CRIZZLING — A PROBLEM IN GLASS CONSERVATION

Robert H. Brill, The Corning Museum of Glass, Corning, N.Y. 14830, USA

1. INTRODUCTION

Crizzled glasses are familiar to all curators or collectors who have handled much early English or European glass, the word 'crizzled' being used to describe the appearance of certain glasses which have a diminished transparency owing to very fine surface crazing. A typical example is illustrated in Figure 1. Under the microscope, a network of fissures can be seen clearly on the surfaces of such glasses, as shown in Figure 2. On those glasses which are most severely afflicted, small bits of glass may have spalled away. The effect is the result of unstable chemical compositions which render the glasses susceptible to chemical attack by water, usually in the form of water adsorbed from the atmosphere.

Crizzling is most often associated with glasses made in the seventeenth and eighteenth centuries, but earlier examples may exist, and nineteenth century examples are by no means rare. The glasses come from rather widespread areas encompassing England, Western Europe (including Venice), Scandinavia, North America, and China. There are numerous pieces, which are known to have been crizzled for a long time, throughout all of the large collections dealing with glass of this period.

Crizzling is one variant of what has often been called 'sick glass' — a persistent, but not very precise term referring to various forms of surface deterioration. These range from a slightly cloudy or dulled appearance, to crizzling, to occasional occurrences of 'weeping glasses' or 'sweating glasses', which repeatedly generate slippery surface films or droplets if exposed to humid conditions. All are related in that they are manifestations of hydrolytic attack by atmospheric water, but we will be concerned here primarily with the crizzling phenomenon.

Perhaps the best known crizzled glasses are those made by George Ravenscroft, the English glassmaker credited with being the first to capitalize on the properties of lead glasses. During his early experimentation, Ravenscroft made some pieces which crizzled within a few months of manufacture, a deficiency which he quickly attempted to correct [1].

Several treatments have been suggested for crizzled glasses. Most of these involve impregnations with polymeric materials which consolidate the surface and restore transparency and a glassy reflectance. The first application of this type of treatment known to the author was that by Professor J. Arvid Hedvall of Uppsala University [2]. Actually, however, none of the treatments we have seen have yielded entirely satisfactory results. Because storage under proper conditions and careful handling seem to forestall further damage to already crizzled glasses, the outlook of The Corning Museum has been to postpone treatment until a completely safe and satisfactory treatment has been perfected. This is still our outlook as far as already crizzled glasses are concerned, since these objects seem to be stable for the present.

However, it has recently become known that there is a related and most urgent problem concerning crizzling [3]. There exists a category of glasses in early stages of crizzling, which have taken up water over the centuries but which do not exhibit very obvious signs of deterioration. Only when they are handled and turned around under correct lighting conditions can the telltale silvery rays of beginning crizzling be seen. These glasses are of the same general origins and dates as the already crizzled glasses. They have become hydrated and 'equilibrated' over the centuries with humid environments. When brought into centrally-heated galleries or apartments, they may be subjected abruptly to very dry conditions during the winter months. For example, in our galleries the relative humidity frequently drops into the 20 — 30% range during midwinter, and upon occasions has even fallen below 15% on extremely cold days. Under such conditions these hydrated glasses become dehydrated, and the crizzling fissures, which were not very evident to begin with, open up and propagate a network of hairline cracks across the surface. Thus, these glasses can become severely crizzled — and this may happen in the course of only a few months. We have observed one serious example of this effect in our museum and suspect that a half-dozen or so other objects have deteriorated to a less marked degree over the years. In addition, we have heard several reports of similar occurrences throughout North America, Europe, and Britain.

While most of the occurrences of this accelerating deterioration which have come to our attention involve vessel glasses, the author has examined one roundel of fifteenth century German glass (a glass bearing painting and silver-stained regions) which has developed an effect akin to crizzling over the past decade or so. Since it had hung adjacent to a heating register during that period, it seems very likely that a dehydration process was the cause of its accelerated deterioration.

By way of definition we have coined the term 'incipient crizzling', to describe this dangerous metastable state of deterioration. It designates glasses which are hydrated and in the initial stages of crizzling (the damage being apparent only under careful inspection) and which are susceptible to a rapid surface deterioration should they be exposed to dehydrating conditions. The object of the research which follows was to arrive at recommendations for the safe storage of glasses with incipient crizzling so as to prevent their disintegration into a severely crizzled state. We are less concerned for the moment with already crizzled or 'weeping' glasses.

