

Strength and Static Fatigue of Abraded Glass Under Controlled Ambient Conditions: IV, Effect of Surrounding Medium

by R. E. MOULD

American Glass Research, Inc., Butler, Pennsylvania*

The strength and static fatigue behavior of abraded glass specimens tested in various surrounding media have been studied. The test media included distilled water, nitrogen atmospheres of varying humidity, methyl and isopropyl alcohol and mixtures of these with distilled water, and various acidic and basic solutions. For intermediate durations of load the strength values in atmospheres of 0.5 and 43% relative humidity were 45 and 20% greater, respectively, than in distilled water. The value of $t_{0.5}$, the characteristic duration for static fatigue, under these three test conditions was 3500, 200, and 8 seconds, respectively, for the particular grit-blast abrasion studied, indicating that liquid water is the most effective agent for promoting a high rate of static fatigue and very dry air with a small concentration of water vapor is least effective. In reagent-grade methyl or isopropyl alcohol (0.01 to 0.05% H₂O) the strength at an intermediate load duration of 10 seconds was about 40% greater than in distilled water and the slope of the static fatigue curve differed somewhat from that obtained for tests in water. With the addition of water to the alcohol solutions the fatigue curve became parallel to that for water, and as the water content was increased, the curves shifted toward the water curve. For tests in acidic and basic solutions the strength at an intermediate load duration was independent of pH over the range pH 1 to 13. For more acidic solutions the strength was slightly less and for more basic solutions slightly greater than in this range. The results are discussed in terms of possible mechanisms for static fatigue. It is concluded that the static fatigue of abraded glass results from changes in the shape or size of surface abrasion cracks under the combined action of stress and the surrounding medium. In general, water or water vapor is the primary agent in promoting fatigue, and, unlike the usual chemical attack, the interaction appears to involve primarily the neutral water molecule and the SiO₂ network of the glass. The presence of other ions or molecules is relatively unimportant except as it may serve to reduce the concentration of water and its availability to the tip of the abrasion crack.

I. Introduction

IT HAS long been recognized that the chemical environment of a glass specimen during a strength test can have a pronounced effect on the results obtained. As long ago as 1929, Milligan¹ observed that the strength of freshly scratched specimens was reduced by 20% if the specimens were wetted immediately before testing and increased by a similar amount

if the cracks were touched with dry paraffin oil before testing. Both the increase and the decrease were relative to the strength in air of unspecified humidity.

Since that time this effect has been studied by several investigators.²⁻⁵ It has been found that for any given rate of loading or duration of load the strength appears to be least when the specimens are tested wet or immersed in water. For tests in air, relative humidity is believed to play a role with the strength decreasing with increasing humidity. In various other liquid media the strength is generally greater than in water. For those liquids giving the greatest strengths (e.g., paraffin oil and methyl alcohol) the values are higher than those in air of intermediate humidity.

By measuring the strength of glass specimens at loads of widely varying durations under different test conditions, Baker and Preston² demonstrated conclusively that static fatigue (decrease of strength with increasing load duration) depends strongly on the chemical environment of the specimen. When specimens were first outgassed and then tested in vacuum, static fatigue was eliminated and strength became independent of load duration. Furthermore, for the shortest durations (0.01 second) the strength under other test conditions tended toward the vacuum strength. Similar results were obtained by Gurney and Pearson,⁴ who also found that complete elimination of static fatigue was not obtained for specimens which were tested in vacuum without previous outgassing.

A similar elimination of the static fatigue effect and a strength level comparable to the vacuum strength are obtained when specimens are tested at very low temperatures. This was first indicated by Vonnegut and Glathart,⁵ who reported that the strength was almost independent of load

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The writer is president and director of research, American Glass Research, Inc.

* Successor to Preston Laboratories, Inc., by change of name.

¹ L. H. Milligan, "Strength of Glass Containing Cracks," *J. Soc. Glass Technol.*, 13 [52] 351-60T (1929); *Ceram. Abstr.*, 9 [7] 516 (1930).

² (a) T. C. Baker and F. W. Preston, "Fatigue of Glass Under Static Loads," *J. Appl. Phys.*, 17 [3] 170-78 (1946); *Ceram. Abstr.*, 1946, August, p. 149.

(b) T. C. Baker and F. W. Preston, "Effect of Water on Strength of Glass," *J. Appl. Phys.*, 17 [3] 179-88 (1946); *Ceram. Abstr.*, 1946, August, p. 137.

³ S. Shurkov, "Influence of Adsorbed Layers on Strength of Quartz Fibers," *Physik. Z. Sowjetunion*, 1, 123-31 (1932).

⁴ C. Gurney and S. Pearson, "Effect of Surrounding Atmosphere on Delayed Fracture of Glass," *Proc. Phys. Soc. (London)*, 62 [356B] 469-76 (1949); *Ceram. Abstr.*, 1949, November, p. 254f.

⁵ V. K. Moorthy and F. V. Tooley, "Effect of Certain Organic Liquids on Strength of Glass," *J. Am. Ceram. Soc.*, 39 [6] 215-17 (1956).

⁶ B. Vonnegut and J. L. Glathart, "Effect of Temperature on Strength and Fatigue of Glass Rods," *J. Appl. Phys.*, 17 [12] 1082-85 (1946); *Ceram. Abstr.*, 1947, November, p. 222a.

duration when specimens were tested at the temperature of liquid air. More recently this result has been confirmed by Kropschot and Mikesell⁷ and by Charles.⁸ Experiments in the present series^{9(a)} have shown that for load durations from 0.0025 to 15 seconds the strength of specimens tested while immersed in liquid nitrogen (77°K.) is independent of the duration of load to within 1%.

Thus glass specimens tested in vacuum after outgassing or at extremely low temperatures do not exhibit static fatigue and may be characterized by a single strength value independent of the duration of load or loading rate employed.* For all durations of load longer than impact durations (about 10⁻⁴ seconds) for tests conducted under the usual conditions in which a contaminating medium (especially water or water vapor) is present, the strength is less than this value and depends both on the duration of load or loading rate and on the nature of the medium.†

Using the apparatus and experimental techniques described in previous papers of this series,⁹ an experimental study of this dependence has been carried out. In particular the effect of the following media on strength and static fatigue has been studied: (1) nitrogen atmospheres with differing relative humidity, (2) methyl and isopropyl alcohol and mixtures of these with distilled water, and (3) acidic and basic solutions.

II. Experimental Methods

The general experimental procedure employed in this study consisted of subjecting the specimens to a standardized abrasion treatment, aging the fresh abrasions under controlled conditions, and then measuring the strength at various load durations with the specimens surrounded by the medium under study. For each experiment the strength of similarly abraded and aged specimens was measured with the specimens immersed in liquid nitrogen. This determination of the "instantaneous strength" (see Part II^{9(b)}) permitted the construction of reduced fatigue curves as a part of the analysis of the data and aided materially in the interpretation of the results obtained. Since the apparatus and methods have already been described in detail, they are reviewed only briefly here with emphasis on those points of particular interest to the present study.

(1) Specimens

As in previous parts of this study the specimens were standard laboratory microscope slides.‡

(2) Abrasion

The abrasion used in this study was the silicon carbide grit blast designated as abrasion (b) in Part II of this series.^{9(b)}

(3) Aging Treatment

All specimens were aged for 20 to 24 hours after abrasion and before testing. Specimens which were to be tested under conditions of controlled humidity were aged under the test condition. Those to be tested while immersed in various liquids were aged in distilled water and then allowed to dry in room air before immersion in the test liquid. In certain cases (e.g., the tests in alcohol) the specimens were immersed briefly in a container of the test liquid and then transferred to fresh liquid for the test itself. In all tests the primary variable under study was the effect of the surrounding medium while the specimen was under stress during the test itself. The purpose of these aging procedures was to eliminate aging as a possible variable by providing a common aging treatment for all specimens, thereby reducing the likelihood of any additional aging occurring during test.§

(4) Test Method

The specimens were tested in cross bending with the grit-blasted spot in the center of the tension face so that all fractures originated in the artificial abrasion. Tests were

conducted with the previously described electromagnetic tester which is capable of applying pulse loads with durations ranging from 0.0025 second up to any desired value. In some cases a complete static fatigue curve, strength vs. load duration, was measured; in others, tests were conducted at a single duration.

