U. S. Department of Commerce
National Bureau of Standards

Research Paper RP1859
Volume 40, February 1948

Part of the Journal of Research of the National Bureau of Standards

Effect of Annealing and Other Heat Treatments on the pH Response of the Glass Electrode

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The effect of annealing and other heat treatments on the pH response of electrodes prepared from Corning 015 glass has been studied and a comparison made with the accompanying changes in hygroscopicity of the glass. New, unleached electrodes continued to give the correct pH response after being annealed near the critical temperature as indicated by the expansion curve for Corning 015 glass. Electrodes that were leached in 0.1 *N* HCl at 80° C lost much of their pH function when given identical heat treatments. The pH response of a typical glass electrode, held 10 minutes at 500° C after being leached in 0.1 *N* HCl for 6 hours at 80° C, was reduced from 59 millivolts per pH (the theoretical value at 25° C) to 22 millivolts per pH. A few seconds in hydrofluoric acid solution restored the pH function of these "dead" electrodes, showing that the inhibiting effect was confined to the outer surface of the electrode bulbs. Evidence obtained by the interferometer indicated that the thickness of this inhibiting layer was less than 5.8×10^{-6} centimeter. Hygroscopicity determinations made on leached samples of the powdered glass showed that the "sorption" power was greatly reduced by heat treatment, whereas for unleached specimens this property was much less affected. From the evidence obtained it seems reasonable to interpret the loss in pH function shown by glass electrodes on heat treatment as being due to the formation of a thin nonhygroscopic silica-rich layer. The resulting electrodes behaved in a manner similar to electrodes prepared from glasses of low hygroscopicity.

I. Introduction

Considerable confusion exists concerning the effect of annealing (release of strain within the glass) on the pH response of the glass electrode. This confusion has been further increased by nonconventional usage of the term annealing. For example, heat treatment of a glass electrode at 120° C should not properly be classified as annealing, as essentially no release of strain within the glass is brought about until much higher temperatures are attained, [1, 2, 3, 4, 5, 6][1] such as the critical temperature, *CT*, indicated by the expansion curve, figure 2. Nevertheless, heat treatment of an electrode for 15 to 20 hours at 120° C is reported to cause a reduction in pH response that is variable and very slow in disappearing [7]. Also, if the electrode is subjected to prolonged or repeated heating at high temperatures, the hydrogen electrode function may disappear completely [8].

The present investigation was undertaken in order to obtain a clearer understanding of the effect of annealing and other heat treatments on the pH response of the glass electrode, with particular attention being given to the accompanying alteration in hygroscopicity of the glass.

II. Experimental Procedure

The pH response was determined by comparing the experimental electrodes against a well-conditioned glass electrode as the reference electrode and measuring the voltage with a Beckman pH meter, model G. The experimental electrodes were blown as thin walled bulbs [9] of Corning 015 glass (72% SiO_2, 22% Na_2O, and 6% CaO) [10] on the end of soft glass tubing and the bulb filled with mercury for the inner connection [11]. Unless otherwise stated, the electrodes were con-

[1] Figures in brackets indicate the literature references at the end of this paper.

ditioned for at least 1 hour in distilled water. The emf values obtained in Britton-Robinson universal buffer mixture [12] of pH 1.9 were taken as the zero voltage departure [2] and the data of the investigation confined to a pH range over which the glass electrode is known to give reliable readings.

For the purpose of rapid aging, some electrodes were leached in 0.1 N HCl at 80.0°±0.2° C in a constant-temperature bath for 6 hours. Following a heat treatment, the electrodes were conditioned again for 1 hour in distilled water before use.

All heat treating was done in a small electrically heated muffle furnace whose temperatures were measured to an accuracy of ±10° C. The annealing schedule consisted of holding the electrodes for 10 minutes at or a few degrees above the critical temperature of Corning 015 glass, cooling slowly to 400° C and then more rapidly to room temperature.

