

Strength and Static Fatigue of Abraded Glass Under Controlled Ambient Conditions: III, Aging of Fresh Abrasions

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The effect of aging under various conditions on the strength and static fatigue of freshly abraded specimens has been studied. For both grit-blast and emery cloth abrasions the liquid nitrogen (fatigueless) strength increased with storage time after formation of the abrasions for specimens stored in liquid water or in an atmosphere containing water vapor. After 1 day of storage in water the strength increase was about 60% of the freshly abraded value for emery cloth abrasions and about 30% for grit-blast abrasions. The aging depended strongly on the medium in which the specimens were stored and on the relative humidity when they were stored in air. In very dry air or vacuum the aging effect appeared to be eliminated. Static fatigue curves (strength vs. load duration) in water were measured for specimens containing fresh abrasions and aged abrasions. Ordinary aging did not change the static fatigue behavior of fresh abrasions. The liquid nitrogen strength and static fatigue also were studied for specimens which had been baked at 470°C. in high vacuum after being abraded. This treatment increased the fatigueless strength by approximately the same amount as aging in water. The rate of static fatigue, however, which was unaffected by ordinary aging, was reduced by a factor of approximately 25 for vacuum-baked as compared with fresh abrasions. Possible mechanisms for aging are discussed in some detail. It is proposed that the observed aging effects on the fatigueless strength can be accounted for by an increase of the radii of the tips of the abrasion cracks in the surfaces of the specimens. The suppression of fatigue for the vacuum-baked specimens is believed to be related to the non-wettability of their surfaces which was observed in the course of the experiments.

I. Introduction

It generally is believed that a piece of glass containing a cut or scratch can be broken more easily and cleanly while the cut is fresh than after it has aged. The scientific validity of this belief has been demonstrated for diamond scratches by Holland and Turner¹ and by Jebsen-Marwedel

and von Stösser.² More recently Levengood³ has reported on the aging of cuts made with a steel wheel glass cutter. All these investigators found that the strength of freshly scratched glass does increase with storage time after the cut or scratch has been formed. The observed increases ranged from 30 to 100% of the strength immediately after scratching and the time scale of the effect varied from a few hours to about 1 day.

These strength changes, which result from aging, are great enough so that they must be considered in any study which aims to make use of standardized abrasions. In the investigation being reported in the present series of papers⁴ a controlled abrasion treatment to the glass surface is employed as a tool in investigating the various factors which affect the strength of glass. It is apparent that aging effects must be taken into account since they are greater, in many cases, than those produced by other variables under study and could easily mask important effects or lead to misinterpretation of the data. Thus one of the goals of the experiments to be reported here was the determination of reproducible aging treatments to be used as part of the standardized abrading and aging of glass specimens in the course of studying other variables.

A second goal was the development of an understanding of the nature of the aging process itself. The previous studies referred to demonstrated the general magnitude and time scale of the effect. One of them showed an apparent dependence on the chemical environment of the specimens.³ Many basic questions remained, however, unanswered. Do the observed changes in strength reflect changes in the "instantaneous strength" as defined in Part II of this series,^{4(b)} or do they rather reflect changes in the static fatigue behavior of aged as compared with fresh abrasions? What is the mechanism for the change? Holland and Turner suggested that it reflected the release of stresses produced by splinters of glass wedged in the fresh cuts. Levengood believed that the aging effects were produced by a partial chemical "healing"

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¹ A. J. Holland and W. E. S. Turner, "Effect of Transverse Scratches on Strength of Sheet Glass," *J. Soc. Glass Technol.*, 21 [87] 383-94T (1937); *Ceram. Abstr.*, 17 [9] 302 (1938).

² H. Jebsen-Marwedel and K. von Stösser, "Der Mechanismus des Schneidens von Glas und die Schwächung des Glases durch den Schnitt" (Cutting of Glass and Weakening of Glass Through the Cut), *Glastech. Ber.*, 17 [1] 1-11 (1939); *Ceram. Abstr.*, 18 [7] 177 (1939).

³ W. C. Levengood, "Effect of Origin Flaw Characteristics on Glass Strength," *J. Appl. Phys.*, 29 [5] 820-26 (1958); *Ceram. Abstr.*, 1958, September, p. 230i.

⁴ (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).

of the cracks produced by the cutter wheel of his experiments. A third possible mechanism is a chemical rounding of the roots of the cuts or abrasions similar to that observed in the case of hydrofluoric acid etching or high-temperature steam autoclaving of damaged glass.⁵

Another question concerns the relation between the aging of abrasions and their geometrical shape. Part II of this series showed that the static fatigue behavior of abraded glass specimens depended on the geometry of the surface cracks produced by the damaging treatment.^{4(b)} Based on the results of strength tests, it was possible to draw a clear distinction between "linear" and "point" flaws in the surface which was consistent with their known geometry as determined by microscopic examination. All the aging studies reported previously have dealt with diamond and steel wheel cuts which would fall into the category of linear flaws. It therefore was of considerable interest to determine the aging behavior of point flaws as produced by a grit-blast type of surface damage, and to compare this with that of linear flaws.

Using the apparatus and experimental techniques described in the previous papers of this series⁴ an experimental study of the effect of the aging of fresh abrasions on the strength of the resulting specimens was carried out. In particular the following topics were studied: (1) the effect of aging on the liquid nitrogen or fatigueless strength, (2) the effect of aging on the static fatigue curve, (3) the time dependence of the aging process, (4) the effect of the chemical environment on the aging process, and (5) the effect of surface crack geometry on the aging behavior.

II. Experimental Methods

As in previous parts of this study⁴ the specimens were standard laboratory microscope slides.* The general experimental method consisted of abrading, aging, and testing the specimens where each of the three steps was carefully controlled and was carried out in a controlled environment.