Each strength value reported represents the average of twenty specimens. The standard deviations of the results were between 5 and 10% of the average value in each case so that the standard error of the mean was between approximately 1 and 2%.

III. Results and Analysis

(1) Effect of Relative Humidity

Two series of specimens were grit blasted, stored for 24 hours, and tested at various load durations in the controlled-condition chamber (see Part I^{9(a)}) in the presence of nitrogen atmospheres containing two different vapor pressures of water. The two conditions used corresponded to relative humidities in air of 43 and 0.5%. A third similar series of experiments was carried out for specimens which were abraded and then stored and tested immersed in distilled water.

The results of these experiments are reported in Table I along with the strength as measured in liquid nitrogen (σ_N) for specimens given the same abrading and aging treatment as each series. From the table it appears that among the three conditions the strength as measured in water was least at all load durations whereas that measured at 43% relative humidity was greatest at short durations and that measured at 0.5% relative humidity was greatest at long durations. This result is, however, misleading and, in fact, is a good illustration of the way in which strength tests on glass can lead to a wrong conclusion if all factors affecting the results are not taken into account.

An examination of the values of σ_N , the liquid nitrogen strength, as shown in the table indicates that there were in fact appreciable differences in the amount of healing which

⁷ R. H. Kropschot and R. P. Mikesell, "Strength and Fatigue of Glass at Very Low Temperatures," *J. Appl. Phys.*, 28 [5] 610-14 (1957); *Ceram. Abstr.*, 1957, September, p. 203f.

⁸ R. J. Charles, "Static Fatigue of Glass, I-II," *J. Appl. Phys.*, 29 [11] 1549-53, 1554-60 (1958); *Ceram. Abstr.*, 1959, March, p. 76j.

⁹ (a) R. E. Mould and R. D. Southwick, "Strength and Static Fatigue of Abraded Glass Under Controlled Ambient Conditions: I, General Concepts and Apparatus," *J. Am. Ceram. Soc.*, 42 [11] 542-47 (1959).

(b) R. E. Mould and R. D. Southwick, "Strength and Static Fatigue of Abraded Glass Under Controlled Ambient Conditions: II, Effect of Various Abrasions and the Universal Fatigue Curve," *ibid.*, 42 [12] 582-92 (1959).

(c) R. E. Mould, "Strength and Static Fatigue of Abraded Glass Under Controlled Ambient Conditions: III, Aging of Fresh Abrasions," *ibid.*, 43 [3] 160-67 (1960).

* As discussed in earlier parts of this series (footnote 9) this value will, of course, depend markedly on the surface condition of the specimens, i.e., on the nature and severity of the surface damage present.

† Although delayed failure and static fatigue may play a role in some practical situations involving glass, the much greater magnitude of the effect of surface damage should never be overlooked. A very low breaking strength always implies severe surface damage or severe flaws regardless of the presence or absence of static fatigue. For example, an applied stress of 2000 lb. per sq. in. will not produce breakage, regardless of its duration or of the surrounding medium, without the previous existence of surface damage in the form of cracks which are of sufficient size to be readily visible to the naked eye.

‡ As given by the manufacturer the chemical composition of these slides is (weight %): SiO₂, 71.96; Fe₂O₃, 0.037; Al₂O₃, 1.42; CaO, 8.11; MgO, 4.23; Na₂O, 13.62; K₂O, 0.29; SO₃, 0.29; total 99.957.

§ For a detailed discussion of the effect of aging on the strength and static fatigue of glass see Part III of this series (footnote 9 (c)).

Table I. Effect of Relative Humidity on Strength*

Load duration (sec.)	Strength (lb./sq. in.)		
	0.5% relative humidity	43% relative humidity	Liquid water
0.0025	9620	10,830	9,710
0.012	9440	9,870	9,180
0.050	9000	9,400	8,440
0.226	8850	8,680	7,750
0.82	8440	7,830	7,150
4	7410	7,080	6,530
15	6900	6,500	6,070
60	6220	6,040	5,420
600	5350	5,330	4,780
3600	5100	4,490	4,530
0.82 (σ_N)	9870	11,230	12,450

* Specimens grit blasted, stored 24 hr. under test condition, and tested in nitrogen atmosphere of controlled humidity or in water.

took place under the three conditions of aging employed between abrasion and test. Only if these differences are compensated for can a true picture of the effect of the conditions during test be obtained. For this purpose reduced strength values (σ/σ_N as described in Part II^(b)) were calculated for each of the three series of results. These are plotted in Fig. 1 in the form of reduced static fatigue curves.

From the curves of the figure it can be seen that at any given load duration the strength relative to the liquid nitrogen strength increases with decreasing relative humidity or decreased availability of water to the glass surface. From the plot it is also apparent how the strength of initially identical specimens (equal values of σ_N) will appear to depend on the test conditions for tests of different load duration. Thus at a duration of 10 seconds specimens tested in atmospheres of 0.5 and 43% relative humidity will appear to be about 40 and 20% stronger, respectively, than specimens tested wet or immersed in water. On the other hand it appears that if the curve for wet specimens is extrapolated to shorter times, it will intersect the other two curves in the region of 10^{-4} seconds at a value of σ/σ_N of about 1.0. This is in agreement with an observation made in this laboratory that for certain impact tests with an effective duration of about 10^{-4} seconds* on commercial glass articles, the strength was the same for wet or dry specimens although for the same articles the strength under sustained load did exhibit a difference for the two test conditions. Thus the effect of the surrounding medium on the strength of a glass specimen cannot be specified independently of load duration.

Another point which is worthy of note in Fig. 1 is that for the driest condition studied the static fatigue curve has become nearly horizontal for the shortest load durations employed. This occurs for a value of reduced strength, σ/σ_N , of almost 1.0. Thus the very short time "dry" strength at room temperature appears to coincide approximately with the fatigueless strength as measured at the temperature of liquid nitrogen and the latter provides a measure of the instantaneous room-temperature strength as defined in Part II of this series.^(b)

From Fig. 1 it can be seen that the reduced static fatigue curves for the three conditions have very nearly the same slope at any given value of reduced strength. This suggests that the curves can be shifted horizontally to coincide as was

* The effective duration is here taken to be the duration for which the applied stress is greater than 90% of the maximum value. For many typical impacts on commercial articles the total duration is of the order of 10^{-3} seconds and the effective duration is about 10^{-4} seconds (see R. E. Mould, "Behavior of Glass Bottles Under Impact," *J. Am. Ceram. Soc.*, 35 [9] 230-35 (1952)).

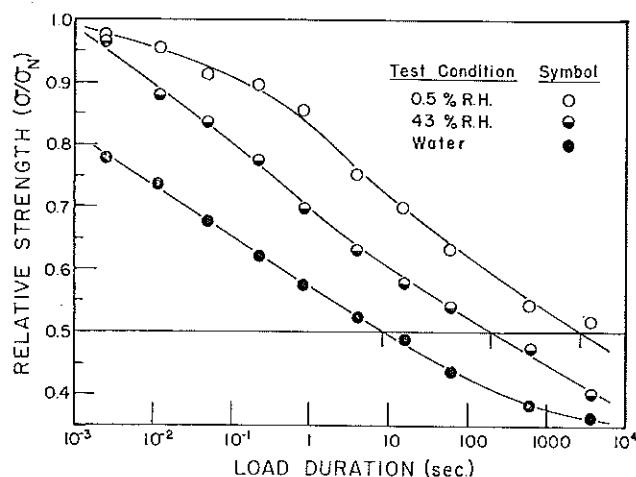


Fig. 1. Reduced strength vs. load duration (log scale) for specimens tested immersed in distilled water and in nitrogen atmospheres of 0.5% and 43% relative humidity (from data of Table I).

done for the reduced curves for various abrasions in the construction of the universal fatigue curve in Part II of this series.^(b) If the curves are thus shifted (which is equivalent to plotting on a reduced time scale), they do in fact coincide very closely except in the case of the shortest load durations for the tests under 0.5 and 43% relative humidity conditions.

