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RADIATION DAMAGE OF GLASS BY ULTRA-VIOLET RAY

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I. Introduction

In the course of development of high power mercury discharge lamps in the factory, stress built-up has been observed in protection bulbs of the lamps after long periods of lighting. In some cases, fracture of bulbs took place spontaneously.

It has been found that the stress was caused neither by the over-heating of the bulbs nor by the electrolysis in their glass, but by the change in glass structure induced directly by ultra-violet irradiation.

The present study has been undertaken to elucidate the machamism of the stress build-up in the glasses caused by the ultra-violet irradiation and to find the methods for preventing the fracture of mercury lamps. Relations between the stress build-up and the chemical composition of glasses has been investigated in detail.

II. Observations of fractured glass bulbs

The fractured bulb, whose inner suface was subjected to severe ultra-violet irradiation for a long time, is illustrated in Photograph 1. Many fine cracks are seen at the inner surface. Photoelastic observation of a cross section of a fragment of the bulb (Te;ex glass; SiO_2 80, B_2O_3 13, Na_2O 4, K_2O 1 and

55

Al_2O_3 2 in weight %) showed the presence of concentrated tension near the inner surface of the bulb as illustrated in Photograph 2. Density increase due to the volume contraction near the inner surface was determined to be 6 x 10^{-3} g/cm^3 by the sink-float method.

In a fractured bulb made of 96 % silica glass, the stressed layer was thicker than in the case of the Tefex glass, as illustrated in Photograph 3, probably due to its better ultra-violet transmission. By heating, the stresses induced in these glasses were released at rather lower temperatures than the annealing points as shown in Figures 1 and 2.

III. Effect of ultra-violet irradiation on various commercial glasses

Various kinds of commercial glasses were irradiated by a 400 W silica glass mercury lamp for 1,000 hr. Specifications of the glasses are given in Table 1. Stresses at the irradiated surfaces and thicknesses of the stressed layers are shown in Table 2. Some of the photoelastic patterns of the stressed layers are illustrated in Photograph 4.

The stress build-up was observed only in some kinds of borosilicate glasses. In the borosilicate glasses containing PbO (Glass 5) or ZnO, (Glass 8), the stress was weak or not detected. For the ultra-violet transmitting borosilicate glass (Glass 8), the stressed layer was considerably thick.

IV. Thermal release of stress in glass induced by ultra-violet irradiation

Thermal release of the stress at various temperatures investigated for fragments of the fractured Terex glass bulb are shown in Figure 3. The stress release was found to occur even at the temperature as low as 250° C, and the stress disappeared completely in a short time at 400° C, which is far below the annealing point of the glass (about 545° C) i.e. the temperature at which the ordinary stress in the glass is released by the viscous flow.

It was concluded from these results that there are several kinds of mechanisms of stress release and that experimental activation energy for the stress release observed in the present experiment was less than 30 kcal/mol (1.3 eV), which is far less than that for its viscous flow (about 100 kcal/mol: 4.3 eV). The value of 1.3 eV is also less than the energy of ultra-violet ray (3 eV or more).

V. Some preperties of glass bulbs damaged by ultra-violet irradiation

Properties of the following two borosilicate glass bulbs, both damaged by the long use as protection bulbs of mercury discharge lamps, were investigated; the Terex glass bulb, made by Tokyo-Shibaura Electric Co., Ltd., used for an ordinary mercury discharge lamp (the sample A) and the Pyrex glass bulb, made by Corning Glass Works, used for a mercury: Tl discharge lamp. The spectral energy distribution of these lamps are shown in Figure 4.

The stressed layer of the sample A showed fluorescence by excitation with the 365 mμ line (Photograph 5) and thermal glow by heating (Figure 5). The stressed layer of the sample B showed neither fluorescence nor thermal glow.

The stressed layers of these samples showed different ESR signals (Figure 6). By heating, both of them showed a thermally released current considerably larger then those reported for the X-or γ-irradiated glasses (Figure 7).

VI. Effects of γ - and ultra-violet irradiation on commercial borosilicated glasses

Effects of γ - and ultra-violet irradiation on commercial Terex and Kovar sealing glasses were compared. In the case of γ-irradiation with dose rate of 5×10^5 r/hr, density change was not detected by the sink-float method for both of the glasses. In the case of the ultra-violet irradiation, stress build-up near the surface of the glasses were found as illustrated in Photographs 6a and 6b, which suggest that there is an increase in density at the portion near the surfaces of the samples.