During this study of aging behavior two different abrasions were used. One was the silicon carbide grit blast which was designated as abrasion (b) in Table III of Part II of this series. The other was hand abrasion with 320-grit emery cloth at right angles to the direction in which the tensile stress was to be applied in testing. This abrasion was designated as abrasion (c) in Part II. As shown in the analysis of Part II, these two abrasions produce examples of point and linear flaws, respectively, on the surface of the specimen. Since each is the only abrasion of its type considered in this paper, they will be referred to hereafter as the standard grit-blast and emery cloth abrasions without repeating the grit and grain sizes on each occasion.

The aging treatments which were used will be described in the course of presenting the results. The strength tests were carried out with the previously described electromagnetic tester. In most cases the specimens were tested while immersed in liquid nitrogen, i.e., at a temperature of 77°K. Since under this test condition the strength (σ_N of Part II) is independent of load duration, such tests provide a valuable means of eliminating static fatigue and measuring the instantaneous, fatigueless strength of a glass specimen in any given condition.

In studying the effect of aging on fresh abrasions such a low-temperature technique has an additional advantage. It is possible to immerse the specimens in liquid nitrogen at any time and hold them thus until test with a reasonable assumption that no further change in their condition will take place. In effect, such immersion "freezes in" the state of the specimen at any given time and permits a determination of its true strength at the instant of immersion.

Each strength value to be reported represents the average strength of twenty specimens. As in earlier parts of this study, the standard deviations of the results for the grit-blasted specimens 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%. For the emery cloth abrasion the corresponding figures were 10 to 15% and 2 to 4% respectively.

III. Results

(1) Aging in Water and the Liquid Nitrogen Strength (σ_N)

Preliminary aging experiments were conducted using an automatic impact tester (see Part I) mounted in the controlled-condition chamber along with the grit blaster.⁶ In these tests the impact strength of grit-blasted specimens was found to increase with storage time after abrading. The results can be summarized as follows: (a) The strength increased approximately linearly with log storage time, (b) it appeared to level off after 24 hours at about 20% above the freshly abraded value, and (c) the rate of increase was approximately ten times as great in 70% relative humidity as in 1%, but the total increase after 24 hours appeared to be about the same.

Because of the humidity dependence observed in these experiments, water was believed to play an important role in the aging process. Therefore, after the development of the liquid nitrogen technique the first experiments which were undertaken on the effect of aging on the liquid nitrogen strength were for specimens aged immersed in distilled water. Freshly abraded specimens (either grit blasted or hand abraded with emery cloth) were immersed in distilled water immediately after abrading and were stored for varying lengths of time. After each specified aging time the specimens were removed from the water, dried by blotting gently with cheesecloth, and immersed in liquid nitrogen where they remained until and during test. For each abrasion one set of specimens was immersed in liquid nitrogen as rapidly as possible after abrading and without contact with water. For these control specimens there was approximately 10 seconds of contact with room air between abrading and immersion.

In addition to these experiments, the effect of aging in an atmosphere saturated with water vapor also was studied for each of the two abrasions under consideration. In this case the specimens were placed over water in a closed container and stored for various lengths of time. They then were removed from the container and immersed in liquid nitrogen where they remained until and during test. The results for both storage conditions for each of the two abrasions are shown graphically in Fig. 1.

An examination of the results shows that the aging behavior of the two abrasions was somewhat different. Consistent with the preliminary impact strength studies, the strength of the grit-blasted specimens increased steadily and approximately linearly with the logarithm of storage time under both storage conditions. The increase was greater for the wet than for the saturated vapor condition for short storage

* (a) 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.

(b) J. E. Stanworth, *Physical Properties of Glass*, pp. 91-92. Oxford University Press, London, 1950. 219 pp.; *Ceram. Abstr.*, 1950, October, p. 199f.

* 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.

⁶ R. E. Mould and R. D. Southwick, "Aging in Nitrogen Atmosphere and Vacuum Baking," Preston Laboratories Report No. 56-084, September 29, 1956 (unpublished results).

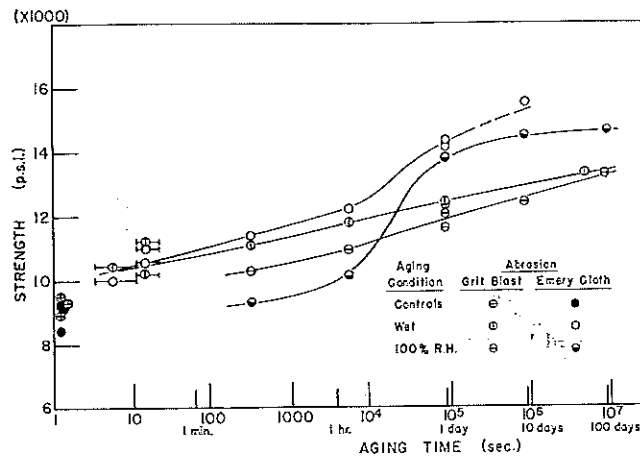


Fig. 1. Aging of fresh abrasions. Strength in liquid nitrogen vs. aging time (log scale).

times, but this difference tended to disappear for long storage times. The previously observed apparent leveling off of the strength after about 24 hours of storage was not observed for the grit-blasted specimens in these tests; rather the increase of strength appeared to continue even after 100 days, the duration of the test. Because of the logarithmic nature of the time dependence, the rate of increase had, of course, become very small by this time.

In the case of the specimens abraded with emery cloth, the aging appeared to be substantially completed at the end of 24 hours and there was little additional change in the strength thereafter.* This general behavior is similar to that observed by Holland and Turner¹ for diamond scratches and by Levengood³ for the cracks produced by a steel cutter wheel. In both experiments the observed strength increases were completed within 24 hours of the formation of the surface damage. A quantitative comparison of the present results with these previous ones are presented later in Section IV.

