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

(11) Publication number: **0 273 884 B1**

(12) # EUROPEAN PATENT SPECIFICATION

(45) Date of publication of patent specification: **16.10.91**

(51) Int. Cl.5: **H01J 29/94**, H01J 7/18, H01J 9/39

(21) Application number: **87830454.2**

(22) Date of filing: **21.12.87**

(54) **Device and composition for liberating nitrogen gas during the manufacture of a cathode ray tube.**

(30) Priority: **22.12.86 IT 2280886**

(43) Date of publication of application:
06.07.88 Bulletin 88/27

(45) Publication of the grant of the patent:
16.10.91 Bulletin 91/42

(84) Designated Contracting States:
DE FR GB IT NL

(56) References cited:
GB-A- 2 076 586
US-A- 3 768 884

(73) Proprietor: **SAES GETTERS S.P.A.**
Via Gallarate, 215
I-20151 Milano(IT)

(72) Inventor: **Martelli, Daniele**
Viale Jenner, 76
I-20100 Milano MI(IT)

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

EP 0 273 884 B1

Description

This invention relates to a device and composition of matter for the release of nitrogen during the manufacture of a cathode ray tube.

The release of nitrogen during the manufacture of a cathode ray tube is well known in the art. See for example US-A- 3.973.816. It is often preferable to release the nitrogen in two stages. For instance US-A-3.669.567 describes a getter device in which there is first a release of nitrogen before evaporation of barium based getter material and there is a second release of nitrogen during the latter part of barium evaporation.

During the manufacture of a cathode ray tube it is customary to perform a sealing process in which a soft glass "frit" is used to join the face plane portion of tube to the conical portion. US-A-4.052.641 describes a heating schedule in performing the frit seal process as follows:

- 25° to 100° C at 3.5° C per minute
- hold 100° C for 30 minutes
- 100° C to 410° C at 8° C per minute
- hold 410° C for 15 minutes
- cool to 25° C at 4° C per minute

It will be realized that different cathode ray tube manufactures use different frit sealing cycles but it will be realized from the aforesaid that temperatures of more than 400° C such as those up to 450° C may be involved for times of the order of 3 to 4 hours. Before the frit sealing process takes place there is very frequently positioned within the cathode ray tube a color selection mask or shadow mask. The shadow mask is often also used as a location for the getter device. However whatever the position of the getter device it will be appreciated that if the getter device is present during the frit sealing process it will also reach temperatures of more than about 400° C and be exposed to these temperatures for several hours. Unfortunately it has been found that with getter devices having a second source of nitrogen and subjected to the above conditions then, on subsequent flashing of the getter device the second source of nitrogen presents certain disadvantages. A first disadvantage is that the nitrogen is released at an undesirable period of time relative to the evaporation of the barium. Another disadvantage is that the nitrogen is released exceedingly quickly and a nitrogen pressure is created within the CRT outside the range of pressures desired to effectively control the distribution and subsequent sorption capabilities of the barium film. Yet another disadvantage is the fact that the extremely rapid production of nitrogen creates a miniature explosion of the nitrogen releasing material thus producing large quantities of loose particles. These loose particles may enter the gun region of the cathode ray tube causing short circuits of the electrodes or the particles may find their way to the shadow mask and block passage of the image producing electron beams thus degrading picture quality.

It is therefore an object of the present invention to provide a means for the controlled release of nitrogen gas after having been subject to a frit sealing process conditions.

It is another object of the present invention to provide a means for the controlled release of nitrogen without the creation of loose particles after having been subject to a frit sealing process.

It is yet a further object of the present invention to provide a composition for the controlled release of nitrogen after having been subject to the conditions of a frit sealing process.

It is another object of the present invention to provide a capsule containing a composition for the controlled release of nitrogen after having been subject to the conditions of a frit seal process.

The invention provides a composition of matter as described in claim 1 and devices comprising such a composition succeeding in these objects.