The hygroscopicity data were obtained from the weight of moisture "sorbed" [14, 15] by powdered samples (approximately 1.5 g) of the glass that passed a Tyler standard 150 mesh sieve. This powder was exposed to the high relative humidity (approximately 98%) maintained by a saturated solution of $CaSO_4.2H_2O$, thermostated at 25° C. The results are reported in terms of grams of water sorbed per cubic centimeter of glass, calculated as follows:

$$\frac{\text{weight of water sorbed} \times \text{density of glass}}{\text{weight of sample}}.$$

III. Results and Discussion

1. Effect of Annealing

To ascertain what effect true annealing (release of strain) has on the behavior of the glass electrode, 12 electrodes of Corning 015 glass were prepared for study and their uniformity of pH responses determined after 1-hour conditioning in distilled water. Nine of them showed no departure from the theoretical value over the range pH 1.9 to pH 9.2, and none of the remaining three exhibited a departure greater than 3 mv over this range (curve A, fig. 1). Two of these electrodes were heated above the critical temperature (500° C) but below the deforming temperature (550° C) indicated by the expansion curve for Corning 015 glass, curve B of figure 2,[3] obtained by the interferometer procedure [4, 17].

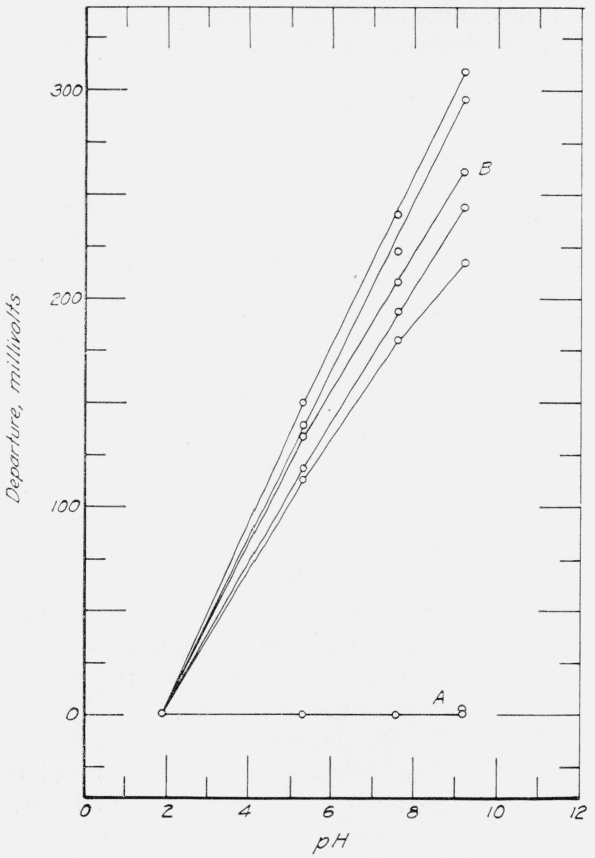

FIGURE 1. *Effect of annealing on the hydrogen electrode function of the glass electrode.*

A, Composite curve of voltage departure for glass electrodes; (1) at time of preparation; (2) unleached and annealed at 500° and 550°C; (3) after leaching in 0.1 N HCl at 80° C; (4) after treatment of "dead" electrodes with hydrofluoric acid. *B*, Voltage departures of five electrodes after being leached in 0.1 N HCl for 6 hours at 80° C and then annealed below 550° C.

After holding for 10 minutes,[4] the temperature of the muffle was allowed to fall slowly to 400° C (curve A, fig. 2), followed by a more rapid cooling to room temperature. These two electrodes, upon being soaked for 1 hour in distilled water, showed no voltage departures (errors) over the range pH 1.9 to pH 9.2 and continued to coincide with curve A, figure 1.[5] To emphasize these

[2] Theoretically, the potential difference between the hydrogen electrode and the experimental glass electrode in a hypothetical solution, normal with respect to hydrogen ions, should have been used as the zero potential [13]. This would have involved experimental difficulties that would add little or nothing to the present data except to displace the departure curves along the pH axis.

[3] The expansion curve for this specimen of Corning 015 glass exhibited a less pronounced critical region than is shown by many other glasses [4, 5, 6].

[4] As the electrodes were very thin, the time for temperature equilibrium to be attained throughout the specimen was very short. However, a holding period of 10 minutes was adopted for the sake of uniformity of procedure, and also as it was a period sufficiently short to avoid devitrification [8].