Based mainly upon intuition and a few preliminary observations, we recommended earlier that glasses which show incipient crizzling should not be exposed to low relative humidities, that the temperature and humidity should be maintained at relatively constant levels, and that localized high temperatures, such as could result from installations with dramatic lighting, should be strictly avoided. Since then, some further progress has been made towards making firm suggestions as to safe exhibition and storage conditions based upon actual laboratory studies. The general approach to this research has been:

1. To obtain fundamental chemical information on susceptible glasses.

Table 1. Analyses of some crizzled glasses

		Venetian(?) c. 1709 colourless 457	Venetian(?) c. 1709 colourless 461	French c. 1750 colourless 449	French 1600-50 grayish 1050	French 1725-50 colourless 1498	Silesian* 1710-30 colourless 4011	American 1790-1810 colourless 1487	American 19th C. colourless 1488	American late 19th C. light blue 1630	Jamestown* 1971 green 1823
SiO_2	d/g	≈ 76	≈ 67	76.0	70.7	≈ 74	≈ 73.5	≈ 69	≈ 77	≈ 81	≈ 67
Na_2O	a	0.13	0.99	0.89	17.7	0.29	0.39	2.62	5.00	12.7	17.5
CaO	a	1.30	0.30	0.22	1.53	2.87	1.61	3.19	2.72	1.96	4.66
K_2O	a	18.7	18.4	18.7	3.42	19.9	16.6	24.2	12.7	2.24	6.82
MgO	a/s	0.04	0.06	≈ 0.1	≈ 0.1	0.22	0.03	0.20	0.32	0.12	0.10
Al_2O_3	a/s	≈ 0.1	≈ 0.05	≈ 0.5	≈ 0.5	1.95	1.03	0.55	1.51	0.44	2.61
Fe_2O_3	a/s	≈ 0.05	≈ 0.1	≈ 0.05	≈ 0.1	0.03	0.002	0.05	0.01	0.03	0.28
MnO	a/s	≈ 0.01	≈ 0.05	0.45	0.38	0.51	0.04	< 0.01	0.00X	0.00X	0.01
PbO	q/s	2.22	12.8	0.002	0.01	nf	5.88	< 0.01	nf	1.5	0.05
As_2O_5	q	1.66	0.24	——	——	——	——	——	≈ 0.5	≈ 0.2	——

Notes:

*All glasses except 1823 and 4011 are heavily crizzled. 1823 is hygroscopic but uncrizzled; 4011 shows incipient crizzling.

Analyses by R. H. Bell and C. A. Jedlicka of Lucius Pitkin, Inc., NYC, and P. B. Adams of Corning Glass Works.

a — atomic absorption.
q — quantitative, various methods.
s — emission spectrography.
g — gravimetry.
d — SiO_2 by difference.
≈ — denotes spectrography.
nf — sought but not found.

Also found in varying trace levels: TiO_2, CuO, CoO, Ag_2O, BaO, SrO, Li_2O, Rb_2O, B_2O_3, ZrO_2. P_2O_5 contents uncertain but generally less than 1.0%. Where no As_2O_5 given, values are uncertain but less than 1.0%.

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2. To characterize the crizzling process physically and chemically.

3. To evaluate the chemical durability of the susceptible glasses relative to other types of glass.

4. To duplicate crizzling in the laboratory on both synthetic glasses and actual pieces of early glass.

5. To identify the primary factors controlling the chemical mechanism of crizzling. (Although it would be desirable to establish the details of the mechanism in the sense of a true reaction and kinetic study, this is not feasible just now.)

6. To arrive at recommendations as to how to prevent susceptible glasses, those showing incipient crizzling, from deteriorating into severe crizzling.

2.   CHEMICAL COMPOSITIONS OF CRIZZLED GLASSES

It has generally been held that crizzling is caused by the attack of atmospheric water, possibly augmented by the uptake of carbon dioxide, and that the susceptibility of the glasses to hydrolysis is the result of a deficiency in lime, the most common stabilizer in glasses. While we also held that view — and still do — it seemed worthwhile to confirm it by chemical analyses. Therefore, chemical analyses were made of several early crizzled glasses, eight of which are reported in Table 1. To simplify the table, only major and minor constituents are reported. Data on trace elements have been excluded. Also included in the table are an example of a glass showing incipient crizzling (no. 4011) and one of a modern glass (no. 1823). Both of the latter were used in experiments aimed at duplicating crizzling in the laboratory. (Descriptions of the glasses analysed are given in the Appendix.)