(2) Other Storage Conditions

To study the effect of various storage conditions, grit-blasted specimens were stored for 20 to 24 hours under various conditions and then tested while immersed in liquid nitrogen. The results are presented in Table I.

From this table one can draw the following conclusions about the aging of fresh abrasions and its effect on the liquid nitrogen or fatigueless strength of specimens containing the abrasions:

(a) The aging of fresh abrasions and the subsequent increase in strength results from an interaction between the glass surface and its environment. In vacuum or very dry air the aging effect appears to be eliminated.

(b) None of the media studied produced an appreciably greater healing effect than did distilled water. For specimens stored in air, water vapor appears to be the active agent in producing aging, since the observed strength increase was directly related to the relative humidity of the air.

(c) Acidic and basic solutions did not differ greatly from water in their effect. The acid appeared to be slightly more effective and the base slightly less so than distilled water.

(d) The aging of fresh damage is less pronounced in methyl alcohol than in distilled water. Thus the increased strength which was observed by Moorthy and Tooley for specimens tested in this medium as compared with water is not produced by a healing effect of the medium as has been suggested.^{3,7} †

Table I. Aging of Fresh Abrasions in Various Media*

Aging medium	Liquid nitrogen strength (lb./sq. in.)	Strength increase (%)
Immediate test	9,470	0
Liquid water	12,340	30
100% relative humidity	12,190	29
50% relative humidity	11,230	19
1% relative humidity	9,870	4
Vacuum (10 μ Hg)	9,840	4
0.1 N NaOH	11,640	23
1 N NaOH	11,960	26
1 N HCl	12,570	33
Methyl alcohol	10,590	12

* Specimens grit blasted, aged 20 to 24 hours in medium indicated, and tested in liquid nitrogen (77°K.).

Table II. Effect of Aging on Static Fatigue*

Load duration (sec.)	Fresh abrasion		Aged 24 hr. in distilled water	
	(lb./sq. in.)	(σ/σ_N)	(lb./sq. in.)	(σ/σ_N)
0.0025	8960	0.82	9645	0.78
0.012	8130	.75	9285	.75
0.050	7090	.65	8314	.67
0.226	6414	.59	7799	.63
0.82	6127	.56	7236	.59
4	5824	.54	6379	.52
15	5147	.47	5822	.47

* Specimens grit blasted, aged as indicated, and tested immersed in distilled water.

(3) Aging and Static Fatigue

All the results reported above have related to the effect of various storage conditions and treatments on the low-temperature or fatigueless strength of specimens containing fresh abrasions. In studies of aging by previous investigators, the strength tests were conducted at load durations and under such conditions that static fatigue must have played a role in the fracture process.^{1,2,3} The question thus remains whether the strength increases which they observed reflect only the change in instantaneous or fatigueless strength as observed in this study or whether these increases also reflect some additional effect of aging on the fatigue mechanism.

(A) *Wet Aging:* To study this question, static fatigue curves were measured immediately after abrasion and after 24 hours of aging in distilled water. The grit-blast abrasion was used and the strength tests were conducted with the specimens immersed in distilled water. The resulting strength values are given in Table II. From the table it can be seen that the strength at all load durations was increased as a result of the aging. From the strength values alone, however, there is no way to determine the nature of this increase, i.e., whether it reflects an increase in the instantaneous strength only or also some change in the fatigue behavior.

* Although the emery cloth abrasions seemed to show some additional aging between 1 and 10 days when stored wet, the 10-day value had an unusually large standard deviation (14% of the average) and must be considered to be somewhat unreliable.

⁷ 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).

† Moorthy and Tooley also considered other explanations for the effect of methyl alcohol on strength, among them a possible reduction in the static fatigue produced by a dehydrating effect of the alcohol.

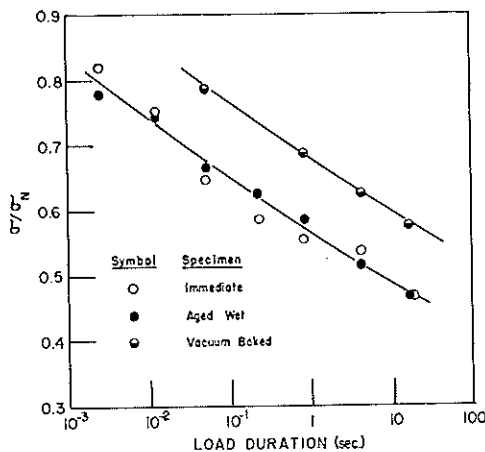


Fig. 2. Reduced strength vs. load duration (log scale) for specimens containing fresh abrasions (immediate test), abrasions aged in water, and abrasions subjected to vacuum-baking treatment. Specimens were immersed in distilled water during testing.

For this purpose it is necessary to analyze the data in terms of the instantaneous (or low-temperature) strength by plotting σ/σ_N , the reduced strength, vs. the load duration for each aging treatment. For this analysis the value of σ_N used for the aged specimens was that given in Table I for specimens stored in liquid water. For the unaged specimens it was necessary to take into account the aging of the specimens in the period during which they were immersed for testing (20 to 60 seconds, depending on load duration). For this reason the value of σ_N for the "immediate" specimens was obtained from Fig. 1. From this figure it can be seen that grit-blasted specimens which have been aged in water for 20 to 60 seconds have values of σ_N ranging from 10,700 to 11,100 lb. per sq. in. In the calculation of σ/σ_N a value of 10,900 was used. The values of σ/σ_N obtained in this way are given in Table II and are plotted vs. load duration in Fig. 2 along with some results for vacuum-baked specimens (see below).