Thermal glow, ESR signals and blackening for the two glasses are shown for comparison in Figures 8, 9 and 10, respectively. They were more conspicuous for the glasses subjected to the γ-irradiation than to the ultra-violet irradiation. These results would sugests that density increase or stress build-up are not directly related to the formation of the centers of thermal glow, ESR or blackening (colour centers).

VII. Stress build-up in binary borate glasses by ultra-violet irradiation

Effects of ultra-violet irradiation on binary borate glasses were investigated. Compositions of these glasses are given in Table 3. After irradiation for 1,000 hrs by a 400 W silica glass mercury lamp, stress build-up at the irradiated surfaces were examined. It was detected only for the binary glasses with alkali oxides. The results are summerized in Table 4. Some results of the photoelastic observations are illustrated in Photograph 7. In binary alkali-germanate glasses, the stress build-up was not observed even after irradiation for 1,000 hr.

VIII. Stress build-up in alkali-borosilicate glasses by ultra-violet irradiation

Effects of kind and amount of alkali oxides on stress build-up in ternary Na_2O- or K_2O-B_2O_3-SiO_2 glasses are shown in Figure 11. The addition of Li_2O to the ternary Na_2O-B_2O_3-SiO_2 glasses was found to suppress the stress build-up considerably (Figure 10). The amount of stress decreased with increase in Na_2O or K_2O contents.

Effects of doping ions such as the Ce or As ions, which absorb the ultra-violet ray strongly, into the ternary Na_2O-B_2O_3-SiO_2 glasses on the stress build-up were also examined (Figure 12). The amount of stress was found to increase with increase in the contents of these ions.

IX. Structure of irradiated surface of glasses observed by electron microscope

Preliminary observations were made on irradiated surfaces of various glasses by an electron microscope. The surfaces were found to become, in some cases, inhomogeneous by the ultra-violet irradiation as illustrated in Photograph 8.

X. Discussion

Experimental results described above showed that the stress build-up occurs only for the glasses containing B_2O_3. The presence of alkali oxides appeared to contribute to this phenomenon, even in little amount such as in the 96 % silica glass. Ultra-violet absorbing ions in glasses, such as Ce or As, also appeared to have some effects on the stress build-up. The experimental activation energy of the thermal release of the stresses seemed to be comparable to those of diffusion of alkali ions or of electric conduction in glasses.

Following the authors' opinion, one of the possible mechanisms of stress build-up in glasses is as follows; The electrons of the non-bridging oxygen ions ejected by photoelectric effect and holes or trapped electrons are formed. Then, under the influence of the electric field thus produced, alkali ions migrate causing structural change of the glasses. This structural change is thought to be the compaction of the glass network, consisting of oxygen polyhedrons such as BO_3 triangles which originally pack loosely. The change of co-ordination number of boron ($3 \rightleftarrows 4$) may be responsible for this compaction.

The efficient methods to prevent the fracture of bulbs of mercury lamps are, to use the borosilicate glasses containing some amount of PbO or ZnO, to lessen the amounts of ions in glass which absorb ultra-violet ray and to heat the bulbs at 400° C certain intervals.

Anyway the experiments are in progress and many fundamental and detailed studies may be required for the com understanding of this phenomenon.

References

K. Ooka and T. Kishii;

J. Ceram. Assoc. Japan, 72 (11-1) 193 (1964);

73 (4) 108 (1965);

73 (7) 147 (1965);

73 (8) 168 (1965);

Table 1 Chemical Compositions of Commercial Glasses

Glass No.		SiO_2	B_2O_3	Al_2O_3	Na_2O	K_2O	Li_2O	PbO	BaO	CaO	MgO	ZnO	As_2O_3	
1.	Silica glass (transparent)	100												
2.	Borosilicate glass	80.6	12.3	2.5	4.5								0.1	
3.	Borosilicate glass with Li_2O	80.6	12.5	2.4	3.9		0.5						0.1	
4.	Borosilicate glass	78.3	14.8	1.5	5.3								0.15	
5.	Lead borosilicate glass	71.2	16.8	2.0	4.5			6.0					0.2	
6.	Barium borosilicate glass	65.4	18.0	7.5	1.9	3.0	1.0		3.0				0.15	
7.	Barium borosilicate glass	63.0	19.4	7.0	1.5	4.0	0.8		3.0					
8.	Borosilicate glass with ZnO	72.4	15.5	2.2	7.6							2.3		
9.	Borosilicate glass with Ce_2O_3	68.5	15.5	2.3	3.4		0.2	10.0						Ce_2O_3 0.5
10.	30% lead glass	56.5		1.4	4.5	7.6		29.5					0.2	
11.	Barium glass	67.6		4.5	7.0	6.8	0.5		13.0				0.2	Sb_2O_3 0.5
12.	Soda lime glass	67.6		2.0	18.4					7.3	4.2		0.3	
13.	Commercial plate glass	72.0		2.0	13.5					8.0	4.0		0.2	