[5] The initial emf readings of unleached electrodes at pH 1.9 were different before and after annealing and other heat tretament, but the pH response, mv per pH, remained unaffected.

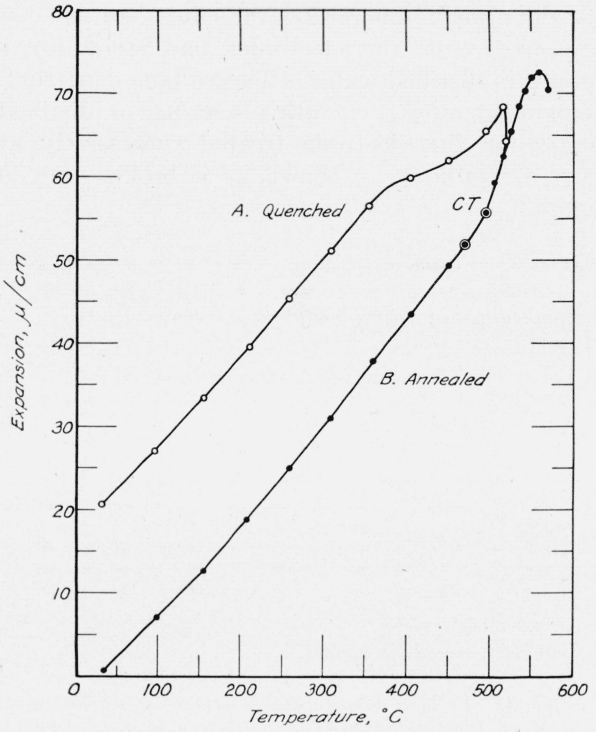

FIGURE 2. *Thermal expansion curve of Corning 015 glass.* *A*, Quenched; *B*, annealed. (Expansion data taken by J. B. Saunders).

results further, one of the electrodes was reheated to the deforming temperature, 550° C, and held for 3 hours before cooling slowly through the annealing range. The bulb was badly deformed by this treatment, but showed no failure of electrode function.

These data indicate that neither annealing nor high temperatures have any pronounced effect, either beneficial or detrimental, on the performance of virgin glass electrodes.

Five of the electrodes from the series were leached 6 hours in 0.1 *N* HCl at 80° C. These electrodes, at the end of the leaching period, still gave pH responses coinciding with curve *A*, figure 1. Upon being heated near 550° C and cooled according to the previous annealing schedule, these electrodes lost much of their electrode function (table 1, curves *B*, fig. 1) and behaved similarly to electrodes prepared from a glass of low hygroscopicity [18, 19]. The values for voltage departure plotted in these curves are those shown by the electrodes after 72 hours conditioning in distilled water. These results indicate the permanency as well as the magnitude of the inhibiting effect brought about by annealing after leaching.

Immersing these "dead" electrodes for a few seconds in hydrofluoric acid (1:1) restored their electrode function immediately, and their voltage departure values once again coincided with curve *A* of figure 1. These results showed that the loss of electrode function was confined to a very thin layer on the outer surface of the electrode bulb. If the swelling, 0.2 interference fringe [20], shown by Corning 015 glass for the period of time that the electrodes were leached in 0.1 *N* HCl is taken as an indicator of the maximum possible thickness of the inactivating layer, it can be no greater than 5.8×10^{-6} cm, calculated from the formula:

$$\text{Thickness} = \frac{\text{fringe displacement} \times \text{wave length of He light}}{2}.$$

TABLE 1. *Voltage departures (errors) of 5 glass electrodes after leaching in 0.1 N HCl, 6 hr at 80° C, followed in turn by annealing at 550° C and stripping with HF*

pH	Departure, millivolts														
	Electrode 1			Electrode 2			Electrode 3			Electrode 4			Electrode 5		
	0.1 *N* HCl	550° C	HF	0.1 *N* HCl	550° C	HF	0.1 *N* HCl	550° C	HF	0.1 *N* HCl	550° C	HF	0.1 *N* HCl	550° C	HF
1.9	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
5.3	0	150	0	0	139	0	0	134	0	0	118	0	0	113	0
7.6	0	240	0	0	223	0	0	208	0	0	194	0	0	180	0
9.2	0	309	0	3	296	0	0	261	0	2	244	0	0	217	0