From the figure it is apparent that the reduced static fatigue curves for the freshly abraded and for the aged specimens agree to within the experimental error. Thus the strength increases produced by aging fresh abrasions in water can be accounted for entirely in terms of changes in σ_N , the liquid nitrogen strength. Both the shape of the static fatigue curve and $t_{0.5}$, the characteristic duration for fatigue, remain unchanged.

(B) *Vacuum Baking:* The effect of baking in high vacuum on the static fatigue of freshly abraded specimens was studied. As shown in Table I, when freshly abraded specimens are stored in vacuum at room temperature, the aging effect is largely eliminated. The early studies showed, however, that vacuum storage at elevated temperatures did produce increases in the impact strength.⁶ This effect increased with increasing baking temperature from about 100° to about 450°C. and appeared to decrease slightly between 450° and 500°C.

For the present study, specimens were subjected to the grit-blast abrasion, stored briefly in dry nitrogen (less than 1 hour), and then transferred to the vacuum furnace which was promptly evacuated to a pressure of about 10^{-5} mm. Hg. The furnace temperature was then raised to 470°C. After 3 hours at this temperature the furnace was allowed to cool overnight to room temperature and was then filled to atmospheric pressure with dry nitrogen. The specimens then were removed and stored in a dry nitrogen atmosphere

Table III. Vacuum Baking and Static Fatigue*

Load duration (sec.)	σ (lb./sq. in.)	σ/σ_N	Test condition
0.050	10,310	0.79	Wet
0.82	9,020	.69	Wet
4	8,260	.63	Wet
15	7,630	.58	Wet
0.82	8,900	.68	Wet†
0.82	13,180		Liquid nitrogen‡
0.82	13,760		Liquid nitrogen§
0.82	13,110		Liquid nitrogen

* Specimens grit blasted; vacuum baked 3 hours, 470°C., 10^{-5} mm. Hg; and tested in water or in liquid nitrogen.

† Stored 1½ hours in distilled water after vacuum baking.

‡ Control set stored 24 hours in distilled water, not baked.

§ Tested immediately after vacuum baking.

|| Immersed in water 20 seconds between baking and testing.

until test. In addition to the vacuum-baked specimens one control set was abraded and stored in distilled water for 24 hours. The liquid nitrogen strength was measured for the control set, for one set which had been vacuum baked, and for a third set which had been vacuum baked and then immersed in water for 20 seconds before immersion in liquid nitrogen. Strength at various load durations also was measured for vacuum-baked specimens tested while immersed in distilled water. One additional set was stored in water for 1½ hours after vacuum baking and then tested in water. The resulting strength values are presented in Table III.

From the table it can be seen that the vacuum-baking treatment produced a slightly greater increase in liquid nitrogen strength than aging in distilled water (13,760 lb. per sq. in. compared with 13,180 lb. per sq. in.). A brief immersion in water after vacuum baking yielded a value almost identical to the 24-hour aging treatment in water. To evaluate the effect of vacuum baking on the static fatigue, examine the reduced fatigue curve for vacuum-baked specimens as shown in Fig. 2. For this curve a value of 13,110 lb. per sq. in. for σ_N was used corresponding to specimens which had been immersed in water briefly after the vacuum-baking treatment to compensate for the immersion occurring during test.

From the figure it is apparent that vacuum baking is in marked contrast to aging in distilled water with respect to its effect on static fatigue. The reduced strength curve for the baked specimens is definitely displaced from that which serves for both immediate and wet-aged specimens. In terms of the characteristic duration, $t_{0.5}$ for vacuum-baked specimens is approximately 200 seconds compared with 8 seconds for specimens aged in distilled water even though both kinds of specimens are immersed in water during testing. Thus vacuum baking, like aging, increases the instantaneous strength of freshly abraded specimens by about 30% and in addition decreases the rate of static fatigue in distilled water by a factor of about 25. Even 1½ hours of immersion in distilled water after baking did not eliminate this suppression of the fatigue effect as can be seen from the 0.82-second test (Table III) for specimens which were thus immersed after baking.

Visual observation of the vacuum-baked specimens showed that they had extremely clean surfaces with an unusually high degree of "sparkle." In addition, they did not wet like the usual specimens. When the specimens were removed from distilled water after dipping or testing, the water would stand in droplets on the surface rather than spread. The slides could, in fact, be almost completely dried simply by giving them a quick shake. This very noticeable behavior persisted even for the specimens which were stored in water for 1½ hours after baking.

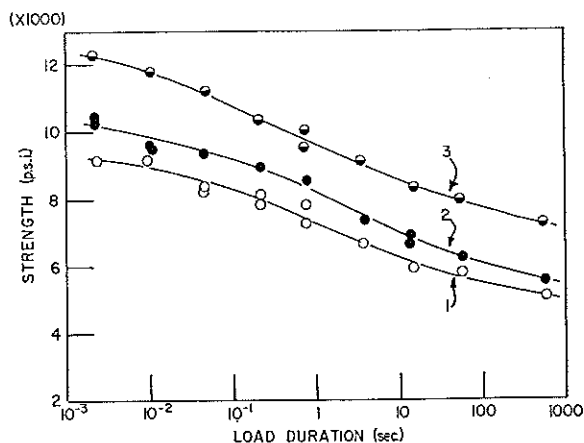


Fig. 3. Strength vs. load duration (log scale) for specimens containing (1) fresh abrasions, (2) abrasions aged in atmosphere with relative humidity of 0.3%, and (3) abrasions subjected to vacuum-baking treatment. Specimens were tested at room temperature in nitrogen atmosphere with relative humidity of 0.3%.

