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(71) Applicant: **SAES GETTERS S.p.A.**
**Via Gallarate, 215/217**
**I-20123 Milano(IT)**

(72) Inventor: **Boffito, Claudio**
**Via Papa Giovanni XXIII, 2/14**
**RHO (Milano)(IT)**
Inventor: **Bolognesi, Massimo**
**Via Bazzini, 24**
**Milano(IT)**

(74) Representative: **Adorno, Silvano et al**
**c/o SOCIETA' ITALIANA BREVETTI S.p.A. Via Carducci, 8**
**I-20123 Milano(IT)**

## (54) Gettering device and system for a cathode ray tube.

(57) A gettering system is provided in a cathode ray tube which have a sensitive cathode that can be damaged when nitrogen is released at first switch-on of the cathode. The gettering system consists of a barium getter providing a high capacity for residual gases throughout tube life and a separate titanium getter which provides a film of titanium having a high sorption speed for the nitrogen which is released at first switch-on of the cathode.

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## "GETTERING DEVICE AND SYSTEM FOR A CATHODE RAY TUBE"

The invention relates to a gettering system for a cathode ray tube and a method of manufacturing a cathode ray tube such as a colour display or television tube using a dispenser cathode which is subject to damage at first switch-on due to a sudden increase of the pressure of gas such as nitrogen within the cathode ray tube. An evaporable titanium getter device is also described.

Cathode ray tubes are well known in the art and have been used for may years for the visual display of information in a wide variety of forms. Cathode ray tubes are generally formed of a screen portion upon which has been deposited one or more phosphors which emit visible light on excitation by a beam of electrons. One or more beams of electrons are generated from an electron gun situated in a neck portion of the cathode ray tube. A cone portion separates the screen from the neck. Frequently there is also incorporated a metal magnetic screening cup within the cone portion.

For the cathode ray tube to function efficiently its internal volume must be maintained at a very high vacuum: that is, its residual pressure must be below $10^{-5}$ mbar. If the pressure is above this value when the atoms as molecules of the residual gas become ionized and, due to the electric fields present, are accelerated towards the cathode, they then impinge upon the cathode and erode the electron emitting materials thus reducing the like of the cathode.

It is required that the image produced on the screen of the cathode ray tube be as bright as possible. This can be accomplished by suitable choice of the phosphors, but also by ensuring that the electron beam which excites the phosphors, has as high a density as possible. This means that the cathode must emit a large number of electrons per square centimeter of its electron emitting area. Such cathodes are well known and are called "dispenser" cathodes. They have also been called "L", "pressed", "impregnated" and "matrix" cathodes, but basically they consist of a chamber of non-porous heat conducting metal such as molybdenum (although other metals such as tungsten, tantalum and niobium can be used) that has a "window" of porous tungsten which constitutes the emitting surface. Unfortunately such dispenser cathodes are extremely sensitive to the residual gas pressure within the cathode ray tube. In order to protect the cathode during normal functioning of the cathode ray tube are used getter devices such as described in US-A-3,381,805 and US-A-4,710,344. These getter devices are capable of sorbing residual gases during the life of the cathode ray tube but are not capable of removing sufficiently quickly the gases, essentially nitrogen, generated during the very first switch-on of the completely manufactured cathode ray tube.

At first switch-on of a cathode ray tube incorporating a dispenser cathode it has been found that the residual gas pressure becomes so high that it compromises the successive behaviour of the cathode during tube life.

It is therefore an object of the present invention to provide an improved gettering system for a cathode ray tube free from one or more of the disadvantages of prior gettering systems.

It is another object of the present invention to provide an improved gettering system for a cathode ray tube which maintains the residual gas pressure lower than $10^{-5}$ mbar during first switch-on of the cathode ray tube.

It is a further object of the present invention to provide an improved gettering system for a cathode ray tube which has a high gettering rate for a nitrogen gas during first switch-on of the cathode ray tube.

It is yet another object of the present invention to provide an improved gettering system for a cathode ray tube in which the cathode is not damaged during first switch-on of the cathode ray tube.

It is yet a further object of the present invention to provide an improved evaporable titanium getter device useful in a gettering system of the present invention.

Other objects and advantages of the present invention will become apparent from the following description whereof and drawings wherein:

**FIGURE 1** is a cross sectional view of a colour cathode ray display tube in which the gettering system of the present invention can be usefully employed;

**FIGURE 2** is a cross section of an evaporable titanium getter device useful in the gettering system of the present invention;

**FIGURE 3** is a diagrammatic sketch of a getter sorption characteristics test apparatus;

**FIGURE 4** is a graph showing the nitrogen sorption characteristics of barium films;

**FIGURE 5** is a graph showing the nitrogen sorption characteristics of titanium films;

**FIGURE 6** is a graph showing the nitrogen sorption characteristics of titanium films on barium films; and

**FIGURE 7** is a graph showing the combined nitrogen sorption characteristics of titanium and barium films when deposited on separate surfaces within the same vessel.