Except for these shortest times, then, the differences in the curves can be considered to arise primarily from differences in the rate at which static fatigue takes place and the effect of the medium can be expressed in terms of this rate or of a characteristic duration corresponding to some particular reduced strength. Vertical lines crossing each curve at $\sigma/\sigma_N = 0.5$ indicate the value of the characteristic duration $t_{0.5}$, i.e., the load duration at which the strength equals one-half the liquid nitrogen strength. The values of this quantity for each test condition are given in Table II.

The reciprocal of the characteristic duration ($R = 1/t_{0.5}$) is also given in the table for each test condition. This quantity provides a measure of the rate at which the static fatigue process is taking place under any given set of conditions and will be referred to as the "fatigue rate" hereafter. From the table it can be seen that the characteristic duration and fatigue rate depend markedly on the availability of water to the glass surface, changing by a factor of more than 400 for the extreme conditions studied.

(2) Effect of Immersion in Alcohol

Among the various organic liquids whose effect on the strength of glass was measured by Moorthy and Tooley, that which yielded the highest values was methyl alcohol.⁹ For a constant-rate-of-loading test with a total time to break of about 6 minutes (estimated to be equivalent to a pulse duration of about 30 seconds) they obtained a strength value in methyl alcohol $36 \pm 9\%$ greater than in water. Of intermediate effect was isopropyl alcohol, which gave a strength value $22 \pm 5\%$ greater than water.

Table II. Values of $t_{0.5}$ and R for Different Test Conditions*

Test condition	Characteristic duration, $t_{0.5}$ (sec.)	Fatigue rate, $R = 1/t_{0.5}$ (sec. ⁻¹)
Wet	8	125×10^{-3}
43% relative humidity	200	5×10^{-3}
0.5% relative humidity	3600	0.29×10^{-3}

* From data of Table I.

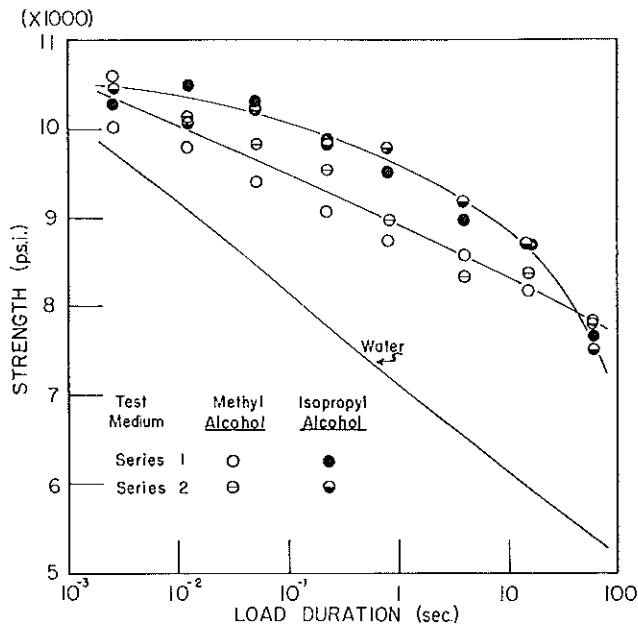


Fig. 2. Strength vs. load duration for specimens tested in reagent-grade methyl and isopropyl alcohol. Specimens received standard grit-blast and aging treatment before test. Curve for specimens in distilled water is shown for comparison.

(A) *Static Fatigue Curves; Pure Alcohol:* Two series of specimens were abraded, stored for 20 to 24 hours in distilled water, and then tested at various load durations immersed in methyl and isopropyl alcohol. Before test the specimens were removed from the aging bath and allowed to dry in room air. Before test each specimen was given a preliminary washing in the test liquid and was then immersed in a second bath for the test. The static fatigue curves obtained for these two test media are shown in Fig. 2 along with the curve for distilled water as a comparison standard. Two complete series of tests were run with each alcohol on separate occasions using different samples of the alcohol, and these are designated as series 1 and 2 in the figure.

At all load durations the strength in both of the alcohols was greater than in distilled water. The difference was least at the shortest load durations and increased with increasing duration. Unlike the various static fatigue curves reported in the foregoing and in previous parts of this series, these curves for specimens immersed in alcohol do not fit the universal fatigue curve (see Part II) when plotted in reduced form with each strength value divided by the instantaneous strength. Thus that curve may apply only where static fatigue involves an interaction between the glass and water or water vapor and not in the case of other media.

Unlike the results of Moorthy and Tooley⁶ and some earlier preliminary experiments of the present study, the specimens tested in isopropyl alcohol were stronger than those tested in methyl alcohol for all load durations of less than approximately 1 minute. At this duration the curves appear to cross with methyl alcohol yielding greater strengths than isopropyl for longer durations. At a load duration approximately equivalent to the loading rate employed by Moorthy and Tooley (30 seconds) the strength values in the two alcohols were approximately equal and were approximately 40% greater than for tests in distilled water at the same duration.

(B) *Alcohol-Water Mixtures:* Since the alcohols used* contained water in minute amounts (from 0.01 to 0.05%) it was believed that the differences between the results of different experiments might involve differences in the water content of various samples. To test this point and to study

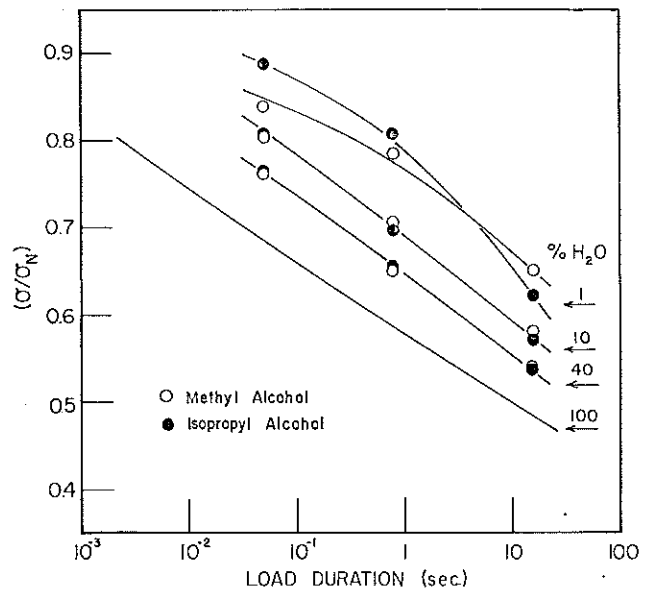


Fig. 3. Reduced strength vs. load duration for specimens tested immersed in mixtures of distilled water and methyl and isopropyl alcohol. Specimens received standard grit-blast and aging treatment before test. Per cent water by volume is indicated at right of curves.

the observed differences in slope of the curves, some experiments were carried out in which sets of specimens were tested immersed in mixtures of alcohol and distilled water.

Specimens which had been given the same abrasion and aging treatment as in the tests described in the foregoing were tested while immersed in methyl and isopropyl alcohol to which had been added 1, 10, and 40% of distilled water by volume. Tests were conducted at three different load durations, and the results, in the form of reduced static fatigue curves, are presented in Fig. 3.

From the figure it can be seen that the results for the alcohols containing 1% water reproduced all the essential features of those for the original, much drier, alcohols. The greatest strength values were obtained in the isopropyl alcohol solution at short durations and in the methyl alcohol solution at long durations. At the shortest durations the strength values in 1% solutions of both alcohols were approximately equal to those in the pure alcohols whereas at the longest duration (15 seconds) they were 10 to 15% lower. For alcohols containing small amounts of water it thus appears that the effect of the water in the solution becomes more apparent as the duration of load is increased.

When the alcohols were diluted by 10 and 40% water, the fatigue curves shifted progressively toward that obtained in pure distilled water and the differences between the two media disappeared. The slopes of the curves also changed so that they became parallel to that obtained in water. Thus for these solutions the interaction between the water and the glass appeared to dominate in determining the rate of static fatigue and the role of the alcohols was simply to dilute the water present.