2. Effect of Heat Treatment at Temperatures Other Than the Annealing Range

Another series of glass electrodes was prepared for the purpose of confirming the findings in the previous section and extending the investigation to temperatures other than the annealing region. Three electrodes from this series were heated to 550° C, annealed by the previous schedule, and then tested for voltage departure after 1 hour of soaking in distilled water. As in the previous case,

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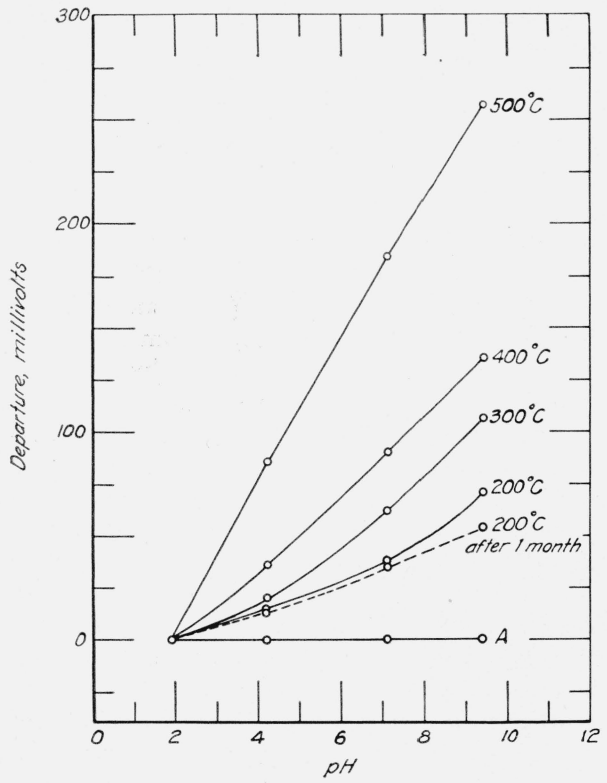

FIGURE 3. *Effect of heat treatment on the hydrogen electrode function of glass electrodes leached in 0.1 N* HCl, *6 hours at 80° C.*

there was no voltage departure brought about by the annealing (curve *A*, fig. 3). The remaining electrodes were leached for 6 hours at 80° C in 0.1 *N* HCl. Three of these, when heated to 550° C and cooled slowly through the annealing region, lost much of their hydrogen electrode function, which they regained immediately upon treatment with hydrofluoric acid. It is of passing interest to note that much of the pH response was restored to these "dead" electrodes by the application of HF to the smallest possible area.

These electrodes, annealed as in the earlier series, served not only to confirm the previous results but also acted as the control experiments for the present series.

Five of the leached electrodes were then heat-treated as a series in temperature steps of 100° C over the range from 100° to 500° C, inclusive. The data from table 2 plotted in figure 3 show the voltage-departure curves resulting from these heat treatments. The effect of the heat treatment at 100° C was not sufficiently permanent or steady to make satisfactory readings possible. However, for the other temperatures the effect had not disappeared after the electrodes had stood for 1 month in distilled water. The voltage departure, remaining after 1 month's soaking in distilled water for the electrode treated successively at 200° C, table 3, is shown as a broken line in figure 3.

TABLE 2. *Voltage departures (errors) of a series of glass electrodes after leaching in 0.1 N* HCl, *6 hr, at 80° C, followed by heat treatments at various temperatures*

pH	Voltage departure after heat treatment at—					
	Room temperature	100° C	200° C	300° C	400° C	500° C
	mv	*mv*	*mv*	*mv*	*mv*	*mv*
1.9	0	0	0	0	0	0
4.2	0	(a)	15	20	36	85
7.1	0	(a)	38	62	90	184
9.4	0	(a)	71	106	136	257

[a] Satisfactory readings not possible.