The present invention provides a gettering system for a colour cathode ray display tube, or a

monochrome projection tube, which has a sensitive cathode such as a dispenser cathode. The gettering system is capable of rapidly sorbing nitrogen gas which is produced when the cathode ray tube is first switched-on. Thus a high pressure of nitrogen is prevented avoiding damage to the cathode by ionic bombardment. The gettering system comprises a first getter metal vapour releasing material capable of releasing barium vapour upon heating and a second getter metal vapour releasing material capable of releasing titanium vapour upon heating.

The term "getter metal vapour releasing material" as used in the specification and claims herein is meant to include both the material prior to and after getter metal vapour release. This term embraces both the material in the form sold with the getter device and in the form in which it is found in an operatingtube wherein the bulk of the getter metal has been evaporated from the material and is in the form of a film on the inside surfaces of the tube.

Referring now to the drawings and in particular to Fig. 1, there is shown a colour cathode ray display tube 100 comprising a screen portion 102, a cone portion 104 and a neck portion 106. Screen 102 is coated with a layer of phosphors 108 near to which is located a screen selection electrode or shadow mask 110 held in place by means of a frame 112. Frame 112 also supports a metal magnetic screening cap 114 within cone portion 104. The surface of cone portion 104 is coated with a graphite layer 116. A dispenser cathode 118 is located within neck portion 106. Cathode 118 is any of the various types of known dipenser cathode such as a tungsten dispenser cathode.

A gettering system within display tube 100 comprises a first getter metal vapour releasing material capable of releasing barium vapour upon heating and preferably comprises a first holder 120 which is preferably of stainless steel having an outer side wall and a bottom wall. Holder 120 supports a getter metal vapour releasing material capable of releasing barium vapour upon hearing. The getter meal vapour releasing material comprises a mixture of a particulate alloy of approximately 50% barium and 50% aluminium together with an approximately equal weight of particulate nickel. It will be realized that small quantities of additional materials such as $Fe_4N$ may be added to this mixture to generate a pressure of nitrogen gas during evaporation of barium in order to control the spacial distribution and porosity of the resulting deposited barium film.

The gettering system also comprises a second getter metal vapour releasing material capable of releasing titanium vapour upon heating such as a titanium-tantalum alloy wire or a tantalum wire clad with titanium. However it is preferably in the form of a second holder 122 which is shown in more detail in Fig. 2. Holder 122 is preferably of ring shape having an outer side wall 124 and a bottom wall 126 in general having a pan-shaped appearance. The holder 122 can be made from a ceramic material but it is preferably made from a metal having a higher melting point than the melting point of titanium. It could therefore be made from molybdenum, niobium (columbium), tantalum or tungsten. The best compromise between workability, cost and other properties makes moybdenum the preferred holder material. Holder 122 supports a getter metal vapour relasing material 128 which comprises a mixture of particulate titanium and a particulate refractory metal. It is desirable to have the titanium in particulate form as it then has a large surface area per unit mass, thus aiding the evaporation of titanium. The particle size should not be too large otherwise the surface area per unit mass is low and excessively long heating times are required to ensure release of sufficient titanium to provide the necessary high pumping speed for removing the nitrogen produced at first switch on of a cathode in a display tube. If the titanium particle size is too small then it becomes difficult to handle during manufacture of the getter device, with dangers of explosion. The titanium particle size should therefore be between 2 and 100 $\mu$m and preferably between 5 and 44 $\mu$m.

When titanium is heated to such a high temperature that its rate of evaporation is sufficiently large it is very near to its melting point and is subject to a reduction of its surface area, if in particulate form, due to thermal sintering. It is therefore preferable to mix the particulate titanium with an anti-sintering material such as a refractory metal. Suitable refractory metals are molybdenum, niobium, tantalum and tungsten. Tantalum is preferred as it is also a getter material at high temperatures but does not oxidize on exposure to air at 400 $^{\circ}$ C. Furthermore it has been found that after evaporation of titanium the residue is firmly held within the holder such that there are no loose particles also ensuring that no molten particles of titanium are released if the temperature accidentally reaches its melting point. The tantalum particle size should be between 2 and 100 $\mu$m and preferably be between 5 and 44 $\mu$m to ensure even and easy mixture with the titanium powder.

The weight ratio of titanium to refractory metal can vary between wide limits. If the ratio of titanium is too high the refractory metal will be unable to perform its antisintering function. If the ratio of titanium is too low it may not be possible to evaporate the required quantity of titanium in an acceptably short time. The weight ratio of titanium to refractory metal should therefore be from 19:1 to 1:19 and preferably be from 5:1 to 1:5.

