

THE ACTION OF PHOSPHORIC ACID ON GLASS

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Phosphoric acid attacks glass at temperatures of 200°C and above, at first etching the surface uniformly and producing a moderate increase in strength. After longer treatment the glass becomes coated with a layer of silicon phosphate which renders it resistant to hydrofluoric acid, but its mechanical strength is reduced because of crystalline inclusions in the surface. Under a microscope the crystalline deposits closely resemble marine barnacles in shape. The rate of reaction of glass with phosphoric acids of increasing degrees of polymerisation has been measured.

1. Introduction

Phosphoric acid attacks quartz at elevated temperatures¹⁾ and when it is evaporated in a glass vessel an insoluble solid is formed which has been identified as silicon phosphate, $\text{SiO}_2 \cdot \text{P}_2\text{O}_5$ ²⁾. Apart from these and other similar observations there has been no systematic study of the effects of phosphoric acid on glass surfaces; the purpose of this investigation was to determine the rate of attack on the surface of glass by phosphoric acid and to examine the effects produced on the mechanical strength and chemical resistance of the glass. Initial experiments showed that the action of orthophosphoric acid alone was inappreciable below 200°C, but at higher temperatures the acid gradually polymerises by dehydration³⁾ and the resulting mixture of partially condensed acids attacked glass more rapidly. Consequently it was impossible to study separately the effects of acid composition and temperature on the rate of reaction since the composition of the acid necessarily alters during an experiment. In order to take account of this, the rate of polymerisation of orthophosphoric acid under the conditions of measurement was determined independently.

2. Experimental procedure and results

2.1. RATE OF POLYMERISATION OF PHOSPHORIC ACID

Phosphoric acid polymerises by dehydration and at a given temperature

the rate of approach to an equilibrium composition is mainly governed by the rate at which water is lost from the system. For this reason all measurements were made in the same apparatus that was subsequently used for studying the reaction with glass. This consisted of a silver beaker 2 inches in diameter and 4 inches tall, half-filled with acid, and heated in an electric furnace controlled to $\pm 1^\circ\text{C}$ by a bare platinum-platinum/rhodium thermocouple immersed in the acid. Samples of the acid were removed at intervals on a platinum wire loop and analysed for orthophosphate and total phosphate by reaction with ammonium molybdate and vanadate⁴).

Determinations were made at 300 and 400°C and the fraction of monomer remaining after various times is plotted in fig. 1; the rate of polymerisation

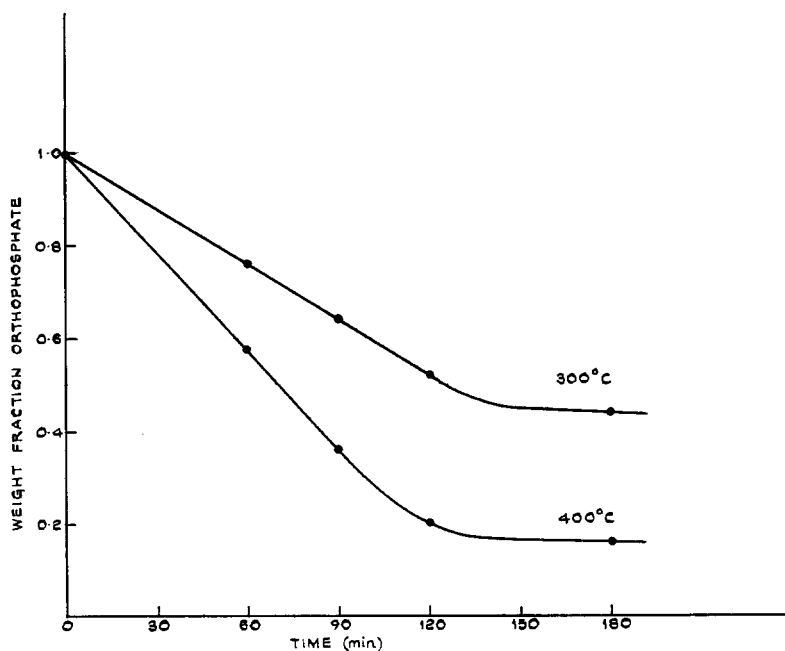


Fig. 1. Rate of polymerisation of phosphoric acid.

was found to be constant at each temperature during the first two hours, and the final concentration of monomer decreased with temperature.

