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CORRELATION BETWEEN CRACK DEVELOPMENT IN GLASS WHILE CONDUCTING ELECTRICITY AND THE CHEMICAL COMPOSITION OF THE GLASS

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When wires are sealed through glass, mechanical strains may occur which owe their origin to differences between the thermal coefficients of expansion of the metal and the glass. The magnitude of these strains should vary somewhat with the chemical composition of the glass and are often sufficient to produce spontaneous cracking An additional factor in crack development, however, is introduced when a difference of potential is applied between the lead-in wires the importance of this factor depending upon the type of glass used. The purpose of the present investigation has been to correlate such crack formation with the chemical composition of the glass.

It is well known that if a difference of potential is applied between two wires which are sealed into a piece of glass there may be for an instant a comparatively large flow of current. At temperatures below 100° this current is practically negligible, one microampere or less, while above 100° the value of the current increases very rapidly with increasing temperature. The initial current flow, occurring immediately after the potential is applied, decreases very rapidly with time, due most probably to polarization. If, after the current has reached a fairly steady value, the polarity of the two wires is reversed, the same effect again takes place, the current, of course, now flowing in the opposite direction, and after each new reversal of potential the current immediately rises to a comparatively large value which falls off with time as described above. It seems reasonable to suppose that this initial current flow plays a part in causing cracks to develop. By determining the number of reversals of current through the glass which different types of analyzed glass could sustain before cracking, it was possible to obtain some results which appear to show a correlation between crack development and the chemical composition of the glass used.

Types of Glass Used

The types of glass worked with, together with their chemical compositions, are given in Table I.

It will be observed that Glasses 1 and 2 are soda-lime glasses; 3 is soda-lead; 4 is a borosilicate of lead and soda; 5 was not analyzed but is known to be a borosilicate glass containing practically no alkalies or heavy metals.

TABLE I

CHEMICAL ANALYSIS OF THE GLASSES USED

	1	2	3	4	5
SiO_2	69.93	69.40	64.64	72.05	Borosilicate glass containing practically no alkalies or heavy metals
Al_2O_3	1.54	0.78	0.20	2.21	
Fe_2O_3	0.19	0.14	0.04	0.05	
PbO	1.44	trace	21.66	6.11	
CaO	3.17	5.15	0.02	0.06	
MgO	0.03	4.09	0.02	0.09	
Na_2O	21.02	16.67	9.10	4.23	
K_2O	0.10	0.20	3.20	1.12	
P_2O_5	0.08	0.16	0.75	trace	
Sb_2O_3	0.05	0.10	..	..	
MnO_2	0.09	0.19	..	0.01	
F_2	..	..	trace	trace	
B_2O_3	2.36[a]	3.12[a]	0.37[a]	14.07[a]	

[a] By difference.

Apparatus and Method

For reasons which will be made evident, the measurements were all made on vacuum tubes[1] containing only a filament and plate, the glass parts of which were made of the different types of glass under test. The lead-in wires which connected the elements inside the tube with external sources of potential served as the electrodes between which the current flowed. The distance between these leads was maintained as near 3.2 mm. ($^1/_8$ inch) as possible. Each tube was placed in an electrically heated oven having a large thermal capacity. A thermocouple of "chromel" and "alumel" was placed close beside the tube in the oven and its leads outside were connected to a Hoskins recording pyrometer. The temperature within this oven as indicated by the pyrometer was kept constant at 300° ±5°. The wires leading to the tube were carefully insulated from each other and the oven. Before each experiment the insulation of the entire circuit was tested. The leakage current was always less than four microamperes.

Fig. 1 shows a schematic diagram of the circuit used.

When the reversing switch was in the position indicated by the dotted lines, a positive potential was impressed on the plate and a current of electrons flowed across the evacuated space between the lighted filament and the plate. The intensity of this current, indicated on Meter 3, was adjusted to five milliamperes by regulating the filament current as shown on Meter 2. When the switch was thrown in the reverse position, the charge on the plate became negative and the "space current" ceased to flow. Any current which might be flowing in the circuit at this time would deflect Meter 3

[1] The tubes used in these experiments were heated to sufficiently high temperatures while being pumped to assure the removal of the adsorbed gases from their glass parts. In some previous work [(a) Harris and Schumacher, *Ind. Eng. Chem.*, **15**, 174 (1923)] it was shown that these temperatures were 200° for the soda-lime and soda-lead glasses and 300° for the borosilicate glasses.

backwards and, since it was so arranged, Meter 5 forwards. The latter, which was capable of indicating current strengths of a few microamperes, gave the value of the current flowing in the glass press of the tube. The switch was manually operated and provided with an electric counter which recorded the total number of complete reversals of potential. An ordinary watch having a second hand was used to time the reversals. Since the current in the glass was changing with time, it was necessary to adopt an arbitrary point at which to read the values of current strength. In all this work this time was at the periods of reversal, or every 15 seconds.