In practice the first getter metal vapour releasing material capable of releasing barium vapour upon heating is located within the cone portion of a cathode ray display tube in such an orientation that, upon heating, the barium vapours are preferentially directed towards the screen portion leaving a part of the cone portion substantially free from deposited barium. The second getter metal vapour releasing material capable of releasing titanium vapour upon heating is located within the cathode ray display tube in such an orientation that, upon heating the titanium vapours are preferentially directed towards the part of the cone portion substantially free from deposited barium. It will be realized that the quantity of titanium deposited and the area over which it is deposited must be sufficiently large to ensure that the nitrogen released at first switch-on of the cathode is quickly removed to maintain its pressure below that which might cause damage to the cathode.

A getter sorption characteristics test apparatus 300 was constructed as shown very schematically in Fig 3. Test apparatus 300 comprised a glass sphere 302 having an internal surface area of 450 $cm^2$, and a cylindrical appendage 304 having a diameter of 3 cm. Provision was made for placing and substituting a barium getter metal vapour releasing material 306 in a position where sphere 302 joined appendage 304. A titanium getter metal vapour releasing material 308 could also be placed centrally of bulb 302 by means of electrical support leads 310, 310'.

Apparatus 300 was also provided with means, not shown, for its evacuation and the introduction of nitrogen gas in such a way as to measure the sorption characteristics of getter materials evaporated within the apparatus 300 according to the procedure described in ASTM F 111.

## EXAMPLE 1

This example is not representative of the present invention and was designed to show the sorption characteristics of a known barium film.

An annular ring getter holder containing a mixture of a particulate alloy of approximately 50% barium and 50% aluminium together with an approximately equal weight of particulate nickel as placed in a test apparatus as described supra. Barium was evaporated from the getter mixture by means of induction heating until approximately 35 mg of barium metal had deposited uniformly on the inside surface of sphere 302. The gettering characteristics for nitrogen gas were measured and are reported in the graph of Fig. 4 as curve 1.

## EXAMPLE 2

This example is not representative of the present invention and was designed to show the sorption characteristics of another known barium film. Example 1 was repeated in all respects except that the mixture contained an amount of $Fe_4N$ capable of producing a nitrogen pressure of between $10^{-3}$ and $5x10^{-2}$ mbar of nitrogen gas during barium evaporation. The resulting sorption characteristics of the barium fim are shown in Fig. 4 as curve 2. This example was repeated resulting in curve 3 in Fig. 4.

## EXAMPLE 3

This example is not representative of the present invention and was designed to show the sorption characteristics of a known titanium film.

In a test apparatus as described supra an 80% tantalum (by weight) - 20% Ti wire of diameter 0.010 inch (0.254 mm) was placed centrally of the test bulb. Electric current was passed through the support leads until about 0.18 mg of titanium had been deposited on the internal surface of the sphere.

The sorption characteristics of the titanium film for nitrogen gas are reported on Fig. 5 as curve 4.

This example was repeated except that 1.8 mg of titanium were deposited, the resulting sorption characteristics are reported on Fig. 5 as curve 5.

## EXAMPLE 4

This example is not representative of the present invention and was designed to show the sorption characteristics of a barium film with a titanium film deposited thereon.

The procedure of Example 2 was repeated to produce a barium film on the internal surface of the sphere. Successively there was evaporated a film of titanium over the barium as described in Example 3. The amount of titanium evaporated was 0.68 mg.

The sorption characteristics of this double film for nitrogen gas were measured and are given as curve

6 on Fig. 6.

This example was repeated except that the amount of titanium evaporated was 1.8 mg. The sorption characteristics of this second double film for nitrogen gas were measured and are given as curve 7 on Fig. 6.

For convenience in later discussions curve 3 of Fig. 4 is also reported on Fig. 6 as curve 3'.

EXAMPLE 5

This example is illustrative of the present invention.

The test apparatus as previously described was used except that the titanium getter metal vapour releasing material was placed in the cylindrical appendage.

A barium film was produced on the inside surface of the sphere as described in Example 2 and titanium was evaporated within the cylindrical appendage. 0.6 mg of titanium were evaporated onto a surface area of 50 $cm^2$ thus the barium and titanium films were deposited on separate surfaces but within cnnecting volumes. The sorption characteristics for nitrogen gas were measured and reported on Fig. 6 as curve 8.

For convenience in later discussion curve 3 of Fig. 4 is also reported on Fig. 7 as curve 3".

EXAMPLE 6

This example describes a less preferred embodiment of getter metal vapour upon heating.