To study this effect further, a series of experiments was carried out in which the specimens were tested at a single load duration (0.82 second) in mixtures of alcohol and water over a wide range of concentrations. Using the resulting strength values and the reduced fatigue curves of Fig. 3, it was possible to estimate the static fatigue rate relative to

* Fisher Scientific Company reagent-grade absolute alcohols. As given by lot analyses on labels, the water content varied from 0.01 to 0.05% for various samples.

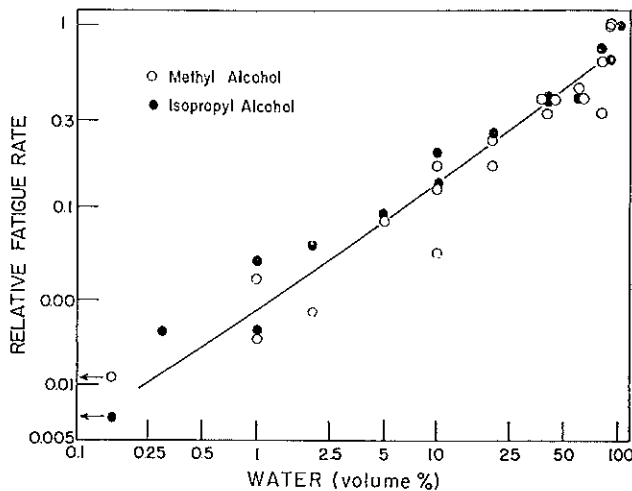


Fig. 4. Fatigue rate (see text) relative to that in distilled water for specimens tested in mixtures of alcohol and water (log scale).

that in pure water for each of the mixtures.* These rates are plotted in Fig. 4 versus the per cent water present by volume in each of the test solutions.

Because of the logarithmic nature of the dependence of strength on load duration a small difference in strength corresponds to a relatively large change in the static fatigue rate. This is reflected by a rather large scatter of the points in Fig. 4. It is apparent, however, from the figure that there is a definite relation between the water content of the solutions and the rate at which the strength decreases with increasing load duration. This relation appears to extend even to solutions containing very small amounts of water and it is possible that even for the driest alcohols studied, water played some role in the static fatigue process. The slope of the line in Fig. 4 is approximately one-half, implying that the fatigue rate varies approximately as the square root of the concentration of water in the solution. Because of the scatter of the data, however, this conclusion must be regarded as highly tentative.

(C) *Liquid Nitrogen Strength after Alcohol Immersion:* The foregoing analysis of the data for specimens immersed in alcohols and in alcohol-water mixtures has contained the implicit assumption that the only effect of such immersion during test was to change the static fatigue behavior of the specimens, i.e., to reduce the loss of strength under load as compared with that in water. Another possibility to be considered is that the increased strength values relative to those for tests in water may arise, at least in part, from some effect of the alcohol on the instantaneous or fatigueless strength of the specimens as it would be measured at extremely short durations, in vacuum, or at very low temperatures.

To test this possibility, some specimens were subjected to the standard grit-blast abrasion, aged overnight in distilled water, dried and immersed for 1 minute in methyl or isopropyl alcohol, and then tested in liquid nitrogen. These tests indicated that the liquid nitrogen strength of specimens which had been exposed briefly to alcohol after aging in water was approximately 4% greater than that of specimens which were not so exposed. Thus the alcohol immersion does appear to have a small effect on the instantaneous strength. It should be noted, however, that this effect, if real, would account for

* The reduced fatigue curves for specimens tested in the various alcohol-water mixtures did not extend to durations of load where the strength was equal to one-half the low-temperature strength. The fatigue rate relative to that in distilled water therefore was estimated by dividing the reciprocal of the load duration at which $\sigma/\sigma_N = 0.7$ in each solution by the corresponding value for tests in water.

Table III. Effect of pH on Strength*

Test solution	pH	Strength (lb./sq. in.)
NaOH	6 N	8010
	1 N	7650
	0.1 N	7230
	0.01 N	7170
	0.001 N	7350
Distilled water	7	7240, 7310, 7420
HCl	0.001 N	7060
	0.01 N	7270, 7230
	0.1 N	7070, 7280
	1 N	6850, 6770
	6 N	6580
	Buffer solutions	10.4
	9.0	7370†
	6.85	7390†
	5.0	7400†
	4.01	7140†

* Specimens grit blasted, stored 24 hr. in distilled water, and tested immersed in indicated solution with 0.82-second load duration.

† Average of forty rather than twenty specimens.

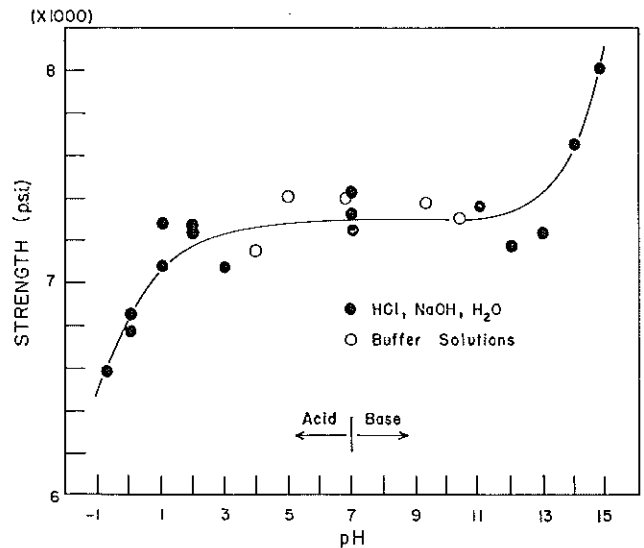


Fig. 5. Strength at 0.82-second load duration vs. pH for specimens immersed in HCl, in NaOH, and in buffer solutions.

only about 10% of the total strength difference between specimens tested in alcohol and in water. As discussed in the foregoing, this difference can therefore be attributed almost entirely to a decrease in the static fatigue rate in alcohol relative to that in water.

(3) *Effect of Acidic and Basic Solutions*

Various investigators have suggested that the static fatigue of glass is related to chemical attack of the surrounding medium on the glass surface and that it should thus be related to the ordinary chemical durability of the glass. Because of the well-known adverse effect of high pH of the attacking medium on the durability, it seemed to be of interest to determine the relation between the strength of glass specimens and the acidity or basicity of the solution to which they were exposed while under stress.

(A) *Effect of HCl and NaOH:* Specimens were given the standard grit-blast abrasion, aged overnight in distilled water, and then tested in HCl and NaOH of varying concentrations at a load duration of 0.82 second. The results are presented in Table III and Fig. 5.

From the table it can be seen that only the most concentrated solutions studied differed appreciably from distilled

Table IV. Effect of Various Acids and Bases on Strength*

Test solution (1 N)	Strength (lb./sq. in.)	Strength difference (lb./sq. in.)†
HCl	7000	-420
HClO ₄	7020	-400
H ₃ PO ₄	6810	-610
H ₂ SO ₄	6720	-700
NH ₄ OH	7420	0
KOH	7580	+160
NaOH	7780	+360

* Specimens grit blasted, stored 24 hr. in distilled water, and tested immersed in medium indicated with 0.82-second load duration.

† As compared with distilled water.

water in their effect on strength. Six normal NaOH yielded a strength value approximately 10% higher than water and six normal HCl approximately 10% lower. One normal base and acid gave intermediate results and the more dilute solutions did not differ significantly from the controls. It should be noted that these results are in direct contradiction to the hypothesis that the static fatigue of glass is directly related to the usual chemical attack by aqueous solutions since, for this soda-lime glass, such attack, especially on the silica network, would be expected to proceed more rapidly in the basic than in the acidic solution. This point is discussed in more detail below.

(B) *Effect of Buffer Solutions:* To study the range of pH near to that of distilled water, tests were conducted with the specimens immersed in buffer solutions.* The results are presented in Table III and shown graphically in Fig. 5. It can be seen that none of the intermediate values of pH yielded results differing significantly from those obtained with distilled water. This is consistent with the lack of effect of dilute HCl and NaOH solutions and is again at variance with expectations based on a theory that static fatigue results from a simple corrosion mechanism.