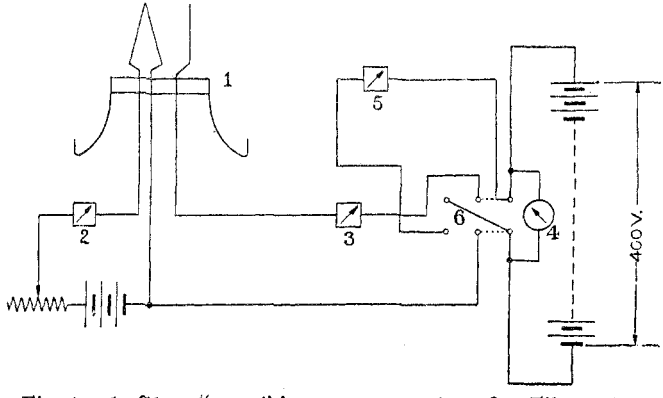

Fig. 1.—1: Glass "press" in a vacuum tube. 2: Filament-current ammeter. 3: Space-current milliammeter. 4: Plate-voltage voltmeter. 5: Glass-current milliammeter (Paul milliammeter). 6: Double-pole, double-throw switch connected so as to reverse plate voltage.

The use of vacuum tubes afforded an extremely sensitive method of determining when the crack occurred, since as long as the gas pressure within the tube remained nearly constant the readings of the space-current meter would be constant during the period when the plate potential was positive. If the pressure increased enough to produce a blue or pink glow in the tube, as would result from a crack in the glass, the readings of the space-current meter would be greatly increased.

Experimental Results

Four samples of each of the five types of glass were tested. These tests showed that glasses of different composition behaved very differently, while those of like composition gave consistent results. Data showing the characteristic behavior of the various types of glass are given in Table II.

In Col. 2 of this table is given the current which flowed through the glasses at the beginning of each experiment, while in Col. 3 is given the current which flowed at the end. The experiments were continued in the cases of the first three types of glass until cracks developed, but since at the end of five hundred reversals of current cracks had not developed in

TABLE II

CRACKING SUSCEPTIBILITY OF THE DIFFERENT GLASSES

	Current in milliamperes								No. of reversals of current before crack occurred.			
	Start of expt. Sample				Completion of expt. Sample				Sample			
Glass	1	2	3	4	1	2	3	4	1	2	3	4
1	0.270	0.245	0.270	0.285	0.400	0.375	0.420	0.400	5	6	4	4
2	.100	.100	.145	.080	.185	.200	.240	.170	8	9	7	9
3	.070	.055	.065	.045	.080	.065	.075	.050	255	300	285	300
4	.060	.055	.055	.040	.020	.018	.020	.017	Had not cracked after 500 reversals			
5	.015	.010	.010	.007	.005	.002	.005	.002	Had not cracked after 500 reversals			

the fourth and fifth types, these experiments were discontinued. A typical case for each kind of glass is represented graphically in Fig. 2 in which the number of reversals of current is plotted against the current in milliamperes which flowed through the glass.

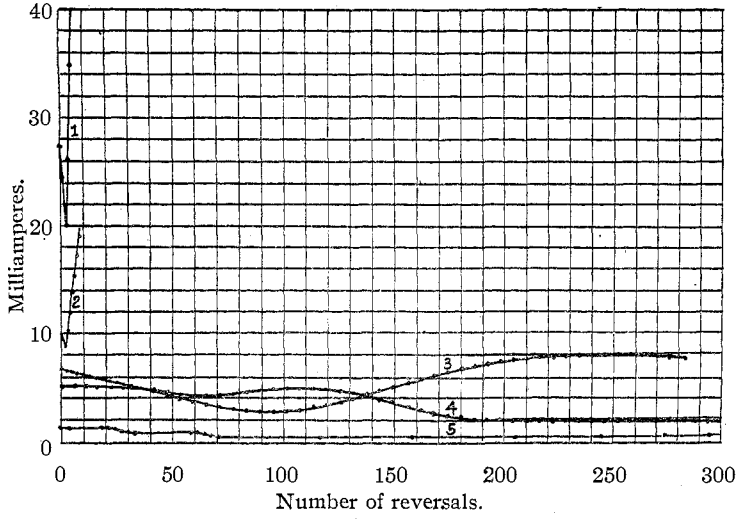

Fig. 2.

It will be noted that all but two of the curves terminate on the graph. This means that the glass press cracked at the time (number of reversals) recorded.

The performance of these various glasses as shown from the curves, when considered from the standpoint of their chemical compositions, is interesting. It appears obvious from the results obtained that a glass becomes more susceptible to crack, when subjected to the above conditions, the higher its soda content. Where lead oxide is substituted for soda, a glass having a far less tendency to crack is produced. Glasses of the borosilicate type showed the least tendency to crack of any of the com-

mercial glasses that were tested. It is also apparent from the figure that the higher the conductivity of the glass the greater the susceptibility to develop cracks.

Discussion

Before trying to interpret the results obtained it might be well to review briefly some of the literature on the subject of electrical conductivity in glass.[2] Warburg[2c] was the first to show that glass conducts electrolytically. He passed a current through a soda-lime-silicate glass at 300°, between mercury electrodes and found that metallic sodium was produced at the cathode. If a current is passed through a glass from a sodium nitrate anode to a mercury cathode, metal is transferred from the sodium nitrate solution to the mercury. This transfer, which takes place through the glass, does not affect the latter in the slightest. This indicates that conduction in some glasses at least is due solely to the motion of the sodium ion and is not due to the motion of the electronegative ion.