(C) *Dry Aging, Vacuum Baking, and Static Fatigue, Dry:* Static fatigue curves for grit-blasted specimens aged and tested under relatively dry conditions are presented in Fig. 3 along with a curve for specimens tested under dry conditions after vacuum baking. The liquid nitrogen strength was not measured for control specimens corresponding to the curves in the figure so that reduced curves cannot be plotted in this case. A comparison of the curves, however, shows that the fatigue curve for the aged and vacuum-baked specimens has very closely the same shape as that for those tested immediately after abrading. It seems almost certain that this slight aging observed in nearly dry nitrogen is similar to that produced by storage in water in that it reflects only a change in the instantaneous strength and not in the static fatigue behavior. With respect to these vacuum-baked specimens tested *dry* (curve (3)) the data are not sufficient to indicate definitely whether or not the fatigue behavior has been affected by the baking treatment as it was for those tested *wet* (above).

With respect to the fatigue curves of Fig. 3 one additional point is worthy of note. All three curves show a pronounced flattening at the short-time end and become almost horizontal. For curve (1), unaged specimens, it is seen that this occurs for $\sigma \approx \sigma_N$, the liquid nitrogen strength (9400 lb. per sq. in.). Thus for these specimens, tested under relatively dry conditions, the characteristic duration of fatigue, $t_{0.5}$, is so great that at the shortest test times employed the strength is nearly equal to the liquid nitrogen strength. Since the curve is nearly horizontal, this value also meets the definition of "instantaneous strength" as proposed in Part II of this series.^{*,4(b)} Thus the instantaneous strength, σ_0 , at room temperature is approximately equal to the liquid nitrogen strength, σ_N . Since the latter is independent of load duration, it is also, of course, equal to σ_0 at 77°K., the temperature of liquid nitrogen. It follows that the temperature dependence of σ_0 must be very small and may in fact be almost zero. This subject will be discussed in more detail in Parts IV and V of this series† dealing respectively with the effect of the ambient medium and temperature to which the specimen is exposed at the time of test.

* The strength measured at a load duration (or loading rate) such that any decrease in duration (or increase in rate) will produce no further increase in strength.

† To be submitted.

(4) Other Observations on Aging

In the general course of this study, the effect of certain other aging treatments on the fatigue behavior of both dry and wet specimens has been studied. The experiments were not, in general, as well controlled as those reported in the foregoing and are not described in detail here. All the tests which have been conducted lead, however, to the same general conclusion. The strength increases which are produced by storing freshly abraded specimens for varying lengths of time under "ordinary" conditions† can be accounted for almost entirely by changes in the instantaneous strength of the specimens. Although there is some slight experimental evidence that the very short time fatigue behavior may depend to a certain extent on the state of aging of the specimens, this subject has not yet been explored in detail. All the apparent changes in fatigue behavior which have been observed for ordinary aging treatments are small compared with the changes in the instantaneous strength.

Finally it should be noted that the presence of contaminants in the atmosphere can sometimes produce marked changes in the aging behavior. As an example, it was observed in the present study that the presence of fumes from a coal-fired hot-air furnace produced a noticeable decrease in the amount of aging observed for specimens stored in the room atmosphere. It was believed that previous adsorption of a film (probably largely SO_2) had decreased the access of atmospheric water vapor to the glass surface.

Thus the relative humidity of an atmosphere is not adequate to specify completely its effectiveness as an aging medium. In the present study overnight storage in distilled water was adopted wherever practicable as being the most easily controlled and the most reproducible treatment for fresh abrasions before test.

IV. Discussion

(1) Comparison with Previous Investigators

In the foregoing sections it has been shown that the type of aging behavior which previous investigators had noted for diamond scratches and cutter-wheel cracks also occurs for the linear and point abrasions of the present study. Of the two types of surface damage the linear flaws (emery cloth scratches), as might be expected, age most like the diamond and cutter-wheel cracks studied previously.^{1,2,3} These three types of damage show a fairly rapid initial increase of strength with storage time after formation followed by a leveling off with only a very slight further increase after about 24 hours. The current results are compared with previous ones in Table IV.

As noted from the table there is reasonably good agreement among the various investigators with respect to the magnitude and general time scale of the aging effect. The somewhat greater effect noted for the emery cloth scratches in the present study than for the diamond scratches and cutter-wheel marks in previous ones may result from the use of the liquid nitrogen quenching technique. This may provide a better estimate of the strength of the "fresh" or unaged scratch than the methods previously employed and thus yield a larger value for the aging effect.

The shorter time observed by Levengood than by others for the completion of aging may result from the fact that his cracks were formed under water. This treatment presumably would permit very rapid access of water to the newly formed crack and might appreciably accelerate the aging process in comparison with specimens which are immersed in water after being damaged in air.

† "Ordinary" is meant to exclude such treatments as vacuum baking and severe chemical attack.

Table IV. Aging Results for Various Investigators

Investigator	Type of damage	Approx. initial strength (lb./sq. in.)*	Storage condition	Total strength increase (%)	Completion time†
Present work	Emery scratch	9,000	Water	60	24 hr.
	Grit blast	9,000	Water	45‡	
Holland and Turner (footnote 1)	Diamond scratch	3,200	Air	43	24 hr.
Jebsen-Marwedel and von Stösser (footnote 2)	Diamond scratch		Water-air§	30	(II)
Levengood (footnote 3)	Steel cutter wheel	1,700	Water-air§	45	4 hr.

* Since test methods differed widely, these values indicate only general strength level.

† Aging time to produce 90% of total strength increase.

‡ After 100 days; increase apparently still incomplete (see Fig. 1).

§ Scratched wet, stored in air without drying.

¶ Only a single aging time of 48 hours was employed.