TABLE 3. *Voltage departures (errors) of a leached glass electrode showing the effect of successive reheating to 200° C*

pH	Voltage departures after reheating to 200° C.					
	First reading	Second reading	Third reading	Fourth reading	Fifth reading	
					1 hr	1 mo [a]
	mv	*mv*	*mv*	*mv*	*mv*	*mv*
1.9	0	0	0	0	0	0
4.2	15	12	13	14	14	13
7.1	38	41	46	48	46	35
9.4	71	78	76	80	82	54

[a] Continuous soaking in distilled water at room temperature.

When the values of voltage departure are plotted against temperature of heat treatment from table 2 or figure 3, the resulting curves (fig. 4) present a sharp increase in effect on the electrode function beyond 400° C. This can be readily rationalized with the critical temperature and annealing region indicated by the expansion curves of figure 2. It shows that the electrode function is destroyed much more strongly by heating near the critical temperature. If the procedure adopted in earlier publications [16, 19] of plotting the pH response as millivolts per pH in acid buffers is followed, the extent to which the electrode function of the glass has been adversely affected by heat treatment is apparent at a glance (table 4 and fig. 5).

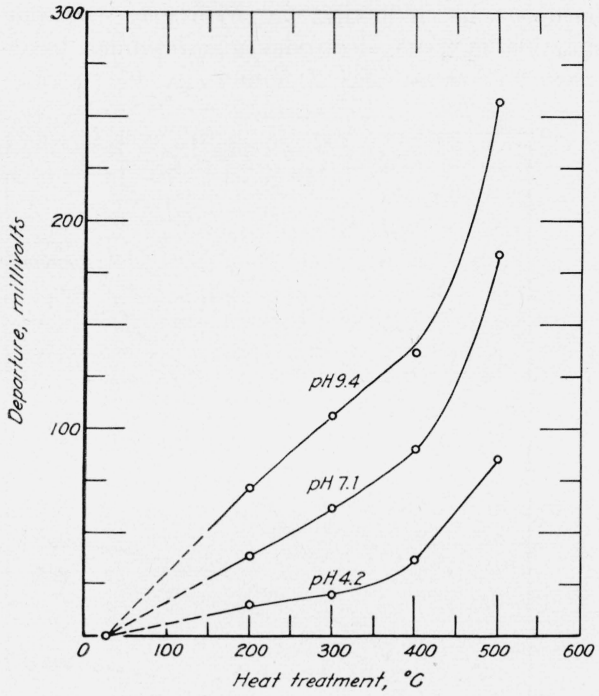

FIGURE 4. *Effect of the temperature of heat treatment on the hydrogen electrode function of glass electrodes at constant pH values.*

Data from figure 3 and table 2.

TABLE 4. pH *response of unleached and leached glass electrodes after heat treatment at various temperatures*

[The pH response values for the leached electrodes were calculated from the voltage departure data for pH 1.9 and pH 4.2 given in table 2]

Heat treatment	pH response	
	Unleached	Leached
	mv/pH	*mv*/pH
Room temperature	59	59
200° C	59	53.4
300° C	59	50.3
400° C	59	43.4
500° C	59	22.0

3. Effect of Heat Treatment on the Hygroscopicity of the Glass

Voltage anomalies (errors) of glass electrodes are normally associated with the hygroscopicity [16, 19], and changes in the chemical durability [18, 20] of the electrode glass. In the present investigation, as all pH measurements have been confined to a pH range over which little or no voltage departure can be accredited to durability shift of the glass, it seems reasonable to expect that the changes in hydrogen electrode function

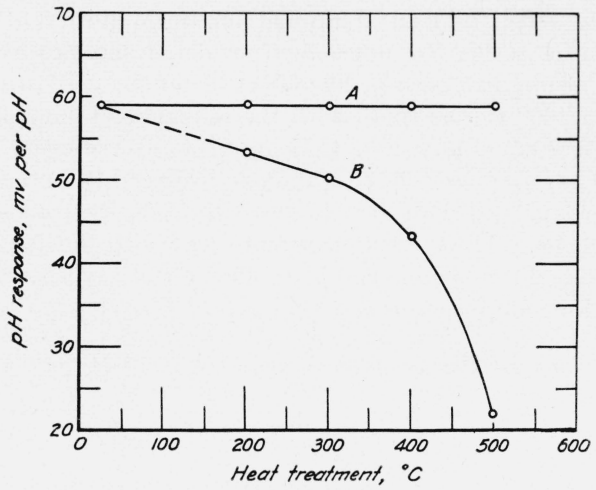

FIGURE 5. *Effect of heat treatment on the* pH *response of glass electrodes.*

A, Unleached; *B*, leached in 0.1 *N* HCl for 6 hours at 80° C. (Values calculated from the data in table 2, fig. 3 for pH 1.9 and pH 4.2).

