Preprint of The Annual Meeting of The Intern. Congress on Glass Sept 1967 Praha



# Some Observations on the Effects of Color Centers on Stress Build-Up in Glasses by Ultra-Violet Ray

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**Abstract**

Ultra-violet ray builds up stress in borate and borosilicate glasses. It was examined how the prior $\gamma$-ray or neutron irradiation would affect the stress build-up in glasses. In glasses not subjected to irradiation there was induction period of about 100 hr, and then the stress increased until it got saturated after about 800 hr. In $\gamma$-irradiated glasses the kinetics of stress build-up was similar to those of unirradiated glasses except that the induction period was about 100 hr longer. This retardation seemed to be caused by absorption of ultra-violet ray in the glasses colored by $\gamma$-irradiation. In neutron irradiated glasses the kinetica was quite different and the stress itself was far greater than those of unirradiated and $\gamma$-irradiated glasses. This should be the results of disordered structure of the glasses caused by thermal spikes and nuclear reaction $B^{10} + n \longrightarrow Li^7 + He^4$.

## I. Introduction

Stress build-up in borate and borosilicate glasses by ultra-violet irradiation was found and investigated by the authors. It was proved that the stress is a result of contraction (density increase) of the glasses in irradiated surface layers. The similar effect has not been found in inorganic materials except in cases of photolysis of silver

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halides. So the structural interpretation on the mechanism of stress build-up is a problem to be elucidated in the future. Many experimental results are necessary to be referred to for the establishment of a new theory to solve the problem.

In the course of the authors' investigation, there were many evidences that the stress build-up is a property which is rather sensitive to structural defects and impurities in glasses. Atmosphere during the melting of the glasses and rather small amount of oxides doped in the glasses distinctly affected the stress caused by ultra-violet ray.

Ionizing radiations form various kinds of structural defects in glasses and in many cases the defects are accompanied by optical absorption in visible and ultra-violet regions. In case of $\gamma$-irradiation, driving out and trapping of electrons and translation of mobile alkali ions take place and various kinds of electronic centers (for example, color, thermoluminescent, electron spin resonance centers, etc.) are created. In case of neutron irradiation, in addition to the defects described above, even the changes of atomic configuration by thermal spikes and of chemical composition by nuclear reaction $B^{10} + n \rightarrow Li^{7} + He^{4}$ occur.

It seemed natural to the authors to suppose that prior irradiation by ionizing radiation has distinct effect on the stress in glasses caused by ultra-violet ray, and that the investigations on the effects should give a clue to the structural interpretation of the phenomenon.

## II. Experimental Methods

Three kinds of borosilicate glasses were tested (Table 1.). Tetragonal columns (10 x 10 x 5 mm) with polished surfaces were made from each of these glasses. Some

Samples of each of these three were subjected to prior irradiation with $\gamma$-ray, some to prior irradiation with neutron flux and some were left unirradiated. Conditions of the irradiation were as follows: $\gamma$-ray; $Co^{60}$ source, $1 \times 10^5$ r/hr, 30 min, 4hr and 24hr: neutron flux; $3 \times 10^{11}$ n/cm$^2$-sec nuclear reactor with power out put of 100 kW, 10 min, 30 min, and 2.5 hr. The columns which were not subjected to irradiation with any of these ionizing radiations were also used as reference samples for the tests.

Those three groups of the samples were then exposed to ultra-violet radiation for 1100 hr. The source of ultra-violet ray was a 400 W mercury discharge lamp made of fused silica. The length and the outer diameter of the lamp were 150 and 17 mm, respectively. Distances between the outer surface of the lamp and irradiated surface of the glasses were 20 and 30 mm, respectively. During the irradiation stresses in the irradiated surfaces and light transmission of the glasses were measured from time to time.

The stresses were measured photoelastically with polarized light which propagates in the direction parallel with the irradiated surfaces. The transmission of the samples was measured with light propagating in the same direction.

## III. Experimental Results

The results of the experiments on Terex glass will be described below. The experimental results on the other two kinds of the glasses were qualitatively the same.

### 3.1 Reference glasses

Time-stress curves of the reference glasses during ultra-violet irradiation are shown in Fig. 1 with 1 as a parameter. At the initial stage of ultra-violet irradiation, induction periods are observed. Then the rates of building-up of the stresses increase and finally the stresses get saturated. Transmission curves of the glasses are shown in Fig. 2.

3.2 The $\gamma$-ray irradiated glasses

The time-stress curves of glasses subjected to prior $\gamma$-irradiation for 30 min, 4 hr and 24 hr are shown in Fig. 3, 4 and 5 respectively. Induction periods in these curves are longer than those of the reference glasses. In the later stage of ultra-violet irradiation, kinetics of stree build-up is approximately the same with that of the refernce ence glasses. Total dose of $\gamma$-ray hardly affects the time-stress relation in the glasses.