(2) The Fresh Abrasion

Before discussing possible mechanisms for the aging effect, the nature of a fresh abrasion in a glass surface is considered. The most readily apparent feature of an abrasion is the surface flaw or crack from which glass has actually been displaced by fracturing, perhaps accompanied in some cases by plastic flow. This is the visible evidence of the abrasion and generally can be seen with the naked eye or a microscope.*

Beneath this for an additional distance into the glass extends the hidden abrasion. This is a crack with no glass removed and perfectly matching surfaces. Unless it is held open by chips of glass it may be so narrow as to be invisible to optical examination. To the tip of this crack is assigned an "effective tip radius," which is generally considered to be of the order of atomic dimensions. If the total depth of the crack, c (visible plus hidden portions), is much greater than the tip radius, ρ , the localized stress at the crack tip can be written as⁸

$$\sigma_1 = \sigma_a 2\sqrt{c/\rho} \quad (1)$$

where σ_1 = local stress at crack tip and σ_a = applied macroscopic stress. If the limiting strength of the material is s_1 , fracture will occur when $\sigma_1 = s_1$ or when

$$\sigma_a = \frac{1}{2}\sqrt{\rho/c} s_1 \quad (2)$$

Although it must be recognized that both "tip radius" and "limiting strength" are somewhat artificial concepts with respect to volumes of atomic or near-atomic dimensions,⁹ equations (1) and (2) will be useful in discussing possible mechanisms for changes in the observed macroscopic strength.

If one examines a fresh abrasion or scratch in a polarizing microscope, one generally can find a region of strain surrounding the tip of the abrasion crack. Holland and Turner observed such strain in the case of diamond scratches, and it also was found to be present in the case of the abrasions studied in the present experiments.

Finally, one other aspect of the fresh abrasion should be noted, viz., the chemical nature of the freshly formed surface

in the abrasion crack. These surfaces, formed by fracture as distinguished from fire-formed surfaces, are highly active chemically. Such surfaces are reported by Weyl¹⁰ to react with O₂, producing atomic oxygen. As discussed by Weyl there are various ways for such a "nascent surface" to become an "equilibrium surface" with a lowering of its surface energy. These are (a) polarization of the surface ions, (b) rearrangement of the surface ions, (c) electron transfer from one surface ion to another, and (d) chemical interaction with the surrounding medium. Of these, (d) is likely to be most important for soda-lime glass at ordinary temperatures and conditions and one can expect the fresh surfaces of an abrasion to react strongly with their environment.

(3) Possible Aging Mechanisms

Three mechanisms for the aging of fresh abrasions are considered. These are (1) release of the polariscopically observable stress around the crack tip, (2) changes in the crack depth, c , and (3) changes in the effective tip radius, ρ .

A release of stress around the tip of the newly formed scratch was proposed by Holland and Turner¹ as a possible mechanism to explain the aging which they observed for freshly made diamond scratches. Two considerations based on the results of the present studies appear to conflict with this explanation. The first is the dependence of aging on the surrounding medium as shown in Table I. Although it could be argued that the breaking down of chips which wedge the cracks open is accelerated by the presence of water, it seems unlikely that such a mechanism would lead to the marked dependence on surrounding medium or relative humidity which was observed.

The second argument is based on the static fatigue behavior of glass. Consider, for example, the 320-grit emery cloth abrasion studied in the present work. After aging for 1 day in water the liquid nitrogen strength associated with this abrasion is about 14,000 lb. per sq. in. When the abrasion is fresh, the corresponding value is about 9000 lb. per sq. in. If this entire strength increase of 5000 lb. per sq. in. results from the relief of "wedge" stresses produced at the crack tip during the abrasion process, then the actual strength of the abraded specimen must be 14,000 lb. per sq. in. at all times, and a wedge stress equivalent to an applied macroscopic tension of 5000 lb. per sq. in. must be present when the abrasion is fresh to yield the observed value of 9000 lb. per sq. in. Based on the static fatigue behavior of this abrasion as reported in Part II (Figs. 3 and 5) an *applied* stress of 5000 lb. per sq. in. will produce failure for specimens immersed in water at room temperature after a load duration

* A good summary of some recent work on grinding and polishing which is pertinent to the nature of abrasions is given by Brüche and Poppa (E. Brüche and H. Poppa, "Polishing of Glass," *J. Soc. Glass Technol.*, 40 [197] 513-19T (1956); *Ceram. Abstr.*, 1958, September, p. 231i).

⁸ Heinz Neuber, "Kerbspannungslehre; Grundlagen für genau Spannungsrechnung" (Theory of Notch Stresses; Principles for Exact Stress Calculation). Springer Verlag, Berlin, 1937. (English translation, J. W. Edwards, Ann Arbor, Mich., 1946. 181 pp.)

⁹ (a) H. A. Elliott, "Analysis of Condition for Rupture Due to Griffith Cracks," *Proc. Phys. Soc. (London)*, 59 [Pt. 2] 208-23 (1947).

(b) C. Gurney, "Effective Stress Concentration at End of a Crack in Materials Having Atomic Constitution," *Phil. Mag.*, [7] 39, 71-76 (1948).

¹⁰ W. A. Weyl, "New Approach to Surface Chemistry and to Heterogeneous Catalysis"; Chapter II, Bulletin No. 57, Mineral Industries Experiment Station, The Pennsylvania State College, State College, Pa., March, 1951. 118 pp.

of about 1 to 5 seconds. Since only a small amount of aging is produced by an immersion of this duration, a wedge stress equivalent to 5000 lb. per sq. in., if present, would produce spontaneous failure during the time-dependent aging process itself. Actually such failures were never observed during the much greater 24-hour immersion of the aging treatment.* One is thus led to the conclusion that the tensile stress produced around the crack tip during the abrasion must be much less than that produced by 5000 lb. per sq. in. of applied stress and could not be responsible for the observed aging behavior. As a final point it also should be noted that the polariscopic appearance of the abrasions changed only slightly as a result of the aging treatments reported in this paper.