Since it is obvious that the result of any motion on the part of the sodium in a glass would tend to give a different distribution of volume, causing development of strains in the glass, if it could be shown that this motion is always more pronounced the higher the soda content of the glass, then one might conclude that this motion is a factor in determining how readily a glass will crack. One point that seems to favor such a notion is that in general whenever the sodium in a glass is replaced by any one of the other metals ordinarily found in commercial glasses, the resistance of the glass is increased. This indicates that either the number of carriers mi-

[2] (a) Ekman, *Phil. Mag.*, [4] **39**, 437 (1870). (b) Gray, *Proc. Roy. Soc.* (London), **34**, 199 (1882). (c) Warburg, *Ann. Physik*, **21**, 622 (1884). (d) Warburg and Tegetmeier, *ibid.*, **35**, 455 (1888). (e) Tegetmeier, *ibid.*, **41**, 18 (1890). (f) Gray and Dobbie, *Proc. Roy. Soc.* (London), **63**, 38 (1898); *Science Abs.*, **5**, 414 (1898). (g) Gray and Dobbie, *Proc. Roy. Soc.* (London), **67**, II, 197 (1900). (h) Bollé, *Thesis*, Friedrich-Wilhelm University, Berlin, A. Lüdtke, 1900. (i) Hovestadt, "Jena Glass," trans. and ed. by J. D. Everett and Alice Everett. Macmillan Co., London, **1902**, p. 372. (j) Rood, *Am. J. Sci.*, [4] **14**, 161 (1902). (k) Phillips, *Electrician*, **57**, 707 (1906). (l) Phillips, *Proc. Roy. Soc. Edinburgh*, **28**, 627 (1908). (m) Le Blanc and Kerschbaum, *Z. physik. Chem.*, **72**, 468 (1910); *C. A.*, **4**, 1928 (1910); *Science Abs.*, **1910A**, abs. 1795. (n) Ambronn, *Thesis*, Göttingen, **1913**, pt. 1. (o) Campbell, *Proc. Phys. Soc. London*, **25**, 336 (1913); *C. A.*, **7**, 3443 (1913). (p) Ambronn, *Physik. Z.*, **14**, 112 (1913); *C. A.*, **7**, 2150 (1913). (q) Schröder, *Z. physik. chem. Unterricht*, **26**, 367 (1913); *Chem. Zentr.*, **85**, I, 330–31 (1914). (r) Speranskii, *J. Russ. Phys.-Chem. Soc.*, **47**, 52 (1915); *C. A.*, **9**, 1419 (1915). (s) Bryson, *Engineering*, **101**, 517 (1916). (t) Ambronn, *Physik. Z.*, **19**, 401 (1918); *Ann. Physik*, [4] **58**, 139 (1919); *C. A.*, **13**, 1375 (1919). (u) Clarke, *Beama*, **8**, 235 (1921). (v) Bush and Connell, *J. Franklin Inst.*, **194**, 231 (1922). (w) Rebbeck, *Trans. Roy. Soc. Canada*, **16**, 272 (1922). (x) Kraus and Darby, THIS JOURNAL, **44**, 2783 (1922). (y) Holladay, *J. Franklin Inst.* **195**, 229 (1923). (z) Addenbrooke, *Phil. Mag.*, **45**, 516 (1923). (aa) Dudding and Smithells, *World Power*, **1924**, pp. 106–110.

grating through the glass has been decreased by the substitution or their speed has been materially lessened; in either case the motion in the glass would be decreased.

Another factor, however, that may be quite important in such development of cracks in glass is the amount of absorbed gas in the glass. It has been definitely shown[2v] that gases, in particular water vapor, penetrate throughout the volume of glass and quartz and radically affect their volume conductivity. For one particular glass that was tested[2v] the measured values of volume resistivity were increased in the ratio approximately of 6:1 by the removal of water vapor and other gas from the glass. From the data in a previous paper[1a] it may be concluded that the total amount of gas dissolved in a glass bears a direct relationship to the alkali content of the glass. Also since the conductivity has been shown to depend upon the amount of absorbed gas, the observation that the highest conductivity is shown by the glass of highest soda content may be due either to the fact that such a glass contains the most ions or that the ions can move more easily due to the lower viscosity, or to the presence of this absorbed gas. Hence, the development of cracks in glasses by repeated reversals of the current may be due in part to the amount of absorbed gas which they contain.

Acknowledgment

This work grew out of an investigation which was being carried on by Mr. F. L. Hunter on the conductivity of glass. The author wishes to acknowledge his indebtedness to the earlier work of Mr. Hunter for certain of the material used in this paper.

Summary

A study has been made of the susceptibility to crack development shown by five different kinds of glass when these were subjected to the action of an electric current. The results indicate that the tendency to crack increases with increasing alkali content of the glass and with increasing electrical conductivity. These conclusions are shown to be in accord with previous observations made on the conductivity of glass.

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