(C) *Different Acids and Bases:* Tests were conducted in 1 N solutions of several acids and bases. The results are given in Table IV.

In all cases the acids yielded strength values below that for distilled water and two of them appeared to be more effective than HCl in promoting fracture. The weak base NH₄OH did not differ from water whereas KOH appeared to be intermediate between water and NaOH in its effect.

IV. Discussion

In this section the complete static fatigue curve for abraded glass as disclosed by the results of this and previous parts of this study is presented and discussed. Possible mechanisms for static fatigue are reviewed and discussed briefly, and finally, the current results are considered in terms of these mechanisms.

(1) Complete Static Fatigue Curve

In Part II of this study static fatigue curves were presented for specimens containing a variety of artificial abrasions and all tested immersed in distilled water.^{9(b)} It was shown that when the reduced strength values, σ/σ_N , were plotted vs. a reduced time scale, $t/t_{0.5}$, all the data could be fitted within experimental error by means of a single universal fatigue curve. The complete strength and static fatigue behavior of each abrasion could be specified by means of this curve in conjunction with the values of σ_N and $t_{0.5}$ associated with the particular abrasion. Using the data of that study the universal fatigue curve could be constructed for a range of $t/t_{0.5}$ from 10^{-4} to 10^5 over which σ/σ_N decreased from 0.82 to 0.21.

In the current study the tests in low humidity conditions led to large values of the characteristic duration so that, for

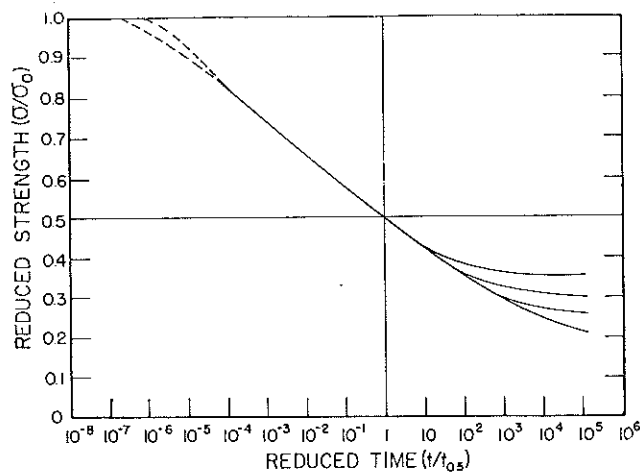


Fig. 6. Complete reduced static fatigue curve. Strength divided by instantaneous strength vs. load duration divided by characteristic duration. The curve applies for specimens tested in water and in atmospheres of varying relative humidity. See text for discussion of short- and long-time regions.

the actual load durations available, the reduced time reached very small values. If one assumes that the static fatigue follows the same general curve under these different conditions, these new data permit the continuation of the universal fatigue curve to shorter reduced times, and in fact to durations where $\sigma \approx \sigma_N$. The complete universal fatigue curve as constructed from the current data plus that reported in Part II is shown in Fig. 6.† In this figure the curve is shown as dotted for durations less than $t/t_{0.5} = 10^{-4}$. This reflects a lack of agreement in the shortest-time points for the two upper curves of Fig. 1 when those curves are plotted on a reduced ($t/t_{0.5}$) time scale.‡ Since there is some small uncertainty in the duration and amplitude of the load for the shortest (0.0025-second) duration, it is not certain whether this lack of agreement at the smallest durations results from some such instrumental variable or reflects a real variation in fatigue behavior from that which would correspond to the existence of the universal fatigue curve.

It will also be seen that multiple curves are shown at the extreme long time end. Unlike the case for short durations this does not reflect any possible uncertainty in the position of a single curve. Rather it reflects the knowledge that more than one curve is necessary in this time range depending on the conditions of the test. At these durations, under certain conditions, the aging or healing of abrasions with time as discussed in Part III of this series^{9(c)} becomes comparable to the static fatigue effect, and compensates for it, with the result that an "endurance limit" is observed; i.e., the fatigue curve becomes horizontal and there is an applied stress below which breakage will not occur regardless of the duration of the stress. Other studies at this laboratory have shown that various factors such as temperature§ and composition of the glass¹⁰ can affect the healing of abrasions to a greater or lesser degree than they affect static fatigue. This leads to different values of reduced time at which the endurance limit can be said to be

* Fisher Scientific Company.

† In the figure, σ_0 , the instantaneous strength is used rather than σ_N , the low-temperature strength. As discussed above, these two quantities are, as nearly as can be determined, equal to each other.

‡ See Section III (1).

§ The effect of temperature will be discussed in Part V of this series.

¹⁰ M. Watanabe, R. V. Caporali, and R. E. Mould, "Effect of Chemical Composition on Strength and Static Fatigue of Soda-Lime Glass," *Phys. and Chem. of Glasses*, 2 [1] 12-23 (1961).

reached and to different values of σ/σ_N for the long-time horizontal asymptote of the static fatigue curve. In the current experiments observed endurance limits have ranged from $\sigma/\sigma_N = 0.2$ to $\sigma/\sigma_N = 0.4$. The statement which is often met in the literature that the very long time strength of glass or the endurance limit is about one-third of the very short time strength appears to be approximately correct in most cases.^{11,12}

Bearing in mind the uncertainty at the shortest load durations and the somewhat variable nature of the long-time behavior, the complete universal fatigue curve of Fig. 6 is believed to represent the static fatigue behavior of glass to within about 5% over the entire range of time and strength values. This method of analysis of the results of static fatigue tests provides a dual criterion for the evaluation of physical theories for the fatigue mechanism. A complete theory must explain the nature and shape of the universal fatigue curve. It must also be consistent with the observed dependence of the characteristic duration, $t_{0.5}$, on such experimental variables as the surrounding medium during test and the nature and severity of the abrasions present in the test specimens.

(2) Physical Basis of Static Fatigue

In Part II of this series the shape of the universal fatigue curve and the dependence of $t_{0.5}$ on the severity of the abrasion were discussed in terms of various theories which have been proposed for the static fatigue of glass.^{9(b)} It was concluded that none of the existing theories completely explained the results but that those which were most successful assumed that fatigue arose from the growth, under stress and the action of an attacking medium, of minute cracks in the surface of the specimen until they reached a size such that the instantaneous strength equaled the applied stress and rupture occurred. It was further concluded that the rate of crack growth probably depends on the instantaneous localized stress at the crack tip as determined by the applied stress and the instantaneous depth of the crack and also, independently, on the crack depth itself. The dependence on the crack depth was believed to reflect the influence of this depth on the availability of the surrounding medium to the tip of the growing crack.

The experiments reported in Part III of this series dealt with the aging of fresh abrasions and disclosed further information which should be borne in mind in discussing static fatigue.^{9(c)} When a specimen containing a fresh abrasion is exposed for a period of time, in the absence of stress, to water or to an atmosphere containing water vapor, its strength is observed to increase by as much as 50%. It was concluded that the most likely cause of this increase was an increase in the effective radius of the crack tip under the action of water or water vapor and a corresponding decrease in the stress concentration factor associated with the abrasion. This raises the possibility that at least part of the static fatigue effect may result from the reverse of this mechanism. Thus the initial stages of static fatigue may involve a change in the shape of the crack tip and an increase in the stress concentration factor. At values of applied stress which are a large fraction of the instantaneous strength this change alone could be adequate to produce failure whereas for smaller values of stress it could be the initial stage in a process of crack growth which ultimately leads to failure.

In any case, regardless of its exact nature, the change in the size and shape of the abrasion crack appears to depend on both the magnitude of the applied stress and on the availability of an interacting medium at the tip of the crack. There are two important aspects of this process which must be taken into consideration. These are (1) the nature of the interaction between the attacking medium and the glass at the tip of the tiny abrasion crack and (2) the mechanisms governing the motion of the medium to the tip of the crack and the variables which determine its concentration at that point.

Both of these aspects have been discussed in the literature in terms of various models and mechanisms. The points of view advanced by various investigators are now summarized and discussed briefly.

