said material A' is either the aluminum hydroxide norstrandite or the aluminum oxo-hydroxide boehmite, and said thermal treatment is carried out at a temperature of 300 °C and 250 °C, respectively.
20. A process according to claim 13 wherein said mixture comprises several materials A' and the thermal treatment is carried out at such a temperature to ensure effective conversion of all materials A' into related sorbing components A.
21. A process according to claim 13 wherein said material A' is used in form of powders having particle size lower than about 100 µm.
22. A process according to claim 13 wherein said component A is calcium oxide and said mixture comprises up to 50% by weight of calcium hydroxide.
23. A gas sorbing device comprising a composition according to any of claims 1 to 12, obtained by depositing the mixture of precursors A' and B' on a support through brush work, spraying, or screen-printing, and subjecting the deposit to thermal treatment.
24. A gas sorbing device according to claim 23 wherein the support is a wall of the final destination device.
25. A gas sorbing device according to claim 23 wherein the support is an additional support.
26. A gas sorbing device according to claim 23 wherein the support is metallic or made of glass.
27. A gas sorbing device according to one of claims 23 to 26, wherein the composition has a thickness from about 20 to 150 µm.
28. An OLED screen comprising a gas sorbing device according to any of claims 23 to 27.