These and other objects and advantages of the present invention will become clear to those skilled in the art of reference to the following description and drawings wherein:

Fig. 1 is a cross sectional view of a capsule containing nitrogen releasing material of the present invention; and

Fig. 2 is a cross sectional view of a getter device utilizing a capsule containing nitrogen releasing material of the present invention.

It has surprisingly been found that a mixture of particulate Fe_4N, particulate Ni and particulate Al are capable of providing the controlled release of nitrogen gas after having been subject to a frit sealing process consisting of heating in air at a temperature of up to about 400° C for a period of up to about 4 hours. The particulate Fe_4N can have any particle size distribution which is capable of withstanding the frit process when in admixture with nickel powder

and aluminium powder. Preferably however the particulate Fe_4N has a particle size distribution of:

10-50	percent	by	weight	smaller	than	5μm
60-90	"	"	"	"	"	10μm
83-98	"	"	"	"	"	15μm
92-100	"	"	"	"	"	20μm
97-100	"	"	"	"	"	30μm

The particulate Ni has a particle size distribution of:

0- 9	percent	by	weight	smaller	than	5μm
7-28	"	"	"	"	"	10μm
21-46	"	"	"	"	"	15μm
35-56	"	"	"	"	"	20μm
49-65	"	"	"	"	"	30μm
58-75	"	"	"	"	"	40μm
69-86	"	"	"	"	"	60μm
78-93	"	"	"	"	"	80μm
at least 92	"	"	"	"	"	100μm

The particulate Al may have any particle size distribution which is capable of withstanding a frit seal process and preferably has a particle size distribution of:

4.5- 9	percent	by	weight	smaller	than	40μm
7-16	"	"	"	"	"	60μm
15-25	"	"	"	"	"	80μm
20-45	"	"	"	"	"	100μm
30-60	"	"	"	"	"	150μm
at least 95	"	"	"	"	"	250μm

The weight percentage of the components Fe_4N, Ni and Al can vary over a wide range. It is preferable that the particulate Fe_4N is present at a percentage of from 40 to 80%. At percentage compositions less than 40% there is insufficient Fe_4N to create a suitable pressure within CRT whereas if the percentage is greater than 80% there is an insufficient Ni and Al to cause a sufficiently exothermic reaction to aid the release of N_2. The Ni should be present in a weight percentage of from 20 to 40%. At a percentage weight less than 20% there is insufficient Ni for the exothermic reaction to aid release of N_2 whereas if the percentage Ni is higher than 40% there is a risk of too much heat being produced with an excessive speed in the release of N_2. The Al should be present in a weight percentage of from 5 to 20%. If the percentage weight of Al is less than 5% there is insufficient Al present to produce sufficient heat in the exothermic reaction to cause release of N_2 from the Fe_4N, whereas if more than 20% of Al is present then the exothermic reaction may take place too violently causing excessive speed in the release of N_2. Preferably the nitrogen releasing composition comprises 60% Fe_4N, 30% Ni and 10% Al.

In the broadest aspects of the present invention the ratio of Ni to Al can vary widely but generally is chosen to produce the maximum amount of heat when the Ni is combined with the Al. The maximum amount of heat is generally produced within weight ratios of Ni to Al of 1 : 10 to 10 : 1. An ideal ratio of Ni to Al is about 3 : 1.

In the broadest aspects of the present invention the ratio of Fe_4N to the combined weight of Ni and Al is chosen to release substantially all the nitrogen from the Fe_4N within a very short period of time generally less than five and preferably less than three seconds. The Fe_4N is generally present in the composition within a weight ratio of 1 : 5 to 5 : 1 and preferably 1 : 2 to 2 : 1 compared to the combined weight of Ni and Al.

In use the composition is preferably adopted as a second source of nitrogen in a N_2 doped getter, and is preferably contained within a holder such as a capsule. The capsule may be of any suitable material for holding the mixture for instance ceramic. Preferably it is of metal. Even more preferably it is of nichrome or stainless steel. Any suitably shaped holder may be used but it is preferably in the form of a hollow cylinder closed at one end.