For working within the system $Na_2O:CaO:SiO_2$ (soda-lime-silica glasses), a lime content of less than about 4% by weight would be regarded as very unstable by present-day standards. Even among ancient glasses, lime contents are ordinarily greater than 5.5—6.0%, and many of them are heavily weathered. It will be seen, however, that only two of the early glasses in Table 1 (nos. 1050 and 1630) are actually soda-lime glasses. The others are in the $K_2O:CaO:SiO_2$ system (potash-lime-silica glasses) or are glasses containing some lead (PbO). The minimum concentration of lime required to stabilize a potash glass may not be just the same as the 4% level cited above for the soda-lime glasses, but it is certainly not very different from that level.

It is quite apparent from the table that all of these glasses are indeed seriously deficient in lime and should be expected to be prone to hydrolysis. Only nos. 1487 and 1823 might be judged to have borderline lime contents and these both have such excessively high total alkali contents that they would also be expected to be very unstable. (A total alkali content of 20% or greater would not be tolerated by modern commercial standards, and ancient glasses with that much alkali are usually very heavily weathered.) Nos. 461 and 4011 are the only glasses of this group which really qualify as lead glasses, and while we have not yet completed our literature search on durabilities within the system $K_2O:PbO:SiO_2$, the potash levels are substantially greater than would be used in modern manufacture.

The explanation of the compositional imbalance of these glasses is of some interest to the historian of chemical technology. Whenever glassmaking is in an ascendency, the glassmaker seeks technological means for improving the quality of his wares. In attempting to make more nearly colourless glass, 'cristallo' in the case of Venice, it was recognized that the purification of raw materials would have a beneficial effect. When leaching and recrystallization processes were introduced for the purification of plant-ash alkalis, this would have had the effect of lowering the concentrations of calcium, magnesium, and aluminum in the resulting alkali, because these elements have a tendency to be present in less soluble chemical forms than the soda and/or potash. Consequently, when purified alkali was used for making glass, the resulting product would have been deficient in lime, magnesia, and alumina. Such glasses then would have unstable compositions until the glass technologists of the day became aware of this effect and compensated for it by adding additional lime in the form of some other ingredient. The net result in the interim would have been the production of purer and possibly more nearly colourless glass, which would have been susceptible to crizzling in the years to follow. There is ample evidence, in fact, that this is just what did happen in the descriptions of Neri regarding the purification of alkali as well as in the story of Ravenscroft's perfection of his lead-glass compositions [4]. We have under way some experiments with barilla plant ashes to verify this.

This effect would have been magnified if a greater percentage of alkali were used in the basic formulation, as might have been done in Venice in an effort to produce a glass with a longer working range, that is, a glass which would remain softened for a longer time and allow the glassmaker to perform the more elaborate manipulations required to make complicated decorative forms.

In connection with the chemical compositions, it is worth commenting upon a common misunderstanding. One often hears the remark that it is the pink glasses which tend to crizzle, and there are, indeed, a great many crizzled glasses which have a pronounced pinkish colour. However, this pink colour is confined to the crizzled surface of the glass and the objects were initially colourless. Since manganese was often used as a decolorant, or might even have been present in some of the plant ashes, many early glasses contained manganese. When these glasses are attacked by water and alkali is leached out, the structures are opened up and the manganese becomes oxidized, yielding a pink colour in the crizzled layer. That this is true has been verified by the fact that when a crizzled layer is removed from one of these pink objects, the remaining glass is perfectly colourless.

3.   ELECTRON MICROPROBE ANALYSES

Electron microprobe analyses of five of the glasses appearing in Table 1 were carried out by W. T. Kane and T. W. Bierweiler of Corning Glass Works. The analyses were made on small samples of glass removed from each of the objects. The samples were mounted in cross-section so that both the crizzled layer and the unaffected glass were exposed for analysis. Individual analyses of both regions on all samples were made for silicon, sodium,

potassium, calcium, and lead (where present). Concentration maps for each element on each glass were obtained so that it is possible to see how the concentration of each element varies over an area including the glass, the crizzled layer, and their interface. The maps covered areas of about 100 x 25 μm. Profiles for each element were also constructed to see how their concentrations varied along a continuous path from the unaffected glass out through the crizzled layers. The concentration maps and profiles established the following points, to which are added our interpretations.

