United States Patent

La Grouw

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[54] GLASS FOR TELEVISION DISPLAY CATHODE-RAY TUBES

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[30] **Foreign Application Priority Data**

Oct. 28, 1968 Netherlands 6815397

[52] **U.S. Cl.** **106/53**

[51] **Int. Cl.** **C03c 3/04,** C03c 3/10, H01i 29/10

[58] **Field of Search** ..... 106/53; 313/89; 252/301.4 F

[56] **References Cited**

UNITED STATES PATENTS

2,856,303	10/1958	Armistead	106/53
3,422,298	1/1969	De Gier	106/53

FOREIGN PATENTS OR APPLICATIONS

1,123,857	8/1968	Great Britain	106/53

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[57] **ABSTRACT**

Glass for envelopes of television display cathode-ray tubes, particularly screen glass for color television, which transmits at most 0.5 mr/h of X-ray radiation at an acceleration voltage of 40 to 45 k. volt, and which has a composition in percent by weight:

SiO_2	58–67	PbO	2–7
Li_2O	0–1	MgO	0–3
Na_2O	2–3	Al_2O_3	1–4
K_2O	11–14	$-As_2O_3 \pm Sb_2O_3$	0.3–0.7
CaO	3–4.5	CeO_2	0.05–0.6
BaO	11–14		

2 Claims, No Drawings

GLASS FOR TELEVISION DISPLAY CATHODE-RAY TUBES

The invention relates to glass for an envelope of a television display cathode-ray tube, particularly glass for the face-plate of the tube.

Particular requirements are imposed on glass for envelopes of cathode-ray tubes for the display of colored television images as compared with that for the display of monochrome television images. Such special glasses are known, for example, from the British Pat. specification No. 1,123,857 the composition of which in percent by weight lies within the following range of compositions:

SiO_2	62–66	BaO	11–14
Li_2O	0–1	MgO	0–3
Na_2O	7–8.5	PbO	0–2
K_2O	6.5–9	Al_2O_3	1–4
CaO	2–4.5	As_2O_3+ Sb_2O_3	0.3–0.7
CeO_2	0.05–0.3		

The special requirements which, as compared with glass for the envelopes for monochrome display, are imposed on glass for envelopes for color display, are connected with differences in the manufacture and in the use of these tubes. In the first place, the glass components of envelopes for color display unlike those for the monochrome display envelopes cannot be sealed by fusing them together but must be connected together with the aid of an enamel. This is connected with the fact that a shadow mask is provided in these tubes, which mask determines the path of the required three electron beams. Furthermore, an extremely fine grating-like pattern of three different luminescent substances corresponding to the apertures of the shadow mask is provided on the inner side of the screen. The requirements relative to the maximum permissible distortion of the glass are in this case much more stringent in connection therewith than for glass of envelopes for monochrome display. In addition, the temperature at which the tube must be heated during evacuation and sealing must be approximately 20° higher and the heat treatment is of a longer duration than for the tubes for monochrome display.

The glasses within the above-mentioned range are eminently satisfactory in a technological respect relative to the softening point, the quality and the thermal coefficient of expansion. For the acceleration voltages until recently used on the electron guns, the absorption of these glasses for the X-ray radiation generated during operation as a result of the electron bombardment on the glass and on the shadow mask is sufficiently great. This even applies when the tube is built in in a cabinet in direct vision construction, thus without a protective cover glass.

The requirement up till now had been that the intensity of the transmitted X-ray radiation may be at most 0.5 milliroentgen per hour (mr/h) at a maximum thickness of 11 mm of the screen glass, an acceleration voltage of 27.5 k. volt and an anode current of 300 μA in a television display tube.

There is, however, a tendency to still further increase the margin of safety to X-ray radiation transmitted by television display tubes. There is a need of a kind of glass in which at most 0.5 mr/h is transmitted at an acceleration voltage of 35 k.volt. The above-described glasses then no longer have a sufficiently high absorption and do not satisfy the stricter safety requirements. For reasons of a technological nature, the thickness of the screen cannot be increased much further than 11 mm. To obtain a sufficiently high absorption while using a glass within the above-mentioned range of compositions, the screen should be thicker by as much as 2.5 mm.

For a satisfactory processing of the glass and moulding face-plates thereof, it is necessary that the temperature dependence of the viscosity is not too great. In practice this means that the temperature difference between the softening point, which is the temperature at which the viscosity of the glass is $10^{7.6}$ poises, and the annealing point, which is the temperature at which the viscosity of the glass is $10^{13.4}$ poises, must be at least 190° C.