(A) Baker and Preston² and Charles³ have considered static fatigue to be produced by the usual chemical attack of water or aqueous solutions on a glass surface as enhanced by the very high localized stresses which the general applied stress produces at the tips of the surface cracks. According to the ordinary concepts of the chemical durability of soda-lime glass, the rate of such attack depends on the pH of the surrounding medium, increasing with increasing alkalinity of the medium. It also depends on the chemical composition of the glass, increasing with increasing Na_2O content. If static fatigue results from the same reactions encountered in the usual durability tests, it would also be expected to show these same dependences.

(B) Orowan has taken a somewhat different approach to the problem by considering it in terms of the Griffith relation:

$$\sigma = \sqrt{\frac{2E\alpha}{\pi c}} \quad (1)$$

where σ = breaking stress, E = Young's modulus, α = surface energy, and c = the depth of the most severe surface crack present.¹³ Noting that the surface energy of mica when cleaved in vacuum is about ten times as great as when cleaved in air, he states that a similar ratio should exist for glass. By equation (1) this would lead to a long-time strength, or endurance limit, in air of about one-third the vacuum or very short time strength. For loads of intermediate duration he believed the fatigue rate in air to be governed primarily by the rate at which an adsorbed film of air or water can be formed on the glass surface and diffuse to the tip of the abrasion crack.

(C) By an analysis of their own data for the static fatigue of glass in atmosphere and in vacuum and that of Vonnegut and Glathart⁶ on the effect of temperature, Gurney and Pearson⁴ arrived at the conclusion that the reaction between glass and air or water vapor does not involve a direct reaction between glass and the gaseous phase. They concluded that, at room temperature, the reaction at the crack tip must be between glass and adsorbed surface layers or capillary liquid in the crack. At elevated temperatures, where the adsorbed layers are driven off, they conclude that the reaction may take place directly with the gaseous phase.

In another paper Gurney considered this and other possible mechanisms for the static fatigue of glass from a theoretical standpoint.¹⁴ He concluded that in addition to the effect of atmospheric attack the approach to homogeneous equilibrium of the highly stressed material at the crack tip might play a role in the fatigue process.

(D) Moorthy and Tooley, in considering their results on the strength of glass as affected by immersion in various organic liquids during test, discussed alternative possibilities for the greater strength values observed relative to those for specimens tested while immersed in water.⁵ One possibility considered was the strengthening of points of weakness in the surface by the bridging of unsaturated oxygens through hydrogen bonding. The second hypothesis, which they

¹¹ A. J. Holland and W. E. S. Turner, "Effect of Sustained Loading on Breaking Strength of Sheet Glass," *J. Soc. Glass Technol.*, 24 [101] 46-57T (1940); *Ceram. Abstr.*, 19 [8] 186 (1940).

¹² E. B. Shand, "Experimental Study of Fracture of Glass: I, The Fracture Process," *J. Am. Ceram. Soc.*, 37 [2] 52-60 (1954).

¹³ E. Orowan, "Fatigue of Glass Under Stress," *Nature*, 154 [3906] 341-43 (1944); *Ceram. Abstr.*, 24 [1] 7 (1945).

¹⁴ C. Gurney, "Delayed Fracture in Glass," *Proc. Phys. Soc. (London)*, 59, 169-85 (1947); *Ceram. Abstr.*, 1951, September, p. 166f.

considered in some respects to be more valid, was that the organic liquids had a dehydrating effect and served to decrease the weakening effect of previously adsorbed water.

(E) More recently Elliott has advanced the idea that the rate of crack growth under stress and thus of static fatigue may be governed by the rate of diffusion of the attacking medium through an amorphous corrosion product remaining in the crack.¹⁵

All the hypotheses described in the foregoing are consistent with the general features of static fatigue as illustrated in Fig. 6. Thus any theory which involves a time-dependent interaction between the glass and the surrounding medium predicts that the strength in vacuum is independent of load duration and that the strength in other media will tend toward the vacuum value as the load duration is decreased. The concept of an endurance limit or stress which the glass will withstand indefinitely arises naturally in connection with Orowan's treatment in terms of surface energies. It is also consistent with a mechanism involving a stress-dependent chemical attack if the aging of abrasions as discussed in Part III of this series^{9(c)} is taken into account. For small enough values of applied stress the healing of flaws produced by chemical etching and rounding of their tips can become more pronounced than the weakening produced by the fatigue mechanism. Baker and Preston² and Charles⁸ recognized that this mechanism could lead to the existence of an endurance limit.

(3) Effect of Relative Humidity

Probably the most important conclusion to be drawn from the results of the present study is with respect to the overriding importance of the effect of water in determining the static fatigue behavior of glass. Nearly all the results obtained can be explained on the basis that the interaction between glass and water is the determining factor in the fatigue process and that the role of various media is primarily that of determining the concentration of water at the tip of the growing crack. The results in atmospheres of differing relative humidity indicate that this effect is a progressive one extending to rather low concentrations of water vapor. With respect to strength and fatigue behavior a glass surface does not appear to be simply "wet" or "dry." Rather it is in equilibrium with its surroundings and its relative "wetness" is reflected in its strength behavior. Whether this equilibrium is with respect to an adsorbed film of water which is diffusing into the advancing crack or whether it involves a direct exchange between the atmosphere and the glass at the tip of the crack cannot be determined from the present results.

(4) Effect of Alcohol

For the tests in mixtures of water with methyl and isopropyl alcohol, the fatigue rate (or, in other terms, the strength at a given load duration) varied monotonically with the concentration of water, by volume, in the solution. Furthermore, when the data were considered in terms of the water concentration, the differences between the two alcohols largely disappeared and both appeared to be acting primarily as diluents for the water present. For concentrations of water of 1% or less there were small differences between the fatigue curves in the two alcohols, but these differences were smaller than have been observed by previous investigators.⁵ In view of the fact that different methods of specimen preparation and treatment before test were employed in the current experiments and in those of Moorthy and Tooley,⁵ this lack of exact agreement is not surprising. Perhaps the most likely source of the difference lies in the fact that Moorthy and Tooley tested specimens which were immersed in the test medium without a previous common aging treatment such as was used in the present study. Thus the aging of any abrasions present on their specimens (as discussed in detail in Part III of this series^{9(c)}) would have occurred during the test itself and exerted an influence on the results obtained.

That such was probably the case is indicated by the fact that in one special test where specimens were tested in methyl alcohol after immersion in water (a procedure similar to that of the present study), they obtained higher strength values than for specimens which were given their regular treatment which did not involve such immersion.

It is possible that even for the driest grades of alcohol used in the present study the small amounts of water present may have played a role in the observed static fatigue behavior. Thus the static fatigue curve for soda-lime glass in completely anhydrous alcohol might differ significantly from those shown in Fig. 2 of this paper. In this connection the results of Berdennikov¹⁶ as summarized in detail by Kuznetsov¹⁷ are of considerable interest. Using the Griffith relation (equation (1)) he determined the surface energies of glass in various media by observing the stress at which a crack of known length would just begin to extend in a specimen immersed in the medium under study. The liquids were distilled *in vacuo* and special measures were taken to dry them. In addition the dryness was checked by measuring the breakdown voltage and dielectric strength of the liquids. Thus in Berdennikov's tests the liquids were probably the driest which have been studied in connection with the fracture of glass.

He found, for cracks of equal initial length, that the stresses which caused the cracks to begin to grow in water and in methyl alcohol were 0.49 and 0.66 respectively times that necessary to initiate propagation in vacuum. According to the surface energy theory of static fatigue as advanced by Orowan, this would imply that the endurance limit in these media should occur at values of applied stress which bear approximately this same relation to the strength as measured in liquid nitrogen. This appears to be inconsistent with the present study in that the endurance limit in water at room temperature was found to be between 0.2 and 0.3 of the instantaneous strength. In addition the static fatigue curve in methyl alcohol showed no signs of flattening at 0.66 of the instantaneous strength as would be expected.