Eight pieces of 80% by weight tantalum 20% titanium alloy wire, 0.010 inches (0.254 mm) in diameter and 10 cm long, weighing about 0.5 g, were each bent at their center and twisted into a bifilar configuration which was then bent into a ring shape. Each ring was then placed in a vacuum environment and heated by induction heating to cause evaporation of titanium. The heating was continued for 30 seconds. The quantity of titanium evaporated from each sample is shown in Table I:

TABLE I

| Sample N° | Titanium evaporated (mg) |
|---|---|
| 1 | 2.0 |
| 2 | 3.2 |
| 3 | 0.8 |
| 4 | 2.8 |
| 5 | 0.9 |
| 6 | 0.4 |
| 7 | 0.3 |
| 8 | 0.5 |

As can be seen from Table I the amount of titanium evaporated varies considerably from sample to sample. Visually it was also observed that the ring was very unevenly heated.

EXAMPLE 7

This example describes the most preferred embodiment presently known of a holder supporting a getter metal vapour releasing material capable of releasing titanium vapour upon heating.

Several pan-shaped holders were pressed from a molybdenum sheet of 0.15 mm thickness. The holders were of 11 mm inside diameter having an outer side wall height of 1.5 mm. Into the holder was compressed, with a force of 4000 kg, 100 mg of a mixture of 80% by weight of particulate titanium and 20% by weight of particulate tantalum. The particle size of both the titanium and tantalum was sich that they passed through a U.S. standard sieve of 325 mesh per inch (128 mesh per cm). The pan-shaped holders

were then placed in a vacuum environment and heated by induction heating to cause evaporation of titanium. The heating was continued for 30 seconds. The quantity of titanium evaporated from each sample is shown in Table II.

TABLE II

| Sample N° | Titanium evaporated (mg) |
|---|---|
| 1 | 4.8 |
| 2 | 4.6 |
| 3 | 8.9 |
| 4 | 6.7 |
| 5 | 6.4 |
| 6 | 5.4 |
| 7 | 7.2 |
| 8 | 10.1 |
| 9 | 4.8 |
| 10 | 4.6 |
| 11 | 6.7 |
| 12 | 11.8 |

As can be seen from Table II considerably higher quantities of titanium can be evaporated with a more uniform yield. Furthermore visual observation showed a substantially uniform heating of the holder and its contents.

EXAMPLE 8

A sample prepared exactly as in Example 7 was subjected to heating in air at 400° C for 10 min. before causing it to evaporate titanium in a vacuum environment. It was found to have evaporated 7.2 mg of titanium in 30 seconds.

DISCUSSIONS OF FIGURES 4 TO 7

Fig. 4 shows that barium films have a high sorption capacity but an undesirable low initial pumping speed for nitrogen gas.

Fig. 5 shows that titanium films have very high initial pumping speeds but very low sorption capacities for nitrogen gas.

In Fig. 6 comparison of the curves shows that if titanium is evaporated onto barium there is a slight increase in the initial sorption speed of the combined gettering system which is not however sufficient to quickly sorb nitrogen gas at first switch-on of a display tube. Furthermore, the more titanium is evaporated the more the sorption capacity is reduced.

Fig. 7 shows that is the barium and titanium films are separated than there is a resultant high initial pumping speed and a high sorption capacity.

EXAMPLE 9

A colour cathode ray display tube is constructed as shown in Fig. 1 . A first stainless steel holder supporting approximately 1000 mg of a mixture of a particulate alloy of about 50% barium and 50% aluminium together with an approximately equal weight of particulate nickel and a small quantity of $Fe_4N$

sufficient to produce a pressure of between $10^{-3}$ and $5x10^{-2}$ mbar of nitrogen during evaporation of barium is attached to the metal screening cap. A second pan-shaped holder manufactured exactly as described in Example 7 is attached to the metal screening cap, between the cap and the cone portion of the display tube. Both first and second getter metal vapour releasing materials are subject to the frit sealing process during display tube manufacture. After evacuation and sealing of the tube the first holder is heated to release barium metal vapours. Then the second holder is heated to release titanium vapours which are deposited on an area where barium has not been deposited. When the tube is first switched on the pressure of nitrogen remains below that which would cause damage to the cathode.

## Claims

1. A gettering system in a cathode ray display tube, having a sensitive cathode, in which a high nitrogen pressure is created at first switch-on of the cathode, characterized by comprising:
   A. a first getter metal vapour releasing material capable of releasing barium vapour upon heating; and
   B. a second getter metal vapour releasing material capable of releasing titanium vapour upon heating.