Such a N_2 releasing capsule for use in a so called "delayed nitrogen doped getter" will now be described with reference to Fig. 1 and Fig. 2 wherein 102 is a nitrogen gas releasing capsule comprising a holder 104 in the form of a cylinder 106 integrally closed at one end by means 108. In this particular case the open end 110 is horizontally flared in the form of a flange 112. Flange 112 has present a series of pips for subsequent projection welding for support purposes 114, 114', 114".

Fig. 2 illustrates the use of a nitrogen gas releasing capsule as a delayed nitrogen doped gas source or second gas source in a nitrogen doped getter. The evaporable getter device 202 comprises a ring shaped holder 204 supporting an evaporable getter metal vapour releasing material 206. Evaporable getter material generally comprises a barium aluminium alloy of composition approximately $BaAl_4$ in admixture with approximately an equal weight of Ni powder. In addition there is usually incorporated a small amount of Fe_4N as a first source of N_2. This mixture is any mixture known in the art, see for example US-A- 4.077.899 which is capable of withstanding the frit process. In this particular embodiment the evaporable getter device 202 further comprises a reflecting shield 208 which serves to hold a ceramic disk 210 to prevent a heated getter device from cracking the nearby glass wall of a cathode ray tube. A nitrogen gas releasing capsule 212 identical in all respects to capsule 102 shown in Fig. 1 is projection welded to the centre portion of reflecting shield 208.

The term "composition of matter for the release of nitrogen gas" as used in the specification and claims herein is meant to include the composition prior to nitrogen gas release.

Furthermore the term "getter metal vapor releasing material" as used in the specification and claims herein is meant to include both the material prior to and after getter metal vapor 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 operating tube 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.

The compositions of the present invention have the property of not releasing particles even after being heated in air at temperatures of 100 to 450°C for a period of two hours.

EXAMPLE 1

This example is designed to show the behaviour of a prior art composition of matter for the release of N_2 gas when held in a hollow cylinder of stainless steel after having been subjected to a frit sealing process in air. A powder mixture is prepared comprising 60% by weight of Fe_4N having a preferred particle size distribution as described above. The mixture further comprises 30% of powdered titanium having a particle size distribution of

2-20	percent	by	weight	smaller	than	10µm
15-40,2	"	"	"	"	"	20µm
30-70	"	"	"	"	"	30µm
50-90	"	"	"	"	"	40µm
80-92	"	"	"	"	"	50µm
at least 90%	"	"	"	"	"	60µm

and 10% of particulate Al having a particle size distribution as described above. About 43 mg of the mixture is placed in a hollow cylinder and is subjected to 450° C for 2 hours in air. The cylinders are then placed in an evacuated system and heated to produce a release of N_2. A violent reaction occurs in which particles of the composition are ejected into the system.

EXAMPLE 2

This example was carried out under the same conditions as Example 1 with the sole exception that in the composition for release of nitrogen gas the titanium was substituted with nickel having the particle size distribution described in US-A- 4.077.899 where its use is disclosed to avoid excessive exothermic reactions. This distribution was as follow:

0%	by	weight	smaller	than	15μm
0.1-0.2%	"	"	"	"	20μm
3-10%	"	"	"	"	30μm
22-60%	"	"	"	"	40μm
70-96%	"	"	"	"	50μm
86-99%	"	"	"	"	55μm
97-100%	"	"	"	"	65μm

Also in this case a violent reaction takes place in which particles of the composition are ejected into the system.

EXAMPLE 3

This Example is designed to show the behaviour of a composition of matter for the release of nitrogen gas of the present invention held in a capsule after having been subjected to a frit sealing process. A powder mixture is prepared having exactly the same weight composition and particle size ranges except that the Ni is replaced by Ni having a particle size distribution according to the Ni distribution as described above. Getter capsules are exposed to air at exactly the same temperature and for exactly the same time as in Example 1. When the capsules are caused to release N_2 in an evacuated system the N_2 is found to be released in a controlled manner without the expulsion of any loose particles from the capsules.