Table 2. Stress at surfaces and thickness of stressed layers measured after 500 and 1000 hours irradiation.

Glass No.	Tension at surfaces (kg/cm^2) 500 hr.	1000 hr.	Thickness (mm)
1.	*	*	
2.	36	69	0.15
3.	25	42	0.15
4.	25	53	0.20
5.	*	*	--
6.	47	74	0.15
7.	47	72	0.15
8.	*	10**	--
9.	*	*	
10.	*	*	--
11.	*	*	--
12.	*	*	--
13.	*	*	--

* : Not recognized

** : 20 kg/cm^2 after 2000 hr. irradiation.

Table 3 Composition of Binary Borate Glasses

Glass No.	Oxides	mol%	Glass No.	Oxides	mol%
1	Na_2O	12	11	PbO	30
2	Na_2O	30	12	PbO	50
3	K_2O	12	13	PbO	70
4	K_2O	30	14	Bi_2O_3	25
5	Li_2O	18	16	Sb_2O_3	25
6	CaO	35	17	Tl_2O	30
7	SrO	35	18	ZnO	45
8	BaO	30			
9	CaO	50			
10	La_2O_3	25			

Table 4 Amount of stress induced at the ultra-violet irradiated surface of glasses of and thickness of the stressed layer

Glass No.	Alkali content in glass (mol%)		Tensile stress (kg/cm^2)	Thickness (mm)
1.	Na_2O	12	~ 20	~ 0.5
2.	Na_2O	10	~ 10	~ 0.5
3.	K_2O	15	~ 15	~ 0.4
4.	K_2O	30	~ 5	~ 0.4
5.	Li_2O	12	~ 5	~ 0.4

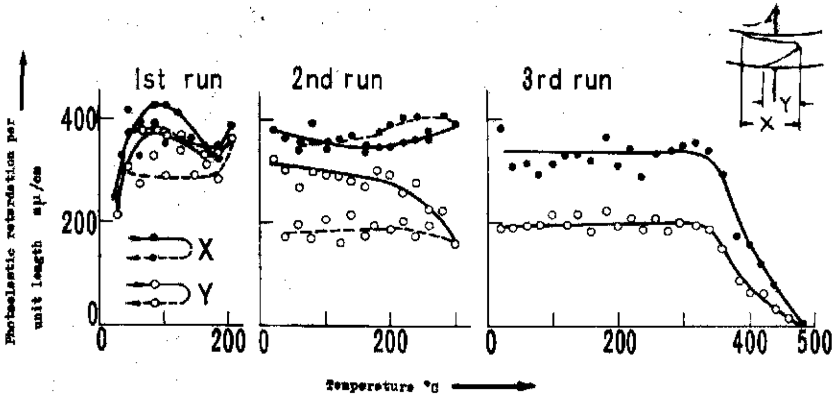


Figure 1 Stress release at the inner surface of a Tere glass bulb

(Annealing point of the glass: about 545 °C)

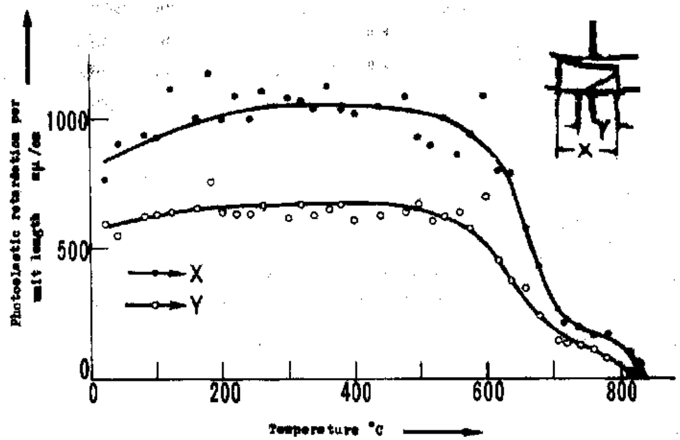


Fig.2 Stress release at the inner surface of a 96 % silica glass bulb
(Annealing point of the glass: about 900°C)