2. A gettering system in a cathode ray display tube (100), having a sensitive cathode (118), in which a high nitrogen pressure is created at first switch-on of the cathode, characterized by comprising:
   A. a first holder (120) supporting a first getter metal vapour releasing material capable of releasing barium vapour upon heating; and
   B. a second holder (122) supporting a second getter metal vapour releasing material (128) capable of releasing titanium vapour upon heating.

3. A gettering system of claim 2 in which the second holder (122) is a refractory metal chosen from the group consisting of: molybdenum, niobium, tantalum and tungsten.

4. A gettering system of claim 2 in which the second getter metal vapour releasing material (128) is a mixture of particulate titanium and a particulate metal antisintering agent chosen from the group consisting of: molybdenum, niobium, tantalum and tungsten.

5. A gettering system of claim 4 in which the particulate titanium has a particle size less than 44 $\mu$m.

6. A gettering system of claim 4 in which the particle size of the antisintering agent is less than 44 $\mu$m.

7. A gettering system of claim 4 in which the weight ratio of titanium to antisintering agent is from 19:1 to 1:19.

8. A gettering system in a colour cathode ray display tube (100) having a screen portion (102), a cone portion (104) and a neck portion (106), a metal magnetic screening cap (114) within said cone portion and a tungsten dispenser cathode (118) within said neck portion, a high nitrogen pressure being created within the display tube (100) at first switch-on of the cathode (118), comprising:
   A. a ring shaped stainless steel first holder (120) having an outer side wall, and a bottom wall, said holder supporting a first getter metal vapour releasing material comprising a mixture of a particulate alloy of approximately 50% barium and 50% aluminium together with an approximately equal weight of particulate nickel; and
   B. a ring shaped molybdenum second holder (122) having an outer side wall (124) and a bottom wall (126), said holder supporting a second getter metal vapour releasing material (128) comprising a mixture of particulate titanium and particulate tantalum.

9. A gettering system for a colour cathode ray display tube having a screen portion (102), a cone portion (104) and a neck portion (106), a metal magnetic screening cap (114) within said cone portion (104) and a tungsten dispenser cathcde (118) within said neck portion (106), a high nitrogen pressure being created within the display tube at first switch-on of the cathode, comprising:
   A. a ring shaped stainless steel, first holder (120) having an outer side wall and a bottom wall, said holder supporting a first getter metal vapour releasing material comprising a mixture of a particulate alloy of approximately 50% barium and 50% aluminium together with an approximately equal weight

of particulate nickel; and

B. a ring shaped molybdenum second holder (122) having an outer side wall (124) and a bottom wall (126), said holder supporting a second getter metal vapour releasing material (128) comprising a mixture of particulate titanium having a particle size less than 44 μm and particulate tantalum having a particle size less than 44 μm and particulate tantalum having a particle size less than 44 μm wherein the weight ratio of titanium to tantalum is from 5:1 to 1:5.

**10.** A holder (122) supporting a getter metal vapour releasing material capable of releasing titanium vapour upon heating in which the holder (122) is ring shaped having an outer side wall (124) and a bottom wall (126) and being made from a material chosen from the group consisting of molybdenum, niobium, tantalum and tungsten, the holder supporting a mixture (128) of titanium and an antisintering agent chosen from the group comprising molybdenum, niobium, tantalum and tungsten, both the titanium and antisintering agent being particulate and wherein the weight ratio of titanium to antisintering agent is from 19:1 to 1:19.