Although the invention has been described in considerable detail with reference to certain preferred embodiments and applications it is intended that variations and modifications can be made within the spirit and scope of the claims.

Claims

1. A composition of matter for the release of nitrogen gas comprising:
A. particulate Fe_4N,
B. particulate Ni, having a particle size
distribution of:

0- 9	percent	by	weight	smaller	than	5μm
7-28	"	"	"	"	"	10μm
21-46	"	"	"	"	"	15μm
35-56	"	"	"	"	"	20μm
49-65	"	"	"	"	"	30μm
58-75	"	"	"	"	"	40μm
69-86	"	"	"	"	"	60μm
78-93	"	"	"	"	"	80μm
at least 92	"	"	"	"	"	100μm

C. particulate Al.

2. The composition of claim 1, wherein the ratio of Ni to Al is that which releases the maximum amount of heat when they are combined; and wherein the Ni and Al are present in an amount sufficient to produce heat which releases substantially all the nitrogen from the Fe_4N.

3. A composition of matter of claim 1, wherein the weight ratio of Ni to Al, namely B : C is 1 : 10 to 10 : 1; and wherein the weight ratio of Fe_4N to the combined weight of Ni and Al namely A : (B + C) is 1 : 5 to 5 : 1.

4. A composition of matter of claim 1 for the controlled release of nitrogen gas after being subjected to heating in air at a temperature of 100 to 450° C for a period of about 2 hours comprising an intimate mixture of:
A. particulate Fe_4N having a particle size distribution of:

10- 50	percent	by	weight	smaller	than	5μm
60- 90	"	"	"	"	"	10μm
83- 98	"	"	"	"	"	15μm
92-100	"	"	"	"	"	20μm
97-100	"	"	"	"	"	30μm

B. particulate Ni having a particle size distribution according to claim 1,
C. particulate Al having a particle size distribution of:

4,5- 9	percent	by	weight	smaller	than	40μm
7-16	"	"	"	"	"	60μm
15-25	"	"	"	"	"	80μm
20-45	"	"	"	"	"	100μm
30-60	"	"	"	"	"	150μm
at least 95	"	"	"	"	"	250μm

5. A nitrogen gas releasing capsule comprising:
   I. a holder; and
   II. a composition of matter according to claim 1
   in which the particulate Al is supported by said holder.

6. A nitrogen gas releasing capsule of claim 5 in which the weight percentages of A, B and C are in the ranges:
   A. from 40 to 80%
   B. from 20 to 40%
   C. from 5 to 20%.

7. A nitrogen gas releasing capsule for use in a delayed nitrogen doped getter for the controlled release of a second amount of nitrogen gas after being subjected to heating in air at a temperature of 100 to 450° C for a period of 2 hours comprising:
   I. a hollow cylinder of stainless steel closed at one end; and
   II. a composition of matter according to claim 4, compressed within said cylinder, wherein
   the weight ratio of B : C is 1 : 10 to 10 : 1;
   and
   the weight ratio of A : (B + C) is 1 : 2 to 2 : 1

8. An evaporable getter device incorporating a composition of matter of claim 1.

9. An evaporable getter device incorporating a capsule comprising the composition of matter of claim 4.

Revendications

1. Une composition de matière pour la libération d'azote gazeux, comprenant :
   A. Fe_4N particulaire,
   B. Ni particulaire, ayant une répartition granulométrique de :

0- 9	pour cent en poids					
	de dimension inférieure à					5 µm
7-28	"	"	"		"	10 µm
21-46	"	"	"		"	15 µm
35-56	"	"	"		"	20 µm
49-65	"	"	"		"	30 µm
58-75	"	"	"		"	40 µm
69-86	"	"	"		"	60 µm
78-93	"	"	"		"	80 µm
au moins 92	"	"	"		"	100 µm

   C. Al particulaire.

2. La composition selon la revendication 1, dans laquelle le rapport de Ni à Al est celui qui libère la quantité maximale de chaleur lorsqu'ils sont combinés ; et dans laquelle Ni et Al sont présents dans une quantité suffisante pour produire de la chaleur qui libère sensiblement tout l'azote à partir de Fe_4N.