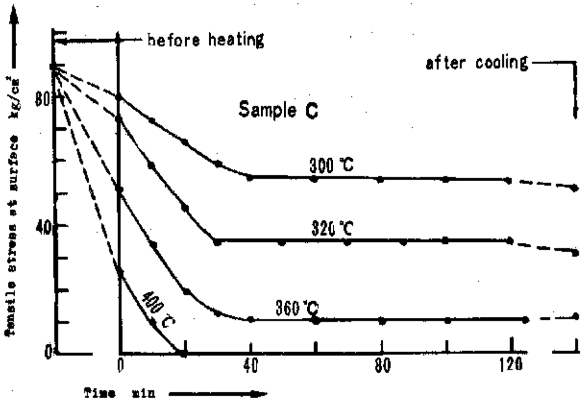


Fig. 3 Stress in a Terex glass bulb at various temperatures

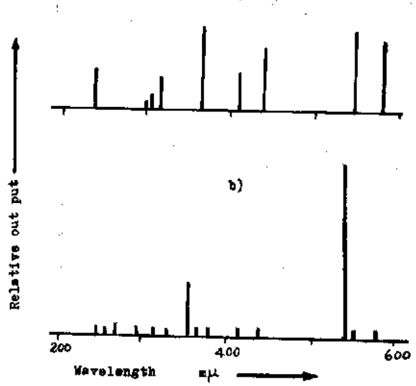


Fig. 4 Relative energy distribution of a) ordinary high pressure mercury lamp and b) high pressure (-cury:TlI lamp

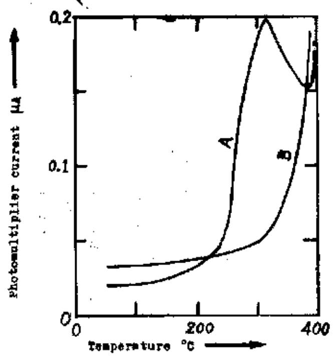


Fig.5 Thermal glow curves for the Terex (sample A) and the Pyrex (sample B) glass bulbs

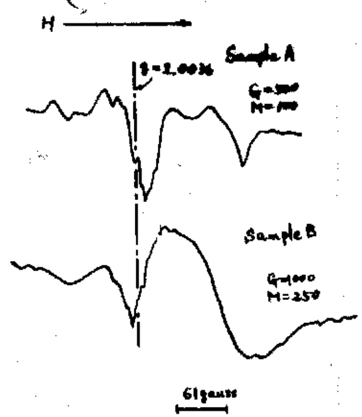


Fig.6 ESR signals of strained layers of damaged Terex glass (sample A) and Pyrex glass (sample B) bulbs
G: index of gain of amplifier of the apparatus
M: index of modulation width of magnetic field
The first derivative curves

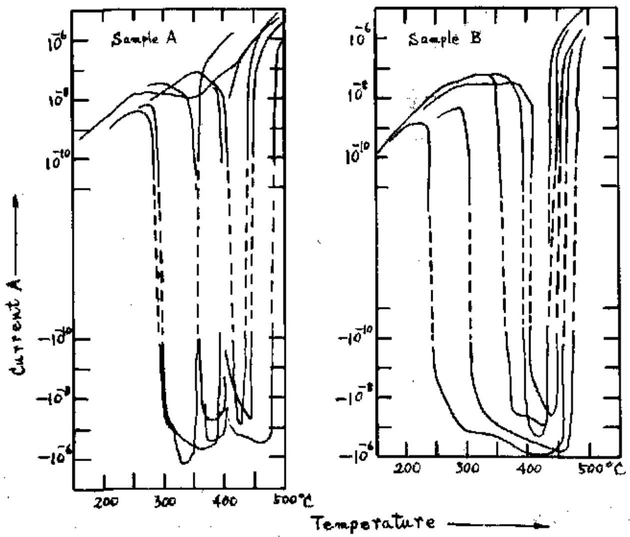


Fig.7 Temperature vs. short circuit current curves for damaged Terex glass bulbs (sample A) and Pyrex bulbs (sample B) showing that the current is reversed by the thermal release of accumulated charge in the glass