1. In the four glasses which were heavily crizzled (nos. 449, 461, 1050, and 1498) the sodium and potassium were very greatly depleted in the crizzled layer, indicating that these two elements had been thoroughly leached out of the glasses and probably removed to a large extent from the surface by washing in the past.

2. The silicon appears somewhat richer on a percentage basis in the crizzled layer than in the unaffected glass. The enrichment is the result of the depletion of the alkali, and it is likely that the total quantity of silica present was about the same before and after the crizzling attack took place.

3. The calcium and lead contents appear to have been unaffected by the leaching process because they, as within the silica, are less soluble than the alkalis. (It would have been difficult, however, to detect changes in the calcium level because the concentration was low to begin with.)

4. A void space could be detected in the four crizzled specimens which clearly marked the separation of the crizzled layer from the glass beneath. The analysts likened the appearance of the profiles to a 'step function', showing extensive depletion of the alkali outside the fissure in the crizzled layer. In two instances a second fissure was revealed beneath the crizzled layer, but this underlayer does not show complete depletion of alkali, only a tendency towards lower concentration. This indicates that the hydration and leaching reactions have proceeded onward into the glass beyond the first fissure separating the depleted layer from the glass. This serves as a reminder that we are dealing with a dynamic system, and that the process does not stop when a flake of crizzling products appears.

5. In a few places, highly localized concentrations of alkali showed up indicating that alkali had redeposited within the fissures. We believe we have also seen such deposits during microscopic examinations of various crizzled glasses. This would be the fate of alkali which had been exchanged by water but had never been washed off the glass during its history of human handling.

6. In sample no. 4011, a glass which showed only incipient crizzling, the alkalis have not been entirely removed from the glass, and the profile does not show the step-like appearance of the crizzled glasses. The alkali concentration shows a gradual depletion gradient sloping down from the unaffected glass to the surface. The profile has the character of a diffusion front. There is some evidence of the beginning of a fissure within the hydrolysing layer. (In anticipation of suggestions which might be prompted by the demonstrated presence of some alkali within this layer, we regard it as doubtful that the process could be reversed successfully and the glassy structure of the layer reconstituted by reintroducing alkali.)

7. The overall thicknesses of the reaction zones as seen through a light microscope measure between 45 and 100 μm, but the microprobe profiles yield additional information. From the spacing of the fissures in the profiles, the thicknesses of the separated layers (the crizzled layers) can be estimated. They range from 25 to 55 μm. In three of the four 'already crizzled' glasses, the layer which had separated is totally depleted in alkali. In the fourth glass, the front of the reaction zone is still within the crizzled layer, and the undersurface of the crizzled layer is quite rich in alkali. In the three instances where the reaction zone had advanced beyond the fissure separating the crizzled layer, the depletion/hydration fronts had penetrated between 40 and 80 μm from the 'original' surface. On the piece showing only incipient crizzling, the depletion/hydration front had penetrated 23 μm into the glass.

If one takes the thicknesses of the crizzled layers and ages of the glasses at face value, the hydration/alkali depletion rate of these five glasses averages out to about 0.3 μm per year. Compared to ancient glasses which are heavily weathered (those suitable for layer-counting), this is not as rapid a rate of hydration. The latter glasses hydrate at a rate of about 0.5—3.0 μm per year. However, lightly weathered ancient glasses, such as those showing iridescence, hydrate more slowly than the crizzled glasses. Iridescent Roman and Islamic glasses hydrate at a rate of only about 0.1 μm per year or less.

4. SYNTHETIC CORROSIBLE GLASSES

In order to learn more about the crizzling process a series of synthetic glasses was prepared. The compositions of the glasses, which are given in Table 2, were patterned like those obtained from the chemical analyses of four of the early glasses reported in Table 1. The glasses were prepared by A. A. Erickson of Corning Glass Works and his co-workers. The compositions given in Table 2 are theoretical values calculated from batch compositions, but chemical analyses of the glasses match them closely. These glasses were used for several types of experiments.