Coloration of the $\gamma$-irradiated glasses was optically bleached away gradually during ultra-violet irradiation. An example of the results of transmission measurements is shown in Fig. 6.

3.3 Neutron-irradiated glasses

The time-stress curves of glasses subjected to prior neutron irradiation for 10 min, 30 min and 2.5 hr are shown in Fig. 7, 8 and 9, respectively. Kinetics of stress build-up is quite different from those of the reference and $\gamma$-irradiated glasses. The stresses at forst increase rapidly getting to the first saturation after 200 - 300 hr of ultra-violet irradiation. The stresses then increase again and reach the second saturation. On one hand the final stresses were twice or more greater than those of both reference and $\gamma$-irradiated glasses but on the other hand the effects of intensity of ultra-violet ray are not so distinct as in the other cases. Dependence of the final stress on the dose of neutron flux is not distinct.

Discoloration process of one of the glasses is shown in Fig. 10.

# IV. Discussion

## 4.1 Reference glasses

Induction periods and saturation of reactions are often observed in photochemical and photosensitized catalytic reactions. The equations which express the kinetics of stress build-up shown in Fig. 1 were looked for by trial and error method. The following simultaneous equations were obtained:

$$\left.\begin{aligned} \frac{dn}{dt} &= \alpha L - \beta n - \delta p n \\ \frac{dp}{dt} &= \varepsilon \frac{dn}{dt} - \delta p n \end{aligned}\right\} \cdots\cdots (1)$$

Here $\alpha$, $\beta$, $\delta$ and $\varepsilon$ are constants, L is the intensity of ultra-violet reay, t is time, n and p are populations of sites N and P, respectively, and the stress is assumed to be proportional to a linear combination of n and p, for example $n-\nu p$ ($\nu$ = const.).

The equations can be interpreted as follows: N is the site in the glass which changed its atomic configuration by the action of ultra-violet ray and it is formed with the rate of $\alpha$ L and disappeares by backward reaction with the rate of $\beta n$ and by recombination with the site P with the rate of $\delta$ pn. P is the site which is formed by structural strain around the site N and it partially compensates the effect of the formation of the site N. The rate of the formation of the site P is assumed to be equal to $\varepsilon \times (dn/dt)$. Here $\varepsilon$ is less than unity. The site P disappears due to the recombination with the site N with the rate of $\delta$ pn. These processes are illustrated schematically with a reaction model shown in Fig. 11. Examples of t vs ($n - \nu$ p) curves calculated with the initial conditions ($p_0 = 0$, $n_0 = 0$ at t = 0) are shown in Fig. 12 with L as a parameter. These curves are similar to those in Fig. 1.

4.2 $\gamma$ -irradiated glasses

In case of $\gamma$ -irradiated glasses induction periods are about 200 hr; about 100 hr longer than in case of the reference glasses. The color of the glasses caused by $\gamma$ -irradiation fades away distinctly in several hundred hours. In case of the surface layers irradiated most severely by ultra-violet ray, fading would take place in much shorter time, namely, about 100 hr. This is comparable with the difference between the induction periods of the reference and $\gamma$ -irradiated glasses. The absorption of ultra-violet ray in extremely thin surface layers of the colored glasses seems to be a cause of retardation in the building-up of the stresses. After bleaching due to the ultra-violet irradiation the prior $\gamma$ -irradiation has hardly any effect on the kinetics of stress build-up. As absorption of ultra-violet ray and stress build-up occur in thin surface layers of colored glasses, it is difficult to conclude experimentally whether the stress build-up is accelerated or retarded in the colored glasses themselves.

In the early stage of the study the authors supposed that the induction period in the reference glasses corresponds to the period in which color centers are formed by ultra-violet ray and after which density of photon energy absorbed in the glass begins to increase. However, since the induction periods are not shortened in case of the glasses colored by $\gamma$ -irradiation, this supposition can hardly be true. The induction period of the reference glasses semms to originate from the more fundamental characteristics of the photo-chemical reaction sequences in the glass network.

4.3 Neutron-irradiated glasses

The kinetics of stress build-up is quite different in case of the glasses subjected to piror neutron irradiation. The reaction schema described in 4.1 is entirely inapplicable for the neutron irradiated glasses. It is natural to interprete the results shown in Fig. 7, 8 and 9 as superposition of the two different kinds of mechanism of stress build-up. One of them has very short relaxation time and the other has relaxation time of about several hundred hours. The structural defects created by thermal spikes and nuclear reaction $B^{10} + n \rightarrow Li^{7} + He^{4}$ make these mechanisms possible. The disordered structure of the glasses might fascilitate the process of the stress build-up.