In connection with the conventional manufacturing technique and the very stringent requirements which are imposed on the maximum permissible distortion of the glass components during manufacture of the tube, it is necessary that glass for a color display tube has an annealing point which is not lower than 485° C.

Finally it is of importance that a glass for a color television display tube has approximately the same coefficient of expansion as that of the known glasses (approximately 99×10^{-7} between 30° and 300° C.), so that a better match is obtained with the existing glasses and metal components which must be sealed on or in respectively.

In the kind of glass according to the present invention, a content of PbO is present with an approximately equal BaO content relative to the known glass. It is by no means surprising in itself that the absorption of X-ray radiation is increased as a result thereof. It was, however, not obvious that it was possible to maintain the physical properties of the glass at the same level by means of a few other modifications. Furthermore, it is also known (from U. K. Pat. specification No. 664,769) that no discoloration occurs on the glass of the face-plate due to electron bombardment, provided that the glass contains CeO_2 and provided that the glass contains no more than 1 percent of readily reducible oxides. However, the glass according to the invention which does not satisfy the last-mentioned requirement owing to its content of PbO, does not discolor under the influence of the electron bombardment.

The range of glass compositions according to the present invention is characterized by the following limits in percent by weight:

SiO_2	58–67	PbO	2–7
Li_2O	0–1	MgO	0–3
Na_2O	2–3	Al_2O_3	1–4
K_2O	11–14	As_2O_3+	0.3–0.7
CaO	3–4.5	CeO_2	0.05–0.6
BaO	11–14		

The softening point of these glasses lies between 690° and 710° C.; the annealing point between 485° and 510° C. and the thermal coefficient of expansion is approximately 97 to 100×10^{-7} between 30° and 300° C. The glasses according to the invention amply satisfy the above-mentioned requirement of transmitting at most 0.5 mr/h at an acceleration voltage of 35 K.volt; it was found that this amount was not yet reached at an acceleration voltage of even 44 to 45 k.volt when using these glasses. The electric resistance thereof is at least $10^{9.4}$ ohm. cm and at least $10^{7.5}$ ohm.cm at 250° and 350°, respectively, while these values are $10^{8.5}$ and $10^{6.7}$ ohm.cm for the above-mentioned known glasses.

The following glass is an example of a glass suitable for the relevant purpose. It is obtained in a manner which is common practice in glass technology by melting the relevant oxides or compounds which are converted into the oxides.

SiO_2	59% by weight	PbO 6.3% by weight.
Li_2O	0.4% by weight	Al_2O_3 2.2% by weight.
Na_2O	2.4% by weight	Sb_2O_3 0.3% by weight.
K_2O	12.7% by weight	CeO_2 0.5% by weight.
CaO	3.6% by weight	Softening point 705°C.
BaO	12.3% by weight	annealing point 502°C.
		coefficient of expansion (30–300° C.) 97×10^{-7}
		$\log \rho$ 250°C. = 10.3
		$\log \rho$ 350°C. = 8.2.

What is claimed is:

1. Glass for envelopes of television display cathode-ray tubes, particularly intended for the face-plate of the tube, consisting essentially of the following in percent by weight:

SiO_2	58–67	PbO	2–7
Li_2O	0–1	MgO	0–3
Na_2O	2–3	Al_2O_3	1–4
K_2O	11–14	As_2O_3+ Sb_2O_3	0.3–0.7
BaO	11–14		

wherein said glass transmits less than 0.5 mr/h of X-ray radiation at an electron acceleration voltage up to 45 k.volts. through a thickness of said glass of 11 mm.

2. Glass as claimed in claim 1, consisting essentially of the following in percent by weight:

SiO_2	59
Li_2O	0.4
Na_2O	2.4
K_2O	12.7
CaO	3.6
BaO	12.3
PbO	6.3
Al_2O_3	2.2
Sb_2O_3	0.3
CeO_2	0.5

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,663,246 Dated May 16, 1972

Inventor(s) COENRAAD MARIA LA GROUW

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

In the Index, under "[30] Foreign Application Priority Data" the priority date should read -- Oct. 29, 1968 --.

Column 2, line 35, "As_2O_3 +" should read -- As_2O_3 + Sb_2O_3 --.

In Claim 1, on the line befor "BaO 11-14" insert the following:

-- CaO 3 - 4.5 CeO_2 0.05 - 0.6 --.

Signed and sealed this 1st day of May 1973.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents

Signed and sealed this day of , 1972.

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