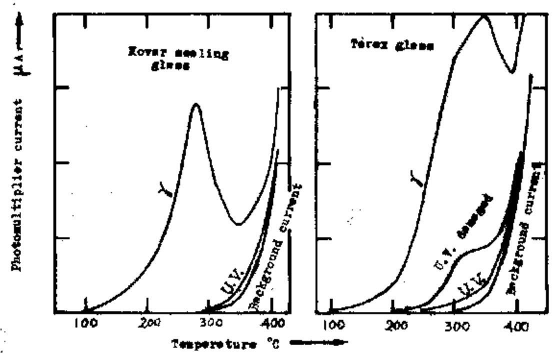


Figure 8 Thermal glow curves for various glasses

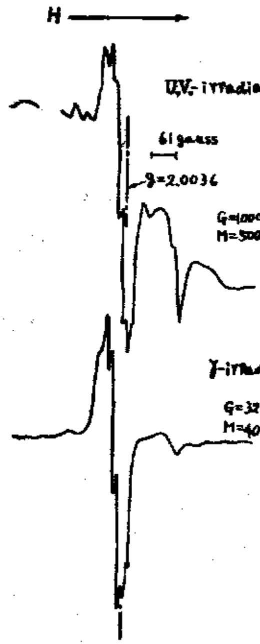


Fig.9 ESR signals of Terex glass irradiated
by γ- and ultra-violet ray
G: index of gain of amplifier of the apparatus
M: index of modulation width of magnetic field
The first derivative curves

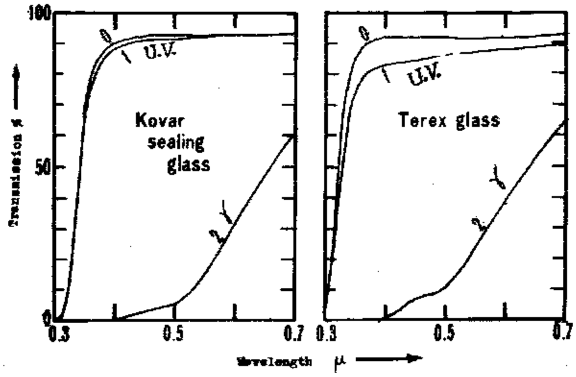


Fig.10 Transmission curves of Kovar sealing and Terex glasses
(4 mm thick) 0: before irradiation, 1: irradiated by ultra-violet ray, 3: irradiated by γ-ray (Co^{60})

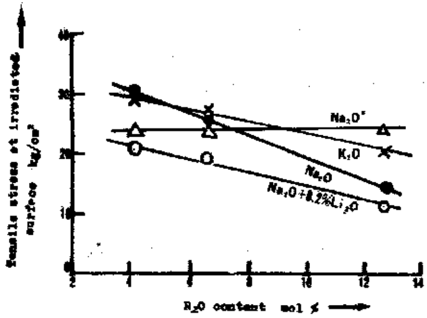


Fig.11 Effect of alkali oxide content (R_2O) in glasses with composition of xR_2O-15.5B_2O_3 -(84.5-x)SiO_2 in mol ratios on tensile stress induced at the glass surfaces by ultra-violet irradiation

*: melted in reducing condition

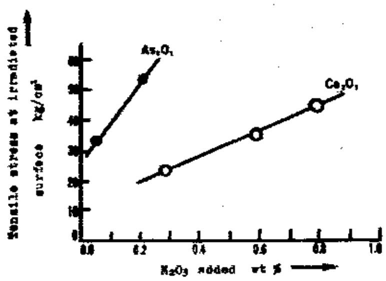
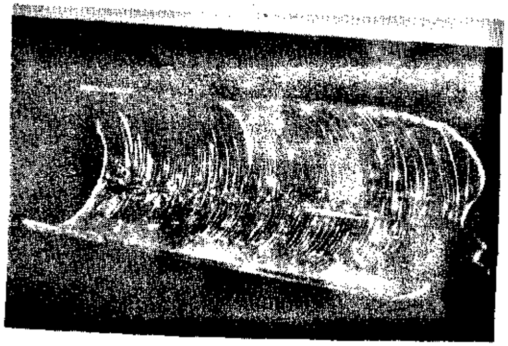