## V. Conclusion

The effects of prior $\gamma$ -or neutron irradiation and also the effects of color center formation on the kinetics of stress build-up in borosilicate glasses during ultra-violet irradiation were examined experimentally. In glasses not subjected to prior irradiation (reference glasses) the induction period of about 100 hr was observed, and then the stress increased until it got saturated in about 800 hr since the beginning of ultra-violet irradiation. A reaction model which expresses the kinetics was proposed.

In $\gamma$ -irradiated glasses the kinetics of stress build-up was similar to those of the reference glasses except that the induction period was about 100 hr longer. This retardation of the stress build-up seemed to be caused by absorption of ultra-violet ray in extremely thin surface layers of colored glasses. The prior irradiation, however, had hardly any effects on the kinetics of stress build-up after fading away of the color centers.

The kinetics was quite different in neutron-irradiated glasses from those of the reference and $\gamma$-irradiated glasses. At first the stress was built up quickly and reached its first saturation and then it began to increase again until it reached its second saturation in about 800 hr since the beginning of ultra-violet irradiation. The stress itself at the end of the test was twice or more greater than those of the reference and $\gamma$ -irradiated glasses. This should be the results of disordered structure of the glasses caused by thermal spikes and nuclear reaction $B^{10} + n \rightarrow Li^7 + He^4$.

**Table 1**

Composition of the glasses used for the tests (wt %)

| | $SiO_2$ | $B_2O_3$ | $Na_2O$ | $K_2O$ | $Li_2O$ | $Al_2O_3$ | BaO | $As_2O_3$ |
|---|---|---|---|---|---|---|---|---|
| Terex | 80.6 | 12.3 | 4.5 | | | 2.0 | | 0.1 |
| Kovar sealing glass | 65.4 | 18.0 | 1.9 | 3.0 | 1.0 | 7.5 | 3.0 | 0.2 |
| soda borosilicate glass | 67 | 28 | 5 | | | | | |

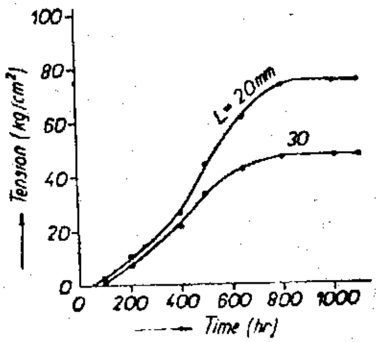



Fig.1 Time-stress curves of the reference glasses
1 : distance between the outersurface of the mercury lamp and the surfaces irradiated by ultra-violet ray

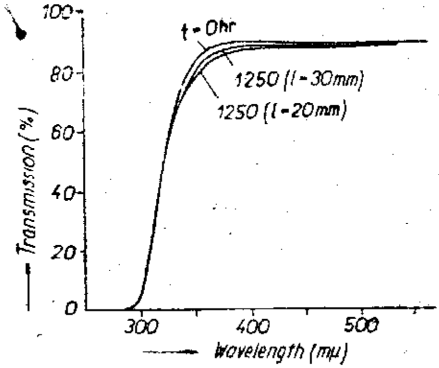



Fig.2 Transmission curves of the reference glasses before and after the ultra-violet irradiation t : time of ultra-violet irradiation

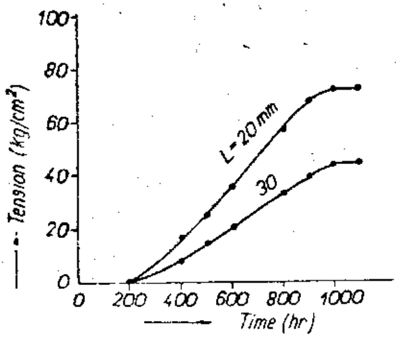



Fig.3 Time-stress curves of the glasses subjected to prior γ-irradiation for 30 min

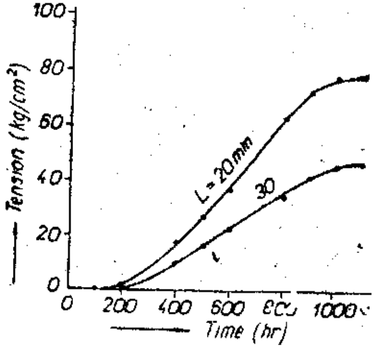
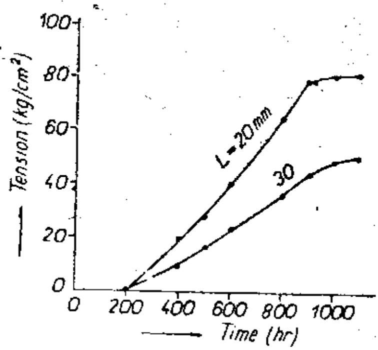