3. Une composition de matière selon la revendication 1, dans laquelle le rapport en poids de Ni à Al, à savoir B : C, est de 1 : 10 à 10 : 1 ; et dans laquelle le rapport en poids de Fe_4N au poids combiné de Ni et Al, à savoir A : (B + C), est de 1 : 5 à 5 : 1.

4. Une composition de matière selon la revendication 1 pour la libération contrôlée d'azote gazeux, après

avoir été soumise à un chauffage dans l'air à une température de 100 à 450 °C, pendant une période d'environ 2 heures, comprenant un mélange intime de :

A. Fe_4N particulaire ayant une répartition granulométrique de :

10-50	pour cent en poids de dimension inférieure à	5 µm
60-90	" " " " "	10 µm
83-98	" " " " "	15 µm
92-100	" " " " "	20 µm
97-100	" " " " "	30 µm

B. Ni particulaire ayant une répartion granulométrique selon la revendication 1 :

C. Al particulaire ayant une répartion granulométrique de :

4,5- 9	pour cent en poids de dimension inférieure à	40 µm
7 - 16	" " " " "	60 µm
15 - 25	" " " " "	80 µm
20 - 45	" " " " "	100 µm
30 - 60	" " " " "	150 µm
au moins 95	" " " " "	250 µm.

5. Une capsule libérant de l'azote gazeux comprenant :

I. un support ; et

II. une composition de matière selon la revendication 1, dans laquelle l'Al particulaire est supporté par ledit support.

6. Une capsule libérant de l'azote gazeux selon la revendication 5, dans laquelle les pourcentages en poids de A, B et C se situent dans les plages :

A. de 40 à 80 %

B. de 20 à 40 %

C. de 5 à 20 %

7. Une capsule libérant de l'azote gazeux destinée à être utilisée dans un dégazeur dopé à l'azote, différé, pour la libération contrôlée d'une deuxième quantité d'azote gazeux, après avoir été soumise à un chauffage dans l'air à une température de 100 à 450 °C pendant une période de 2 heures, comprenant :

I. un cylindre creux en acier inoxydable, fermé à une extrémité : et

II. une composition de matière selon la revendication 4. comprimée à l'intérieur dudit cylindre, dans laquelle :

- le rapport en poids de B : C est de 1 : 10 à 10 : 1 ; et
- le rapport en poids de A : (B + C) est de 1 : 2 à 2 : 1.

8. Un dispositif de dégazage évaporable incorporant une composition de matière de la revendication 1.

9. Un dispositif de dégazage évaporable incorporant une capsule comprenant la composition de matière de la revendication 4.

Patentansprüche

1. Zusammensetzung zur Freisetzung von Stickstoffgas, enthaltend:
   A. teilchenförmiges Fe_4N
   B. teilchenförmiges Ni mit einer Teilchengrößenverteilung von:

0- 9	Gewichtsprozent	kleiner	als	5 µm
7-28	"	"	"	10 µm
21-46	"	"	"	15 µm
35-56	"	"	"	20 µm
49-65	"	"	"	30 µm
58-75	"	"	"	40 µm
69-86	"	"	"	60 µm
78-93	"	"	"	80 µm
wenigstens 92	"	"	"	100 µm

   C. teilchenförmiges Al.

2. Zusammensetzung nach Anspruch 1, dadurch gekennzeichnet, daß das Verhältnis von Ni zu Al so ist, daß es die maximale Menge an Wärme freisetzt, wenn sie vereinigt werden und worin das Ni und Al in ausreichender Menge vorliegen, um Hitze zu erzeugen, die praktisch den gesamten Stickstoff vom Fe_4N freisetzt.