2.2. REACTION WITH GLASS

The glass specimens were 4 mm diameter rods of a soda-line glass containing SiO_2 71.5, Al_2O_3 2.2, CaO 5.7, MgO 3.0, BaO 1.7, Na_2O 14.0, K_2O 1.5%. They were treated in batches of eight held vertically in a platinum

TABLE I
Measurements of rate of attack on Glass by phosphoric acid

Temp. (°C)	Time (min)	Wt. fraction orthophosphate		Total wt. loss of 8 rods (mg)	Vol. glass dissolved per rod (mm ³)	Length immersed (mm)	Average initial diam. (mm)	Average depth of glass removed (μm)	Calculated etching rate (μm/min)
		Initial	Average						
300	30	0.86	0.74	144	7.2	100	4.2	5.4	0.18
300	30	0.68	0.56	282	13.9	100	4.1	10.8	0.36
300	30	0.45	0.44	423	20.9	100	4.1	16.2	0.54
400	30	0.91	0.69	261	12.9	100	4.3	9.6	0.32
400	30	0.46	0.26	846	41.8	100	4.1	32.4	1.08
400	30	0.24	0.22	1036	51.3	100	4.0	40.8	1.36

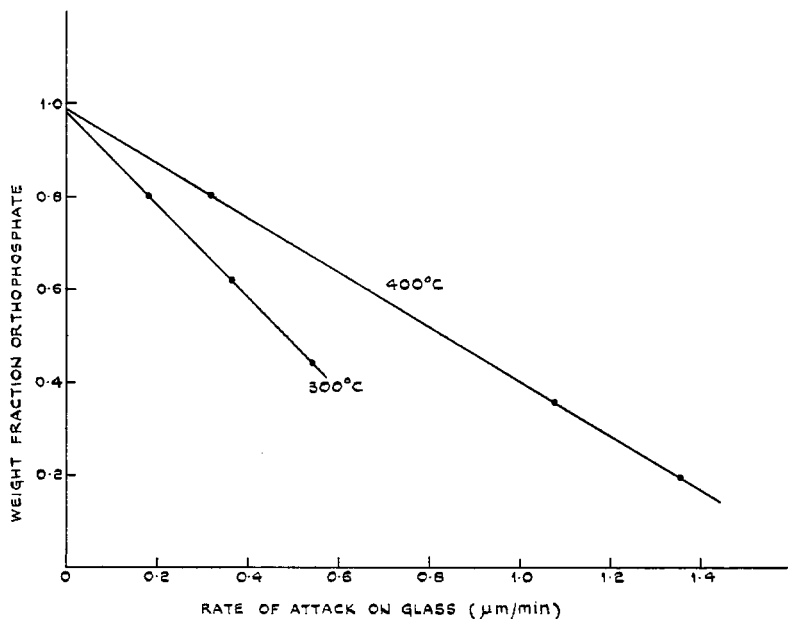


Fig. 2. Rate of attack on glass.

wire frame and gently agitated in the hot acid by rotating the frame at about 1 rpm. The extent of reaction was determined from the loss in weight and the change in diameter of the specimens and their strength was measured in four-point bending over a 1.25-inch span in a Hounsfield tensometer. The duration of each experiment was 30 min and the change in composition of the acid during this time was calculated from fig. 1. The results are given in table 1. The rate of attack on the glass at each temperature is plotted against

TABLE 2
Strengths of rods after treatment in phosphoric acid

Wt. fraction of orthophosphate	Fracture stress after 30 min at stated temperature (kg/mm ² ; mean \pm 95% confidence limits)	
	300°C	400°C
No treatment	25.2 \pm 2.8	25.2 \pm 2.8
0.8	40.6 \pm 3.5	36.4 \pm 4.2
0.48	89.6 \pm 9.1	106.2 \pm 10.5
0.30	77.0 \pm 8.4	46.2 \pm 6.0
0.17	46.2 \pm 6.3	39.8 \pm 7.7
0.14	22.4 \pm 6.3	12.6 \pm 3.5

the average concentration of orthophosphoric acid in fig. 2, and the effects on the strength of the glass are shown in table 2. It was found that the rate of attack on glass was proportional to the concentration of polymeric acid, and extrapolation to zero polymer concentration showed that pure orthophosphoric acid would have no action on glass if it did not undergo polymerisation during the time needed for measurement.

The strength of the treated specimens at first increased with the extent of reaction, indicative of uniform etching; but when the concentration of polymeric acid increased above 50% the strength decreased rapidly reaching a lower value than the untreated specimens.