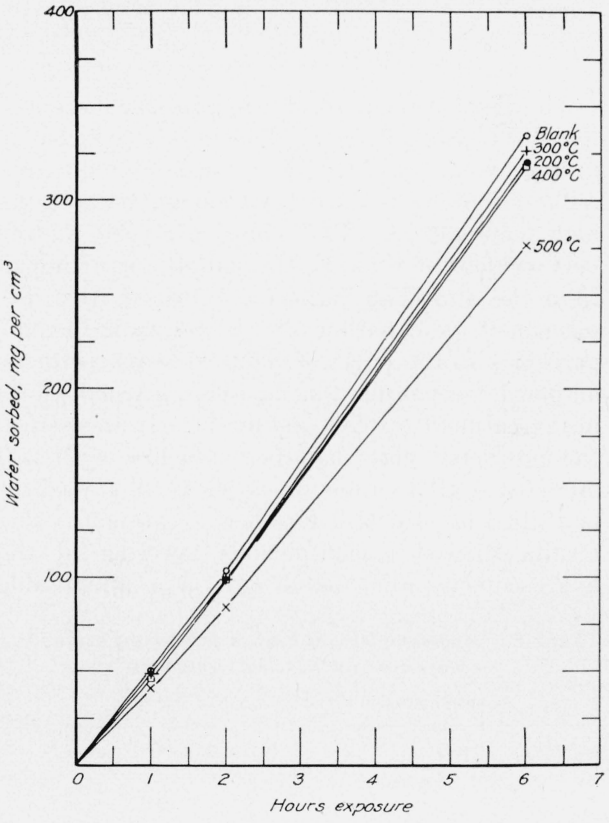

FIGURE 6. *Effect of heat treatment at various temperatures on the hydroscopicity of unleached powdered Corning 015 glass.*

caused by the various heat treatments of the electrodes might be associated with changes in hygroscopicity. Table 5 and figure 6 illustrate

the effect of heat treatment on the quantity of water sorbed by unleached powdered samples of Corning 015 glass. The effect of temperature up to 400° C was small with the sequence of curves for 200° C and 300° C being in a reverse order. The curve for 500° C, although displaced from the group, still indicates a glass of high hygroscopicity. These results correlate well with the fact that the annealing had little effect on the hydrogen electrode function of virgin glass electrodes.

TABLE 5. *Hygroscopicity of unleached powdered Corning 015 glass after various heat treatments*

Heat treatment	Water sorbed for exposures of—		
	1 hr	2 hr	6 hr
	*mg/cm*³	*mg/cm*³	*mg/cm*³
Room temperature	50	103	334
200° C	49	99	320
300° C	48	99	326
400° C	46	98	318
500° C	41	84	276

The displacement of the hygroscopicity curve for 500° C probably is not due entirely to a change in hygroscopicity of the glass, but largely due to a reduction of exposed surface from sintering at the high temperature. This sintering at 500° C was very evident at the time the sample was removed from the annealing furnace. However, this displacement indicated for 500° C was small in comparison with the effect of identical heat treatment on powdered samples that had been leached before heat treatment (table 6 and fig. 7). In this series, the powdered glass had been leached with 200 ml of 0.1 *N* HCl for 6 hours at 80° C, then washed, and dried at 110° C before heat treatment. The results showed a conspicuous lowering of the hygroscopicity that paralleled, in a remarkable fashion, the reduction in hydrogen electrode function of glass electrodes given similar treatment. (Compare figs. 3, 5, and 7.)