Fig.3

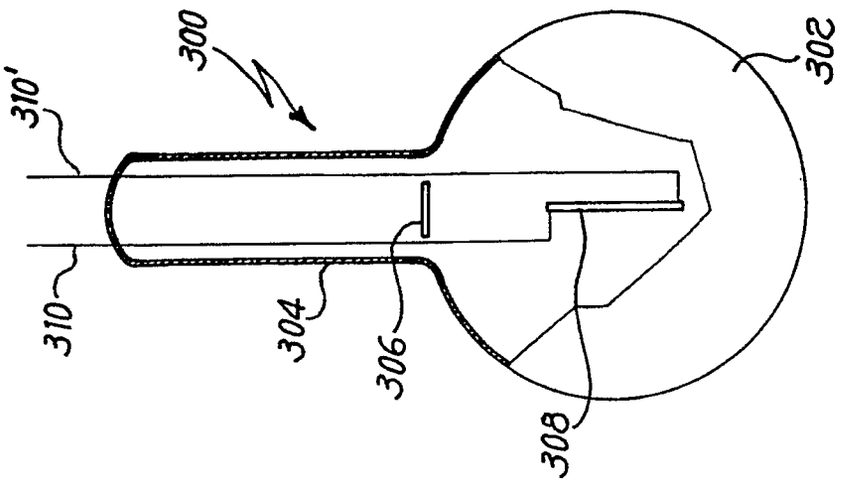



Fig.2

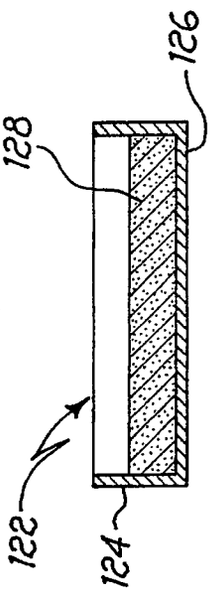
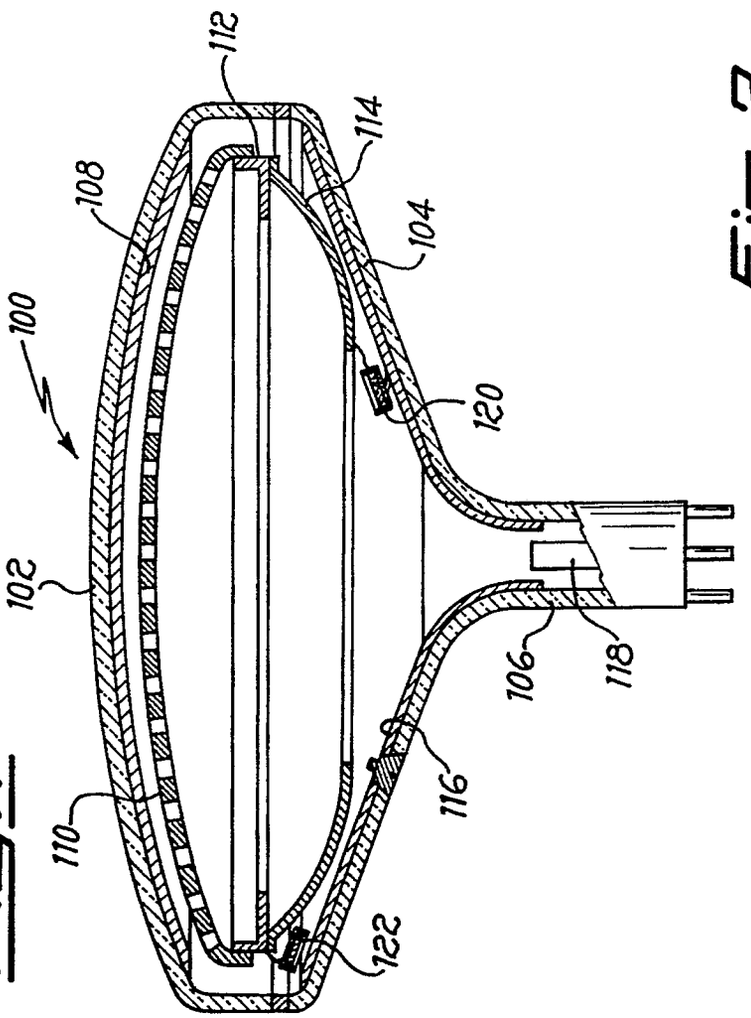
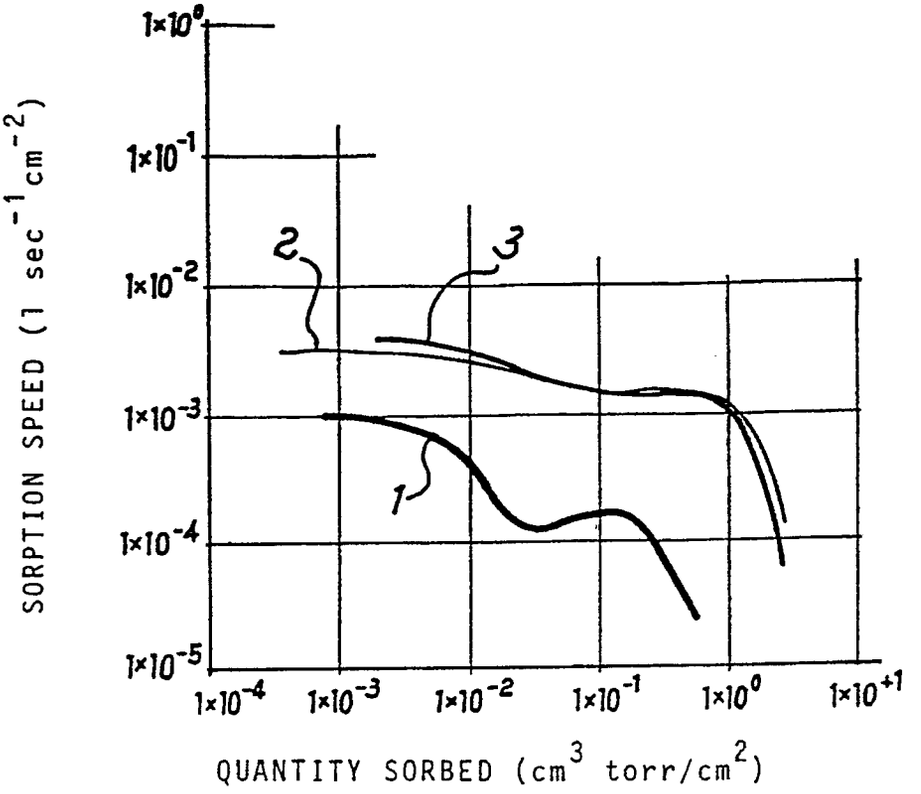