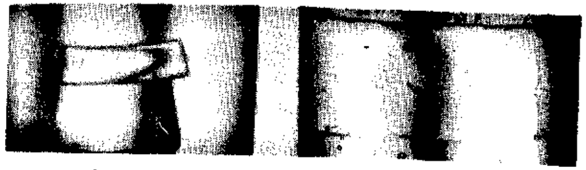
Fig.12 Effect of As_2O_3 or Ce_2O_3 added to glasses with composition of 6.5Na_2O-15.5B_2O_3-78SiO_2 in mol ratio on tensile stress induced at the glass surface by ultra-violet irradiation



Photograph 1 Outer protection bulb of a high pressure mercury discharge lamp damaged by ultra-violet irradiation

a) Thick section b) Thin section

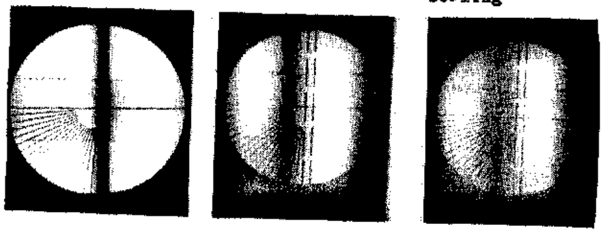
Photograph 2 Photoelastic observation of cross sections of a damaged Terex glass bulb



a) Thick section b) Thin section

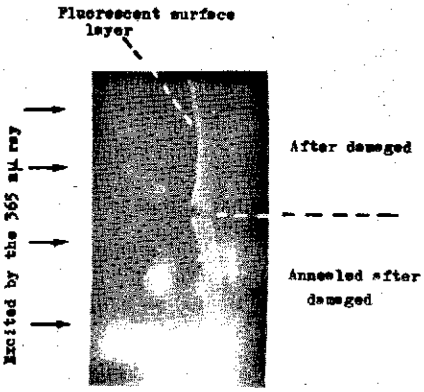
Photograph 3 Photoelastic observation of cross sections of a damaged 96 % silica glass bulb

Silica glass Borosilicate glass Terex Barium borosilicate glass for Kovar sealing

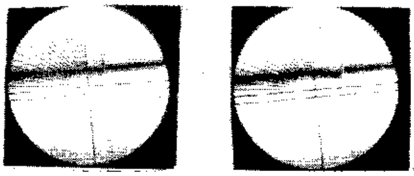


Zinc borosilicate glass (U.V. transmitting) Lead (30 wt %) glass

Photograph 4 Photoelastic observation of surfaces of various commercial glasses irradiated by ultra-violet ray

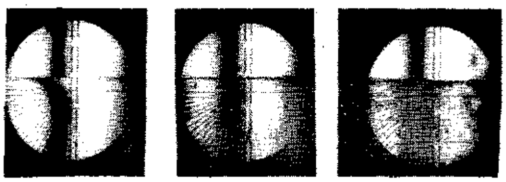


Photograph 5 Fluorescence of a strained surface layer of Teres glass bulb (sample A) by excitation with the 365 mμ ray (photographed through a green filter to cut of the exciting ray)



Terex glass (500hr) Kovar sealing glass (500hr)

Photograph 6 Photoelastic observation of strained layers of the Terex and Kovar sealing glasses irradiated by ultra-violet ray

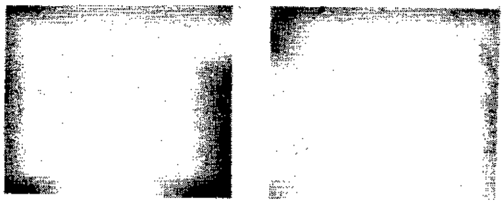


Na_2O 12	Na_2O 30	PbO 50
B_2O_3 88	B_2O_3 70	B_2O_3 50
mol %	mol %	mol %

Photograph 7 Photoelastic observation of the irradiated surfaces of binary borate glasses

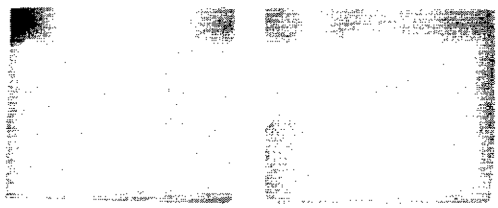
Soda borosilicate glass
(SiO_2 80.5, B_2O_3 15.5, Na_2O 4.0 mol %)

before irradiation after irradiation



Commercial barium glass for kinescope bulb (which contains no B_2O_3)

before irradiation after irradiation



Photograph 8 Electron-microscopic observation of the change of glass surfaces caused by ultra-violet irradiation