Table 2. Compositions of synthetic early glasses

| | Glasses susceptible to crizzling | | | | |
	XS	XT	XU	XV	PP
SiO_2	73.5	75.5	75.0	65.0	75.8
Na_2O	22.0	—	—	—	0.1
K_2O	—	20.0	20.0	20.0	18.7
CaO	2.0	2.0	1.0	1.0	1.30
MgO	1.0	1.0	—	—	—
Al_2O_3	1.0	1.0	1.0	1.0	0.2
PbO	—	—	3.0	13.0	2.25
MnO	0.5	0.5	—	—	—
As_2O_3	—	—	—	—	1.65
Prototype	1050 (French)	449 (French)	457 (Venetian)	461 (Venetian)	457 (Venetian)

Table 3 contains compositions of synthetic mediaeval stained glasses also prepared by Dr Erickson. There are seventeen such glasses in the table. Their prototypes were groups of glasses, analysed by the author, from York, Nürnberg, and the Zerek Camii [5]. Series were also prepared to test various compositional effects on properties related to durability and weathering characteristics. The glasses represent variations in concentrations of Na_2O/K_2O, P_2O_5, MgO, and CuO; the effects of colour on both stable and durable glasses; and the duplication of an extremely interesting group of lead-containing mediaeval glasses. Some of these glasses have been used by Mr Bettembourg* in his research. We have carried out weathering and durability tests on several of these synthetic stained glasses, but they will not be discussed here, since they are beyond the scope of this paper.

5. WEATHERING AND DURABILITY TESTS

Samples of the synthetic corrosible glasses (XS, XT, XU, and XV) were subjected to three types of testing. These were a miniature powder test, weathering cabinet exposure and autoclaving. All the testing was carried out by P. B. Adams, H. V. Walters, and M. L. Nelson of Corning Glass Works using their routine testing procedures.

Since the details of the individual tests are rather complicated, we shall only outline the procedures here, but further information can be obtained by writing to Mr Adams.** The powder test consists of a water treatment of powdered glass at 90°C for four hours. The weight of alkali extracted is then determined by chemical analysis. The weathering cabinet test consists of exposing small pieces of the glass to an environment of 98% relative humidity at 50°C, and making periodic inspections for surface damage, which is then expressed in a standard terminology. The autoclaving was carried out at 121°C, at 15 psi, for various lengths of time, with the glasses immersed in the liquid phase. Small polished plates of the glass were used for autoclaving. (Other variations of the conditions for the tests were also used for exploratory purposes.)

The first two tests were used for evaluation of the durabilities of the glasses. The conditions parallel standard glass-testing procedures, so the results can be used for comparison with more familiar types of glasses.

The autoclaving was undertaken to look for chemical cracking and for the investigation of hydration—dehydration effects. For the latter purpose, autoclaving served to introduce water into the glasses. Different samples of the glasses were then stored under different relative humidity conditions (at room temperature), to see what levels of relative humidity might successfully inhibit the dehydration which produces crizzling. (As will be shown below, this hydration—dehydration treatment produces a kind of deterioration which is indistinguishable from the crizzling seen on actual early glasses.) The results of the tests are summarized in Table 4.

Some of the findings of the tests are listed below, accompanied by our interpretations.

1. In the powder test, glasses XS and XU, the soda glass and the potash glass with the light lead concentration, showed very poor resistance to hydrolysis. Glass XV, the more heavily-leaded glass, shows a considerably better resistance; and XT, the potash-lime glass, is still better. In fact, the durability of XT approaches that of some of the poorer present-day commercial glasses. It is somewhat surprising that XT holds up as well as it does, but it indicates that the addition of even the small increment of CaO (from 1.0 to 2.0%) over XV brings about a marked increase in stability. In comparing the durabilities of XS and XT, it should be noted that although the concentrations of soda and potash are not very different on a weight-percentage basis, in terms of mole percent the alkali content of the potash glass is markedly less (13.7% vs. 21.5%). This undoubtedly accounts for much of its increased durability. The glasses appear to rank as follows, in order of increasing durability: (very poor) XS ≈ XU ≪ XV < XT (fairly stable).

2. In the weathering cabinet exposures, XS was by far the poorest, and XT again the best. While some commercial bulb glasses do not fare much better than XS in this test, container glasses are much more durable. The glasses appear to rank as follows in order of increasing durability: (very poor) XS < XU < XV < XT (fairly stable).

*Laboratoire de Recherches des Monuments Historiques, Château de Champs/Marne, France.
**Corning Glass Works, Corning, NY 14830, USA.