Two explanations for this discrepancy suggest themselves. The first relates to the shape of the abrasion cracks in the present study or of the cracks studied by Berdennikov. The estimation of the endurance limit relative to the vacuum or instantaneous strength from the relative surface energies in vacuum and in the test medium is based on the assumption that the initial stages of flaw growth are the same under both conditions of test. If, as suggested in Part III of this study, the aging of abrasions is related to a slight rounding of the tips of the flaws, it is possible that the effective tip radius changes rapidly during the early stages of the fatigue process and that this change leads to a greater strength decrease than would be expected from the surface energies alone.

A second possible explanation relates to the time scale of Berdennikov's experiments and to the minimum rate of flaw growth which he was able to observe. His values for the relative stress necessary to initiate crack growth in water and in methyl alcohol correspond closely to the relative strength values observed in these media in the present study for load durations of approximately 10 seconds. This suggests that the smallest observable rate of crack growth may have corresponded to that which occurs in fatigue tests for this duration of load. If this explanation is correct, then Berdennikov did not in fact obtain the equilibrium values of surface energy in the various media but rather some higher value associated with the particular time scale of his experiment. A similar

¹⁵ H. A. Elliott, "Stress Rupture in Glass," *J. Appl. Phys.*, 29 [2] 224-25 (1958).

¹⁶ V. P. Berdennikov, "Measurement of Surface Tension of Solids," *Zhur. Fiz. Khim.*, 5 [2/3] 358-71 (1934).

¹⁷ V. D. Kuznetsov, *Surface Energy of Solids* (translated from the Russian), Chapter VI. Department of Scientific & Industrial Research, Her Majesty's Stationery Office, London, 1957. 283 pp.

experiment, carried out at much longer times or with much greater sensitivity to very small rates of crack growth, might then lead to considerably lower values for the surface energies of glass in various media relative to that in vacuum.

It is of interest to note that for tests in vacuum, where static fatigue does not play a role, Berdennikov obtained a value of surface energy of 1260 ergs per sq. cm. This is in reasonable agreement with the value of 1600 ergs per sq. cm. as estimated from the liquid nitrogen strength of specimens with abrasions of known depth as reported in Part II of this series.^{9(b)}

(5) Effect of Acidic and Basic Solutions

The results of the present study for specimens tested in acidic and basic solutions tend to support the general view that the static fatigue of glass depends primarily on the reaction between water and the glass surface. Strength at an intermediate load duration was found to be independent of the pH of the test solution over the range pH 1 to 13. Only for solutions beyond this range was the strength value significantly different from that for distilled water with acidic solutions yielding somewhat smaller and basic solutions somewhat greater values.

The literature on the chemical durability of glass has been reviewed extensively by Morey.¹⁸ For soda-lime glass the rate of attack by aqueous media generally increases with increasing pH, i.e., for more alkaline solutions. For glasses of different compositions the rate of attack increases with increasing alkalinity of the glass, the durability of the glass decreasing as the alkali content is increased. Some of the studies summarized by Morey led to the general conclusion that acid solutions do not differ appreciably from water in their rate of attack on soda-lime glass until high concentrations are reached, at which point the rate of attack is diminished. In a more recent study, however, Raggon and Bacon¹⁹ found that the silica extraction from a commercial container glass by HCl solutions increased with increasing strength of the solutions whereas the Na₂O extraction remained approximately constant.

Pike and Hubbard studied the attack of buffer solutions on a soda-lime glass surface by means of an interferometric comparison of exposed and unexposed areas.²⁰ Judged by this means the depth of attack was independent of pH until a value of about 9.5 was reached. For solutions more alkaline than this the attack increased rapidly with increasing pH.

The effect of pH on the equilibrium solubility of amorphous SiO₂ as determined by studies of colloidal suspensions has been summarized by Iler.²¹ The solubility is essentially independent of pH in the range pH 1 to 9 and increases with pH for values above pH 9. Although, as Iler points out, it is not certain that a true equilibrium was reached in the studies which he summarizes, it appears that both the rate of attack of aqueous solutions on glass and the silica concentration in equilibrium with glass should increase with increasing alkalinity of the attacking medium.

Based on the behavior summarized here, it might be expected that in an aqueous medium the rate of static fatigue would be greatest and the strength least for alkaline solutions,

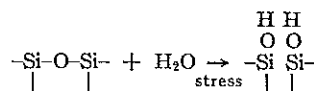
especially for values of pH greater than about 9. The observed behavior was the reverse of this with the strength increasing (i.e., fatigue decreasing) for highly alkaline solutions. Furthermore, it should be noted that this strength increase did not become appreciable until about pH 14 whereas the increase in chemical attack becomes very pronounced above pH 10. On the acid side a small but definite decrease in strength occurs for solutions more acid than pH 1 (0.1 *N* HCl). This appears to be more consistent with the increased silica extraction noted by Raggon and Bacon¹⁹ for increasingly acidic solutions than with the apparent lack of effect of acid as judged by other methods of studying chemical attack.

Considering especially the results for alkaline solutions, it is apparent that the static fatigue of glass cannot be related in a simple way to the ordinary chemical attack of acidic and basic solutions on the glass surface as has been suggested.^{2,8} This conclusion is further reinforced by the results of a systematic study of the effect of chemical composition on the strength and static fatigue of soda-lime glass.¹⁰ In that study it was found that the aging or healing of fresh abrasions depended strongly on the soda content of the glass whereas the static fatigue behavior did not.

A possible explanation for these differences between fatigue and chemical durability may be found by considering the nature of the two processes. The chemical attack of an aqueous solution on a glass surface can be thought of as a two-step process. First the water reacts with the surface to form a complex hydrated layer. This layer is then gradually dissolved or decomposed by the solution, permitting the attack to occur to greater depths. The normal occurrence of a hydrated layer many atoms deep on a glass surface aged in ordinary atmosphere and the very low solubility of silica in neutral water suggest that it is the second stage of the hydrolysis and dissolution reaction which generally limits the rate of chemical attack on soda-lime glass. This view is substantiated by the fact that, as discussed by Iler, the solubility of silica and siliceous ions increases with increasing pH. The value of pH at which the solubility increases markedly is about the same as that at which the rate of attack on soda-lime glass becomes marked. The effect of pH on the attack rate may therefore reflect its effect on the dissolution or decomposition of the hydrated surface layer rather than on its formation.

The lack of a marked increase in the static fatigue rate and of a corresponding decrease in the observed strength for alkaline solutions may then indicate that fatigue involves only the formation of hydrated surfaces in the advancing crack and not their dissolution. As the crack extends, fresh surface is continually exposed to the attacking medium and the process can continue without the necessity for the removal of the hydrated surfaces.

If the reaction between water and the highly stressed bonds at the tip of the crack is a simple hydration which can be represented schematically by



then other ions present in the glass or solution may play a negligible role. Such a picture of the fatigue process is consistent with the lack of dependence of the fatigue rate on pH over a wide range of intermediate values as observed in the present study and with its lack of dependence on the Na₂O content of the glass.¹⁰ Thus the effect of pH like that of alcohol leads to the general conclusion that water is the primary agent involved in the static fatigue of glass.

The foregoing explanation for the static fatigue effect does not, of course, account for the small strength differences noted for specimens tested in relatively strong acidic and basic solutions. For basic solutions of 1 *N* concentration or

¹⁸ G. W. Morey, *Properties of Glass*, 2nd ed.; Chapter IV, "The Chemical Durability of Glass." American Chemical Society Monograph Series, No. 124, Reinhold Publishing Corp., New York, 1954. 591 pp.; *Ceram. Abstr.*, 1954, October, p. 180h.

¹⁹ F. C. Raggon and F. R. Bacon, "Action of Hydrochloric Acid Solutions on Borosilicate and Soda-Lime Glass Bottles," *Am. Ceram. Soc. Bull.*, 33 [9] 267-71 (1954).

²⁰ R. G. Pike and Donald Hubbard, "Increased Chemical Reactivity of the Surface Compared with That in the Bulk Volume of Britton-Robinson Universal Buffers," *J. Research Natl. Bur. Standards*, 59 [6] 411-14 (1957); RP 2811; *Ceram. Abstr.*, 1960, February, p. 46e.