The second possible mechanism, a change of crack depth, c , also is believed to be unlikely. According to equation (2), in order to account for the observed strength changes of up to 50% with aging, it would be necessary for the crack depth to decrease to approximately half its original value. There is no good evidence that cracks in glass can indeed heal with time under ordinary storage conditions in the sense of once-separated surfaces rejoining. Although such healing has been observed in the case of cleaved surfaces of mica, it has occurred only when the surfaces were prevented from "aging."¹¹ Rather than promoting the rejoining of fresh surfaces, a medium such as water is much more likely to contaminate the surfaces and prevent the re-formation of glassy bonds across the crack.

In the presence of water, any healing of the abrasion cracks by closing would have to involve a bonding across the crack by some water-containing material, presumably a form of silica gel. Such a structure would be much weaker than the original glass and the crack actually would have to heal by more than half its initial depth to account for the observed strength increases. In this connection it should be noted that only the "hidden" portion of the abrasion, from which no glass has been removed, would be capable of healing in this manner.

In contrast to the first two mechanisms, the third, a change in the effective radius, ρ , of the crack tip, seems to be highly plausible. A mechanism involving dissolution of glass at the tip of the crack and a resulting increase in the tip radius is much more consistent with the observed dependence of the aging effect on the presence of water and water vapor than are either of those discussed above.

In addition, the magnitude of the effect is about what one would expect of such a mechanism. By equation (2) the observed 50% increase in strength corresponds to an approximate doubling of the effective tip radius. If one assumes that the original tip radius is of the order of an atomic radius, this would correspond to an increase of a few atomic radii. In other words, the strength increase could be accounted for entirely by a dissolution of the few surface layers of molecules which in the fresh abrasion are in a highly nonequilibrium condition. If this effect were to take place only to the depth of some initially disturbed surface layer, this also would account for the saturation of the effect which has been observed in certain cases.

(4) Role of Geometry of Abrasion

In comparing the aging behavior of the grit-blast (point) abrasions with that of the emery cloth (linear) abrasions (Fig. 1), it should be noted that the two abrasions studied had the same liquid nitrogen strength values immediately after abrading and before aging. It is of interest to note

that the linear flaws aged more rapidly in liquid water and less rapidly in saturated atmosphere for the first 90 minutes than did the point flaws. This suggests that at least in the early stages of aging the differences in the behavior of the two types of flaws are related to the ease with which water can penetrate to the depths of the surface cracks. It seems reasonable that capillary forces may facilitate the penetration of liquid water into the deep narrow cracks formed by the emery cloth abrasions whereas this same narrowness and depth inhibits the penetration of atmospheric water vapor, resulting in a more pronounced difference between the two aging conditions for the linear than for the point flaws.

In Part II of this series, the static fatigue (delayed failure under constant applied stress) of specimens containing linear and point flaws was studied, and it was found that with the same instantaneous strengths the former fatigued fifty times more rapidly than the latter when immersed in liquid water. Taking into account the present results it can now be stated that for specimens immersed in liquid water all strength changes which have been studied (both aging and fatigue) take place more rapidly for linear than for point flaws.

(5) Vacuum Baking

Because of the absence of water or water vapor it is apparent that the strength increase associated with the vacuum baking of freshly abraded specimens as shown in Table III must differ somewhat from that associated with room-temperature aging. It is possible that in this treatment atomic rearrangements occurring at elevated temperature may play the same role as chemical attack at room temperature. In this view the disturbed surface layer within the abrasion could revert to a lower surface energy condition and, as above, the resulting strength increase could be associated with an increase in the effective radius of the crack tip. Such a view is supported by the fact that the magnitude of the aging effect is the same in both types of treatment.

To discuss the change in the fatigue behavior of specimens which have been vacuum baked (see Fig. 2), one must again consider the chemical behavior of the glass surface and especially the adsorption and desorption of water from such surfaces. Much knowledge which relates to this subject has been acquired from experimental studies of colloidal silica and has been summarized by Iler.¹² He states that the surface of such silica ordinarily is covered with a monolayer of hydroxyl groups, termed "bound water." When silica is heated to 500° to 600°C., this layer is partly removed, and part of the surface is left in a dehydrated oxide condition which will not physically adsorb water or methyl red dye as does the hydrated surface. This surface will rehydrate only slowly on exposure to water.

The adsorption and desorption of water from the surfaces of massive glass has been studied extensively by Todd.¹³ His results on the vacuum baking of various glasses are consistent with the foregoing summary of Iler with the additional information that aged glass (1 or 2 years) is covered with a hydrated layer many molecules (about 100 a.u.) thick. In the present work one is concerned with the newly formed surfaces in the abrasions, and this thick layer is of no concern.

Since water plays a very important role in the static fatigue behavior of glass,[†] it seems likely that the decreased rate of

¹² R. K. Iler, "Surface Chemistry of Silica and Silicates"; Chapter VIII in *Colloid Chemistry of Silica and Silicates*. Cornell University Press, Ithaca, N. Y., 1955. 324 pp.; *Ceram. Abstr.*, 1956, May, p. 107j.

¹³ B. J. Todd, "Outgassing of Glass," *J. Appl. Phys.*, 26 [10] 1238-43 (1955); *Ceram. Abstr.*, 1956, February, p. 32i.

[†] The role of water and other agents in the static fatigue of glass will be considered in detail in Part IV of this series.

* Spontaneous failure, i.e., in the absence of applied stress, was not observed for any of the specimens in this study.