Fig.1

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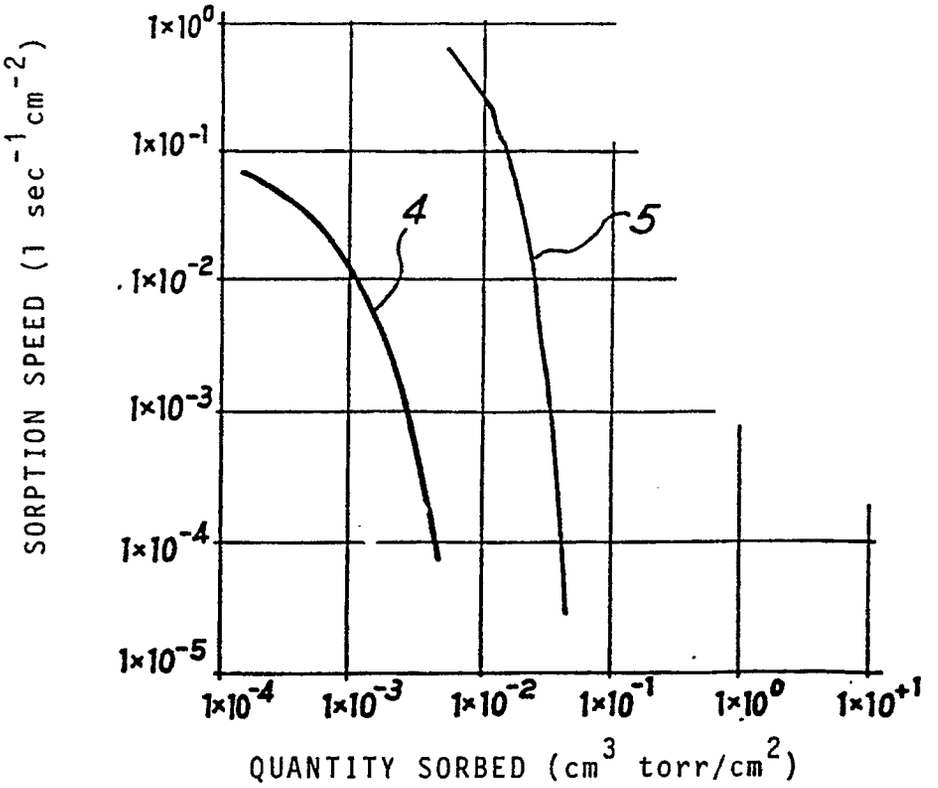
1×10$^{-1}$
1×10$^{-2}$
1×10$^{-3}$
1×10$^{-4}$
1×10$^{-5}$
1×10$^{-4}$
1×10$^{-3}$
1×10$^{-2}$
1×10$^{-1}$
1×10$^{0}$
1×10$^{+1}$
QUANTITY SORBED (cm$^{3}$ torr/cm$^{2}$)
1
2
3