²¹ R. K. Iler, *Colloid Chemistry of Silica and Silicates*; Chapter I, "The Silica-Water System." Cornell University Press, Ithaca, N. Y., 1955. 324 pp.; *Ceram. Abstr.*, 1956, May, p. 107j.

greater it is possible that ordinary chemical attack rounds the tips of the cracks during test and competes with the crack-growth mechanism to lead to somewhat higher observed strength values. In acids of greater than 1 *N* concentration, it is possible that the highly mobile H⁺ ion may diffuse into the glass network and in some way accelerate the crack-growth mechanism slightly. Both of these suggestions must be considered as highly conjectural, however, in terms of current experimental knowledge.

(6) General

Based on all the results of this study the current knowledge of the static fatigue of abraded glass and the role of the surrounding medium can now be summarized as follows. Static fatigue, or the decrease of strength with increasing load duration, results from changes, under stress, in the shape and/or depth of surface flaws and cracks which have resulted from previous mechanical contact with the surface. These changes take place only in the presence of a surrounding medium which can react with the newly formed surfaces of a growing abrasion, thereby decreasing their surface energy. Water appears to be the most effective agent for this process and the rate of crack growth is governed primarily by the localized stress at the crack tip and by the concentration of water or water vapor at that point. In contrast to ordinary chemical attack on glass surfaces, the rate of fatigue is affected only slightly by the presence of other ions or molecules either in the attacking medium or in the glass itself except as these may affect the concentration of water at the tip of the flaw. The reaction generally appears to involve only water and the silica network of the glass and may be thought of as a simple hydrolysis of the surfaces formed during crack growth.

(7) Practical Significance of Static Fatigue and Effect of Surrounding Medium

Because of the very short load durations at which the strength begins to deviate from the instantaneous strength, static fatigue plays a role in almost all breakage of glass except that produced by impact or in vacuum or at very low temperatures. In practice this means that in virtually all testing or breakage of glass, with the exception of impact, the duration of load and the nature of the surrounding medium have an effect on the breaking stress. The effect of load duration has long been recognized and standard tests²² for the strength of glass and glass articles include specifications for the duration of load or the rate of loading to be employed or a provision for including a statement of these quantities in the report of the results.

The weakening effect of water has also long been recognized from a practical standpoint, and a common practice in breaking glass through the use of a glass cutter is to moisten the scratch before applying stress to produce breakage. Perhaps not so widely recognized is the effect of relative humidity on the breaking stress as indicated in Fig. 1. From that figure it can be seen that, for a given intermediate value of load duration, the strength in a very dry atmosphere may be 20% greater than that in an atmosphere of intermediate humidity and 45% greater than that in contact with liquid water. Thus for tests in air, differences in relative humidity can produce differences in the observed strength and for extreme variation (as, for instance, between a rainy summer day and the interior of a heated building in winter) these differences may be great enough to be of practical concern. Probably the simplest way to circumvent this difficulty in many cases is to conduct tests with the specimens wet or immersed in water. Such a procedure has the dual advantage of eliminating differences caused by changes in relative humidity and of testing the specimens under the most severe conditions likely to be encountered. In this connection it should be remembered that the degree of aging of any abrasions present can also have an appreciable effect on the results of a strength test (see Part III⁽⁶⁾).

Of further interest is the nature of the static fatigue curve itself. Because of the logarithmic nature of this curve the strength differences associated with moderate changes in load duration or loading rate are rather small. Over most of the curve, changing the load duration by a factor of 10 produces a change in strength of less than 10% of the instantaneous strength, whereas a change of 10% in load duration produces a change of less than 1% in the strength. Although it is important to control or state the duration of load in testing the strength of glass and glassware, highly exact control is not necessary, and variations of 10 or even 20% in the duration or rate of loading can readily be tolerated in most cases.

In the commercial use of glass it would, of course, be highly advantageous from a strength standpoint if the static fatigue process could be eliminated or suppressed so that the strength at any load duration would equal the instantaneous strength. Such a development would lead to an increase in the very long time strength by a factor of three to four. The results of this and previous studies, however, indicate the very great difficulties inherent in any attempt to achieve this goal. Two characteristics of the fatigue process are important to consider in connection with any attempt to eliminate or reduce static fatigue. The first is the nature of the fatigue curve itself. Any attempt to eliminate fatigue by preventing water or water vapor from reaching the tip of the surface cracks will, unless the elimination of water is very complete, simply shift the fatigue curve to longer times. Although, as shown in Fig. 1, the strength at any given load duration will be somewhat greater, it seems unlikely that the endurance limit will be greatly affected. Thus any treatment which reduces static fatigue without eliminating it entirely may somewhat increase the strength for intermediate durations of load. However, the endurance limit, or safe stress level for very long time loads, will be unaffected. Furthermore, very large changes in fatigue rate are necessary to produce moderate differences in strength at any given duration. As shown by the current results (Fig. 1 and Table II), in a very dry atmosphere the fatigue rate is reduced by a factor of approximately 400 relative to wet specimens but the strength at any load duration is increased by only about 45%.

The second important characteristic is the nature of the reaction between the surroundings and the glass which leads to static fatigue. Since static fatigue appears to involve a simple interaction between water and the silica network of the glass and to be essentially independent of the presence of other materials, it seems highly unlikely that any of the measures, such as surface dealkalization²³ or changes in chemical composition, which successfully improve the chemical durability of glass with respect to water attack will produce a similar improvement in the static fatigue behavior.

V. Summary and Conclusions

The results of this study can be summarized as follows:

(1) At any given intermediate duration of load the strength of glass increases with decreasing relative humidity of the atmosphere in which it is tested. In nitrogen atmospheres of approximately 0.5 and 43% relative humidity, the respective strength values were approximately 45 and 20% greater than in distilled water over an intermediate range of durations.

²² (a) "Tentative Method of Internal Pressure Test on Glass Containers," A.S.T.M. Designation C 147-59T. 1959 Supplement to Book of A.S.T.M. Standards, Part 5. American Society for Testing Materials, Philadelphia, Pa.

(b) "Standard Method of Flexure Testing of Glass (Determination of Modulus of Rupture)," A.S.T.M. Designation C 158-43. 1955 Book of A.S.T.M. Standards, Part 3, pp. 919-21. American Society for Testing Materials, Philadelphia, Pa.

²³ H. S. Williams and W. A. Weyl, "Surface Dealkalization of Finished Glassware, I-II," *Glass Ind.*, 26 [6] 275-77, 290-92, 301; [7] 324-26, 339, 341-42, 344 (1945); *Ceram. Abstr.*, 24 [9] 163 (1945).

(2) For loads of very short (less than 10^{-3} seconds) and very long (greater than about 1 hour) duration these differences tend to disappear and the effect of the surrounding medium on strength is best interpreted in terms of the static fatigue effect and the rate of the static fatigue process.

(3) For the grit-blast abrasion which was studied, the characteristic durations, $t_{0.5}$, at which the strength equaled one-half the instantaneous strength were 8, 200, and 3500 seconds, respectively, for the tests in water and in atmospheres of 43 and 0.5% relative humidity.

(4) For specimens tested in methyl and isopropyl alcohol and in mixtures of these liquids with water, the strength and static fatigue rate depended primarily on the water content of the solution and differences between the two alcohols were relatively unimportant. In the driest solutions studied (0.01 to 0.05% H_2O), the strength at intermediate load durations (about 10 seconds) was about 40% greater than in distilled

water, whereas for very short durations this difference tended to disappear.

(5) For tests in acidic and basic solutions the strength at a given load duration was independent of pH over the range pH 1 to 13. In 6 *N* NaOH the strength was 10% greater than in distilled water, and in 6 *N* HCl it was about 10% less. In 1 *N* concentrations, other acids and bases were comparable to HCl and NaOH in their effect on strength.

(6) Based on the foregoing results the static fatigue of glass appears to result from changes in the size and depth of surface abrasion cracks under the combined action of stress and water or water vapor. The interaction leading to these changes appears to involve primarily the neutral water molecule and the SiO_2 network of the glass. Unlike the usual chemical attack, it is relatively independent of the presence of other ions either in the glass or in the solution except as these may serve to reduce the concentration of water and its availability at the tip of the crack.