¹¹ See p. 14 of footnote 10.

static fatigue observed for vacuum-baked specimens is related to the difficulty in hydrating thoroughly dehydrated glass surfaces. The obvious nonwettability of the vacuum-baked specimens probably reflects the behavior described by Iler for colloidal silica. The failure in one test of 1½ hours of water immersion following vacuum baking to alter this behavior indicates that the rehydration process proceeds extremely slowly.

As outlined above, the healing behavior of the abraded specimens in these experiments is consistent with current knowledge of the behavior of glass and silica surfaces with respect to the adsorption and desorption of water. These experiments emphasize the complex role played by water in the breakage of glass. Thus the presence of water or water vapor can lead to the strengthening of abraded glass as in the present aging studies. As is demonstrated by the studies of previous investigators and by other phases of the present study, it also is a weakening agent in static fatigue tests. Probably the best comprehensive statement is that the presence of water or water vapor encourages *changes* in the strength of abraded glass, either weakening or strengthening, depending on the other conditions present.

(6) Practical Significance of Aging Effect

The present study and those of previous investigators have shown that the aging of fresh abrasions in a glass surface is a real, significant, and probably universal phenomenon. One can state, in general, that any abrasion crack is most severe at, or just after, the instant of its formation. In the absence of an applied tensile stress the strength associated with a given surface flaw either remains constant or increases after its formation, depending on the surrounding environment.

The implication of this fact with respect to the cutting of flat glass is obvious and has been noted by previous investigators¹; i.e., the glass should be broken as soon as possible after the formation of the diamond scratch or cutter mark. With respect to the accidental breakage of commercial glass articles one can conclude that surface damage alone will never lead to so-called "spontaneous breakage" through the growth of cracks in the absence of other factors such as a tensile stress greater than the "endurance limit"^{*} or, in certain rare cases, some extreme type of chemical corrosion.¹⁴

Another instance in which the aging effect should be taken into account is in the use of some form of artificial abrasion in the strength testing of glass and glassware. Both emery cloth and grit-blast abrasions, as in the present study, or artificial glass-to-glass contact can serve to reduce greatly the scatter of results in strength tests and to simulate more nearly actual trade conditions as compared with tests on unabraded specimens.^{15,†} It should be borne in mind, however, that in

such tests the abrasions will age after forming, and that the articles or specimens under test can increase in strength by as much as 50 to 60% over the freshly abraded value. Such differences obviously can influence the results of a series of tests. In general, if artificial abrasions are used, it is almost as important to standardize and to control the aging treatment between abrading and testing as it is to control the method of abrading itself.

Finally, from a practical standpoint, it should be noted that, although aging does lead to some recovery of the strength lost through surface damage to a glass article, this recovery is small compared with the very high initial strength of pristine, undamaged glass. A pristine glass surface with a strength in excess of 100,000 lb. per sq. in. may have that strength reduced to 10,000 lb. per sq. in. by an abrasion. The strength subsequently may increase to 15,000 lb. per sq. in. on aging. Thus, although a 50% strength increase has occurred, only a very small fraction of the initial strength loss is recovered. With the possible exception of etching with hydrofluoric acid and fire polishing (both of which, in effect, create new, undamaged surfaces) none of the aging treatments studied in this investigation led to a recovery of more than a small fraction of the strength loss produced by surface damage. Natural aging, although it helps, does not provide a complete answer to the practical problem of eliminating the effects of surface damage to commercial glass articles.

V. Summary and Conclusions

The results of this study can be summarized as follows:

(1) The liquid nitrogen (fatigueless) strength of freshly abraded specimens increases with storage time in certain media. For storage in liquid water (the most extreme case) the strength increase after 1 day was about 50% for linear abrasions (emery cloth) and about 30% for point abrasions (grit blast).

(2) For the emery cloth abrasions the effect appeared to be largely completed after one day whereas for the grit-blast abrasions the strength was still increasing, although at a very small rate, at the end of 100 days of storage.

(3) The aging effect depended strongly on the medium in which the specimens were stored. Distilled water was highly effective as an aging medium, and in air aging depended strongly on the relative humidity. In very dry air or vacuum at room temperature aging did not appear to take place. Acidic and basic solutions did not differ appreciably from water in their effect.

(4) The effect of aging under "ordinary" conditions could be accounted for entirely by changes in the instantaneous or fatigueless strength and fatigue behavior appeared to be unchanged.

(5) Baking at 470°C. (880°F.) under high vacuum produced about the same strength increase as aging 24 hours in distilled water. In addition, the vacuum-baking treatment decreased the static fatigue rate for specimens subsequently tested while immersed in distilled water as compared with fresh abrasions or those aged in water.

(6) The most reasonable mechanism for aging appeared to be a rounding of the tips of the flaws produced by the abrading process under the action of water.

(7) In the vacuum-baking treatment the high temperature is believed to permit the rounding of the flaws to occur to give the same increase as the water soaking. The suppression of static fatigue by vacuum baking is believed to be related to the observed fact that the baked specimens are nonwetttable on subsequent water immersion.

* The concept of "endurance limit" will be discussed in subsequent parts of this series.

¹⁴ (a) A. Silverman and L. G. Ghering, "Deterioration of Old Whiskey Bottles," *Glass Ind.*, 23 [9] 339 (1942); *Ceram. Abstr.*, 22 [1] 6 (1943).

(b) F. W. Preston, "Bottle Breakage—Causes and Types of Fractures," *Bull. Am. Ceram. Soc.*, 18 [2] 35-60 (1939).

¹⁵ J. M. Teague, Jr., and H. H. Blau, "Investigations of Stresses in Glass Bottles Under Internal Hydrostatic Pressure," *J. Am. Ceram. Soc.*, 39 [7] 229-52 (1956).

† See Part I of this series (footnote 4(a)) for an additional discussion of the value of artificial abrasion as a tool in testing.