TABLE 6. *Hygroscopicity of leached powdered Corning 015 glass after various heat treatments*

Samples leached in 200 ml of 0.1 *N* HCl, 6 hr at 80° C

Heat treatment	Water sorbed for exposures of—		
	1 hr	2 hr	6 hr
	mg/cm ³	*mg/cm* ³	*mg/cm* ³
Room temperature [a]	59	126	334
200° C	77	126	182
300° C	64	114	163
400° C	65	84	117
500° C	49	71	82

[a] Unleached specimen included as comparison control.

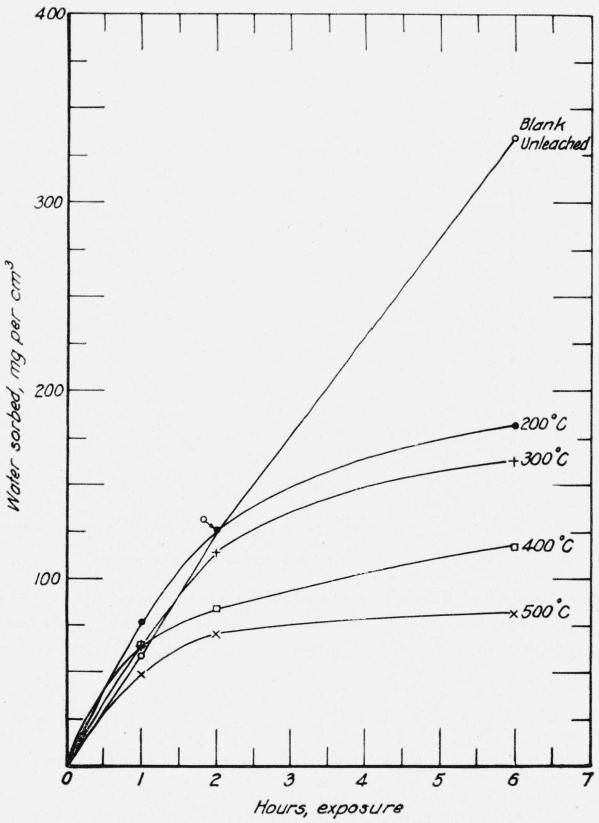

FIGURE 7. *Effect of heat treatment at various temperatures on the hydroscopicity of samples of powdered 015 glass, leached in 0.1 N* HCl, *6 hours at 80° C.*

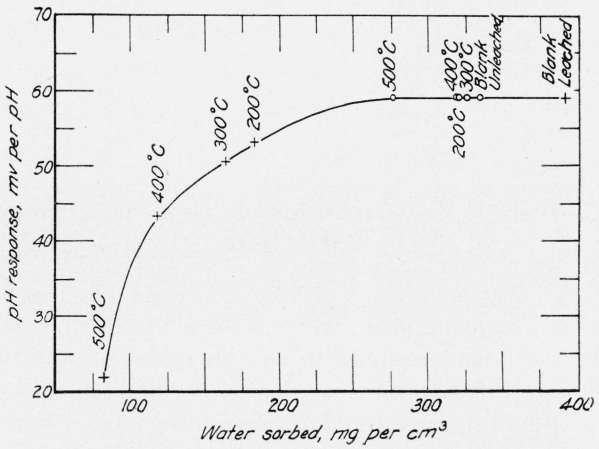

FIGURE 8. *Comparison of* pH *response of heat treated leached and unleached glass electrodes with the hydroscopicity of the glass after similar treatments.*

○, Unleached; +, leached.

An over-all view of the effect of heat treatment on the pH response of glass electrodes and the accompanying effect on the hygroscopicity of the glass is given in table 7 and figure 8. It emphasizes strongly that the pH response of the heat-treated electrodes is dependent on the accompany hygroscopicity of the glass surface as affected by leaching and not on the temperature of treatment alone.

TABLE 7. *Effect of heat treatment on the* pH *response and hygroscopicity of leached and unleached samples of Corning 015 glass*

Heat treatment	pH response		Water sorbed	
	Unleached	Leached	Unleached	Leached
	mv/p*H*	*mv*/p*H*	*mg*/*cm*³	*mg*/*cm*³
Room temperature	[a] 59	[a] 59	[b] 334	392
200° C	59	53.4	320	[c] 182
300° C	59	50.3	326	163
400° C	59	43.4	318	117
500° C	59	22.0	276	82

[a] Values from table 4.
[b] Values from table 5.
[c] Values from table 6.