Fig.4 Time-stress curves
of the glasses subjected
to prior γ-irradiation
for 4 hr




g.5 Time-stress curves
the glasses subjected
prior γ-irradiation
r 24 hr

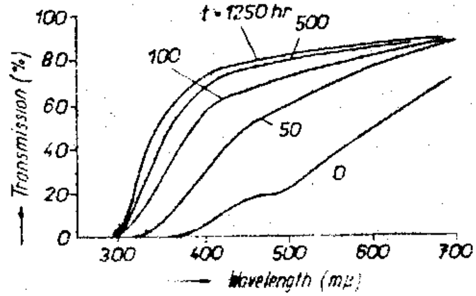



Fig.6 Change of transmission during ultra-violet irradiation of the glass subjected to prior irradiation with γ -ray for 24 hr (l = 20 mm)

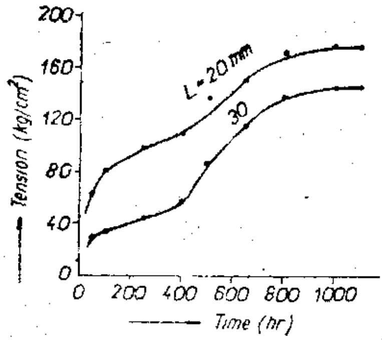



Fig.7 Time-stress curves of the glasses subjected to prior neutron irradiation for 10 min

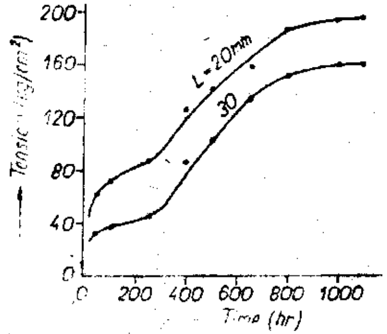



Fig.8 Time-stress curves of the glasses subjected to prior neutron irradiation for 30 min

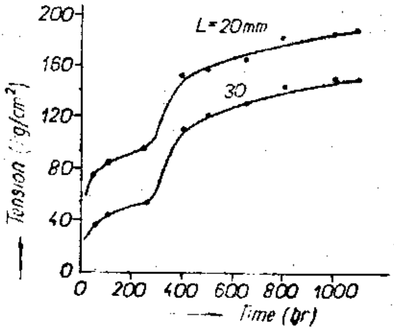



Fig.9 Time-stress curves of the glasses subjected to prior neutron irradiation for 2.5 hr

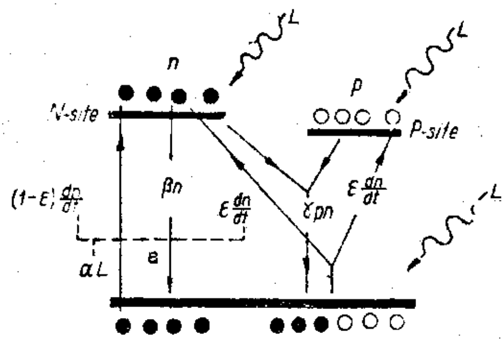



**Fig.11** A reaction model which illustrates the reaction schema expressed t the equation (1)

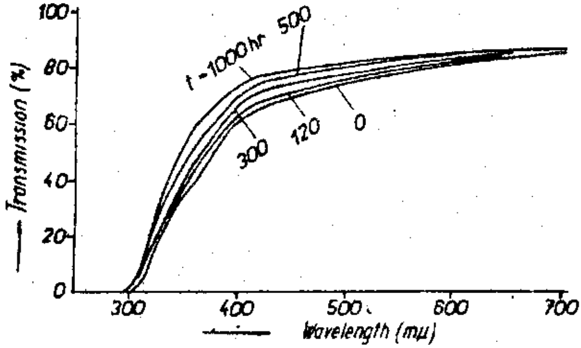



**Fig.10** Change of transmission during ultra-violet irradiation of the glass subjected to prior neutron irradiation for 2.5 hr (l = 20 mm)

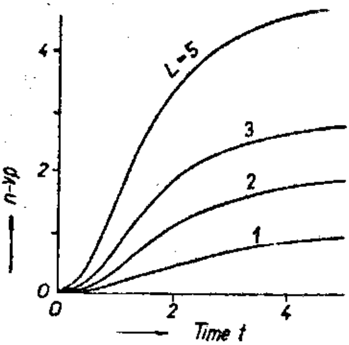



**Fig.12** An example of the groups of curves calculated by the equation (1)