3. Zusammensetzung nach Anspruch 1, dadurch gekennzeichent, daß das Gewichtsverhältnis von Ni:Al, nämlich B:C 1:10 bis 10:1 beträgt und worin das Gewichtsverhältnis von Fe_4N zu dem vereinigten Gewicht von Ni und Al, nämlich A:(B + C) 1:5 bis 5:1 beträgt.

4. Zusammensetzung nach Anspruch 1 zur gesteuerten Freisetzung von Stickstoffgas nach Erhitzen an der Luft bei einer Temperatur von 100 bis 450 °C für eine Zeitspanne von etwa 2 Stunden, enthaltend ein inniges Gemisch von:
   A) teilchenförmigem Fe_4N mit einer Teilchengrößenverteilung von:

10- 50	Gewichtsprozent	kleiner	als	5 µm
60- 90	"	"	"	10 µm
83- 98	"	"	"	15 µm
92-100	"	"	"	20 µm
97-100	"	"	"	30 µm

   B) teilchenförmigem Ni mit einer Teilchengrößenverteilung gemäß Anspruch 1,
   C) teilchenförmigem Al mit einer Teilchengrößenverteilung von:

4,5- 9	Gewichtsprozent	kleiner	als	40	µm
7-16	"	"	"	60	µm
15-25	"	"	"	80	µm
20-45	"	"	"	100	µm
30-60	"	"	"	150	µm
wenigstens 95	"	"	"	250	µm

5. Stickstoffgas-freisetzende Kapsel enthaltend:
   I. einen Halter und
   II. eine Zusammensetzung nach Anspruch 1,
   worin das teilchenförmige Al vom Halter getragen wird.

6. Stickstoffgas-freisetzende Kapsel nach Anspruch 5, dadurch gekennzeichne, daß die Gewichtsprozent an A, B und C in folgenden Bereichen liegen:
   A 40 bis 80%
   B 20 bis 40%
   C 5 bis 20%.

7. Stickstoffgas-freisetzende Kapsel zur Verwendung in einem verzögerten stickstoffdotierten Getter zur gesteuerten Freisetzung einer zweiten Menge von Stickstoffgas nach Erhitzen an Luft bei einer Temperatur von 100 bis 450°C für eine Zeitspanne von 2 Stunden, enthaltend:
   I. einen Hohlzylinder aus rostfreiem Stahl, der an einem Ende geschlossen ist, und
   II. eine Zusammensetzung nach Anspruch 4, die in diesem Zylinder verpresst ist, und worin das Gewichtsverhältnis von B:C 1:10 bis 10:1 und das Gewichtsverhältnis von A:(B+C) 1:2 bis 2:1, beträgt.

8. Verdampfbare Gettervorrichtung, enthaltend eine Zusammensetzung nach Anspruch 1.

9. Verdampfbare Gettervorrichtung enthaltend eine Kapsel mit der Zusammensetzung von Anspruch 4.

Fig. 1

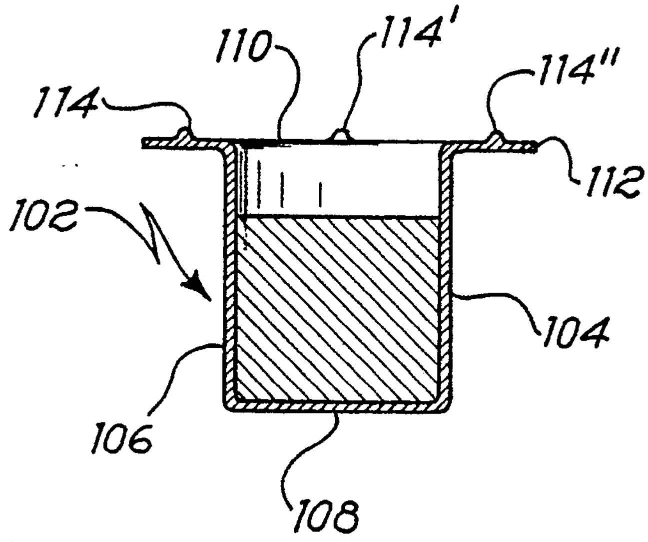

Fig. 2