Figure 7 showed that in most cases the sorption of moisture during the first hour of exposure by the leached powder was more rapid than for the fresh glass. This property is more strongly emphasized by the data presented in table 8 and figure 9. In obtaining these data, additional HCl was added to maintain the solution acid during the period of leaching. The behavior of the powder was noticeably different, with an increase in volume and more rapid rate of settling. The marked increase in the sorption of moisture by this treated glass during the early hours of exposure in the humidity chamber compared with the fresh glass sample, is undoubtedly the result of the difference in the chemical and physical nature of the surfaces presented, the desiccating property of silica gel becoming a decided factor.

TABLE 8. *Hygroscopicity of leached samples of Corning 015 glass after various heat treatments*

The leaching solution was maintained acid by repeated additions of HCl.

Heat treatment	Water sorbed after exposures of—		
	1 hr	2 hr	6 hr
	mg/*cm*³	*mg*/*cm*³	*mg*/*cm*³
Room temperature (unleached)	61	140	360
Room temperature (leached)	131	204	418
200°C	103	169	274
300°C	109	170	257
400°C	88	135	222
500°C	74	103	148

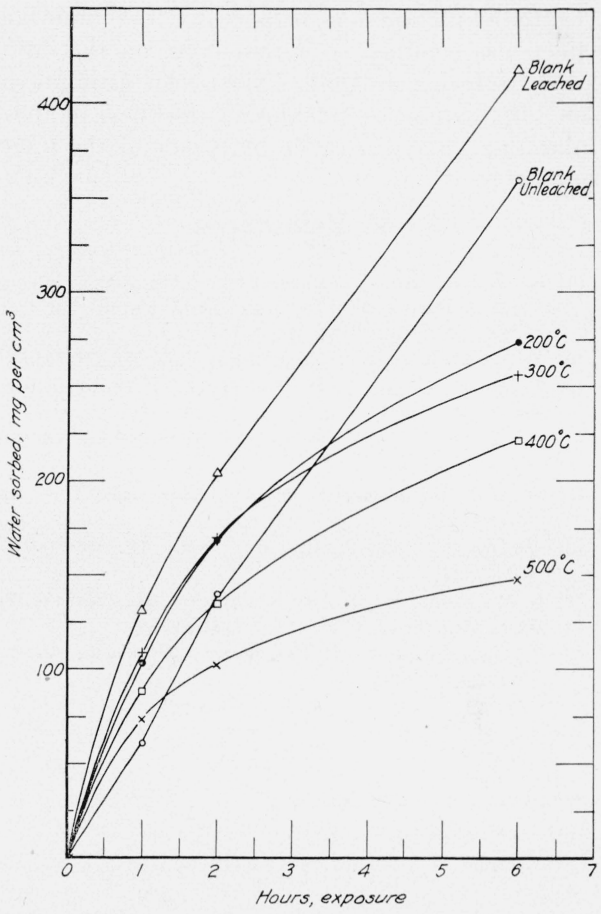

FIGURE 9. *Effect of heat treatment at various temperatures on the hydroscopicity of leached, powdered Corning 015 glass.*

The acid solution that normally becomes alkaline was maintained acid by repeated additions of HCl.

IV. Summary

New unleached glass electrodes were given annealing and other heat treatments without reducing their pH function, whereas electrodes leached in hydrochloric acid lost much of their pH response upon identical heat treatment. This reduction in pH response brought about by heat treatment was found to be accompanied by a reduction in the hygroscopicity of the glass. By treating these "dead" electrodes with hydrofluoric acid, it was possible to restore their hydrogen

electrode function and to show that the inhibiting effect was confined to a thin layer on the outer surface of the electrode bulbs. An estimate of 5.8×10^{-6} cm as the maximum thickness of these inhibiting films was made by means of the interferometer.

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WASHINGTON, October 1, 1947.