2.3. APPEARANCE OF THE TREATED GLASS

Depending upon the extent of reaction, the surface of specimens which had been exposed to acid containing 50% or more of polymeric phosphate was more or less opaque, and after extended treatment the surface was noticeably roughened. Microscopical examination revealed crystalline inclusions in the glass which closely resembled marine barnacles in shape (figs. 3 and 4). Although these crystals projected from the glass surface as shown in fig. 5, they were very firmly attached and could not be detached by scraping. After crushing a portion of a treated specimen to a coarse powder, the sample was stirred in warm 40% hydrofluoric acid until all the glass was dissolved; the residue was then washed by decantation and dried. Micros-

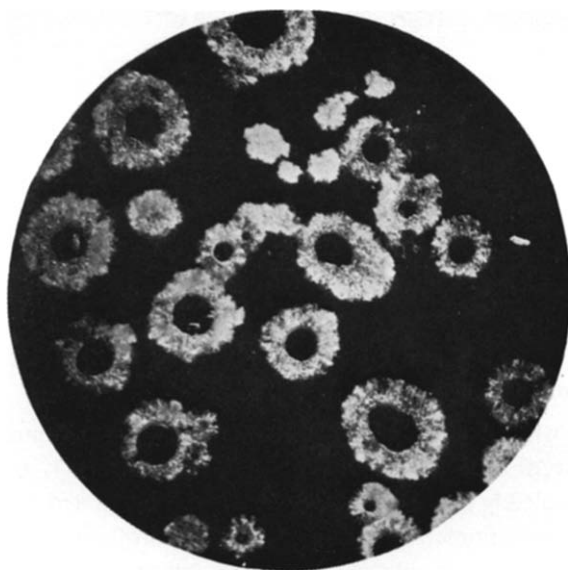


Fig. 3. Appearance of treated surface after 5 min at 400°C ($\times 100$)



Fig. 4. Appearance of treated surface after 15 min at 400°C ($\times 100$).



Fig. 5. Profile of rod after 15 min at 400°C ($\times 120$).

copical examination showed that the barnacle-like clusters of crystals remained, apparently unaltered in form. Elementary analysis of the residue showed it to be silicon phosphate, $\text{SiO}_2 \cdot \text{P}_2\text{O}_5$ (found, Si 14.0, P 30.5; required, Si 13.9, P 30.7%).

2.4. CHEMICAL RESISTANCE OF THE TREATED GLASS

Specimens which had been treated in acid mixtures containing mainly polyphosphate, or in so-called "metaphosphoric" acid HPO_3 at 400°C for 30 min were completely opaque. After washing free from acid and drying, the weighed rods were immersed in 10% aqueous hydrofluoric acid for periods up to 24 hr. No loss in weight was observed in any specimen after 2 hr; after 8 hr some specimens showed a small loss in weight and after 24 hr the same

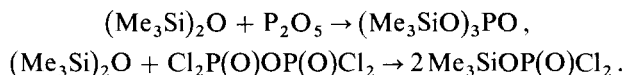
specimens had lost up to 10% in weight, but the remainder were still not attacked. Complete resistance to attack by hydrofluoric acid presumably depends upon complete coverage of the surface by silicon phosphate crystals.

3. Discussion

Van Wazer³⁾ has studied the composition of condensed phosphoric acids and has determined the distribution of monomer and polymer units as a function of the $\text{H}_2\text{O}/\text{P}_2\text{O}_5$ mole ratio. From these data it can be deduced that at the equilibrium compositions reached in the present experiments, which correspond to $\text{H}_2\text{O}/\text{P}_2\text{O}_5$ mole ratios between 2.0 and 2.3, the chief constituent of the acid is the dimer, pyrophosphoric acid. The present results show that pure orthophosphoric acid does not attack glass, and that the rate of attack increases with the concentration of dimer. A possible explanation of these observations is that the first step in the reaction is a mutual interchange of anhydride linkages or "scrambling" reaction such as



Similar reactions are known to occur between organo-silicon compounds and phosphorus pentoxide or pyrophosphoryl chloride^{5, 6)}:



Presumably the silicate network dissolves in the acid as mixed anhydride units containing SiOP linkages. As reaction continues, silicon phosphate may be formed by condensation of these units, but the reason for its being preferentially formed on the dissolving glass surface is still obscure.

References

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