Fig.4


SORPTION SPEED (1 sec$^{-1}$cm$^{-2}$)
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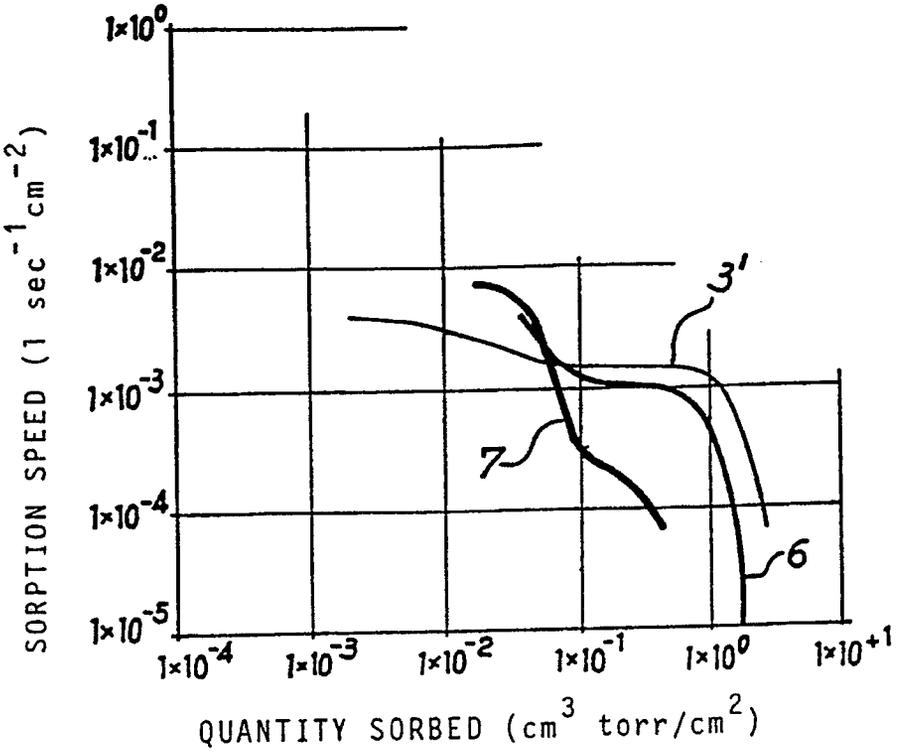
1×10$^{-1}$
1×10$^{-2}$
1×10$^{-3}$
1×10$^{-4}$
1×10$^{-5}$
1×10$^{-4}$
1×10$^{-3}$
1×10$^{-2}$
1×10$^{-1}$
1×10$^{0}$
1×10$^{+1}$
QUANTITY SORBED (cm$^{3}$ torr/cm$^{2}$)
4
5

Fig.5


SORPTION SPEED (1 sec$^{-1}$cm$^{-2}$)
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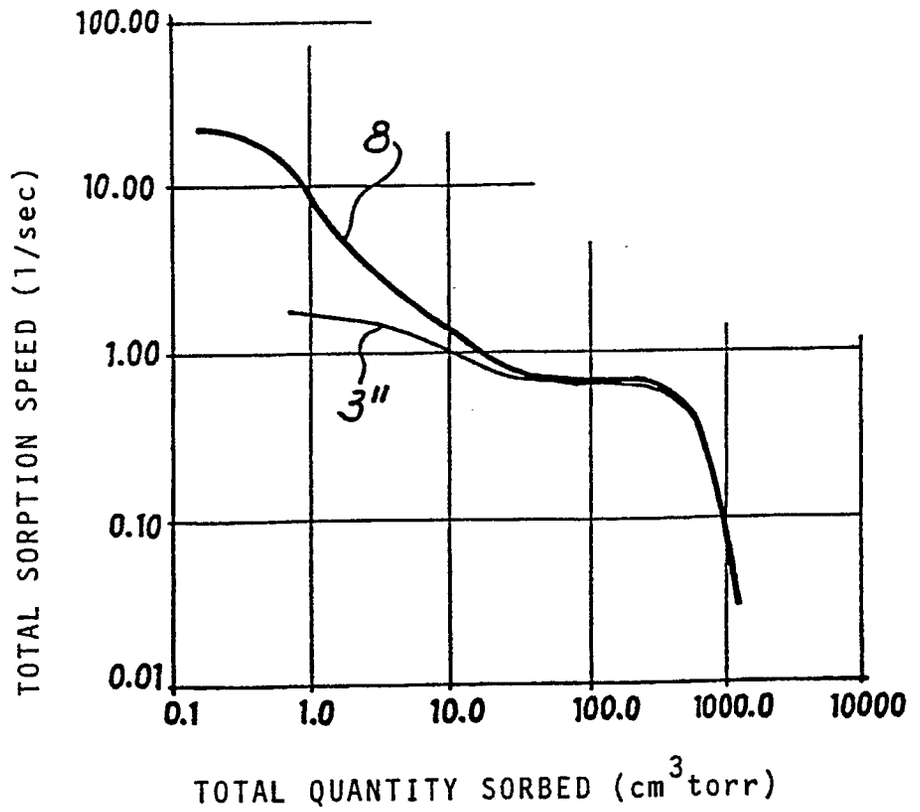
1×10$^{-2}$
1×10$^{-3}$
1×10$^{-4}$
1×10$^{-5}$
1×10$^{-4}$
1×10$^{-3}$
1×10$^{-2}$
1×10$^{-1}$
1×10$^{0}$
1×10$^{+1}$
QUANTITY SORBED (cm$^{3}$ torr/cm$^{2}$)
3'
7
6

Fig.6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10.00
1.00
0.10
0.01
0.1
1.0
10.0
100.0
1000.0
10000
TOTAL QUANTITY SORBED (cm$^{3}$torr)
8
3''

Fig.7