Table 3. Compositions of synthetic stained glasses

	QQ	QR	QS	RC	RD	RE	RF	VS	VW	VX	VY	VZ	FE	FF	FG	FH	FI
SiO_2	58.5	55.5	66.0	60.0	54.0	48.0	48.0	63.0	63.0	56.7	56.7	56.7	50.0	48.4	63.0	61.0	69.5
K_2O	8.5	18.5	1.5	20.0	18.0	16.0	16.0	18.0	—	16.2	16.2	16.2	17.0	16.4	12.5	12.0	1.5
Na_2O	3.0	0.5	14.0	—	—	—	—	—	18.0	—	—	—	3.0	2.9	1.5	1.5	14.0
CaO	16.0	19.0	10.0	20.0	18.0	16.0	16.0	18.0	18.0	16.2	16.2	16.2	16.0	15.4	12.0	11.6	12.0
MgO	7.0	2.5	1.4	—	—	—	—	—	—	—	10.0	—	7.0	6.9	4.0	3.9	—
Al_2O_3	1.0	1.0	2.0	—	—	—	—	—	—	—	—	—	1.5	1.5	1.5	1.5	1.5
P_2O_5	4.0	1.0	—	—	—	—	—	—	—	10.0	—	—	4.0	3.9	4.0	3.9	—
Fe_2O_3	1.0	1.0	1.0	—	—	—	—	1.0	1.0	0.9	0.9	0.9	0.5	0.5	0.5	0.5	0.5
MnO	1.0	1.0	1.0	—	—	—	—	—	—	—	—	—	1.0	1.0	1.0	1.0	1.0
CuO	—	—	3.0	—	—	—	3.0	—	—	—	—	10.0	—	3.0	—	3.0	—
CoO	—	—	0.1	—	—	—	—	—	—	—	—	—	—	0.1	—	0.1	—
PbO	—	—	—	—	10.0	20.0	17.0	—	—	—	—	—	—	—	—	—	—
Prototype	York	Nürn-berg	Zerek Camii	K_2O base glass	PbO effect	PbO effect	PbO effect	K_2O base glass	Na_2O-K_2O subst.	P_2O_5 effect	MgO effect	CuO effect	Un-stable	Un-stable, blue	Durable	Durable, blue	Na_2O-K_2O subst.

3. The autoclaving produced chemical cracking [6] in XS even after only short durations. XU and XV developed a surface haziness, while XT showed no apparent change. The glasses appear to rank as follows, in order of increasing durability: (very poor) XS < XU < XV ≪ XT (apparently stable).

Table 4. Results of durability tests

	XS	XT	XU	XV
Powder test*				
Alkali extracted				
(Wt −% of glass)				
Na_2O	0.48	—	—	—
K_2O	—	0.057	0.71	0.16
Alkali extracted				
(Mmole/100 g glass)				
Na_2O	7.7	—	—	—
K_2O	—	0.61	7.5	1.7
Weathering cabinet exposure**				
Time required to breakdown	2 wks	8 wks	4 wks	6 wks
Chemical cracking***				
Days required	1	none occurs	≈8	≈15

* Sample wt ≈1 gram, adjusted to constant surface area from density; −40 to +50 mesh; 5 ml H_2O. Run for 4 hours at 90°C.
** 98% RH, 50°C. Breakdown = Obvious damage under inspection without magnification.
*** 2.5 x 2.5 x 0.1 cm polished plates in 285 ml H_2O, 95°C, 15 psi, for varying times.

6. INFRARED ANALYSES

Infrared reflectance and transmission spectra were taken for several samples of autoclaved glasses and their untreated counterparts. The spectra were run by H. Hoover and B. Butler of Corning Glass Works.

Reflectance spectra in the 8-12 μm region established clearly that the autoclaved glasses had been depleted in alkali because they showed a sharper reflectance peak than the anhydrous glasses. The shift indicates less disturbance of the Si—O—Si bonds by alkali or other modifiers. It is noteworthy that this was true even of the glass XT, which showed no visible evidence of alteration after the autoclaving.

Infrared transmission spectra in the 2-5 μm region indicated the presence of large quantities of beta-hydroxyls, or loosely-bound water. A sample of glass XV which had been hydrated through autoclaving was crizzled by heating it to 135°C for 1½ hours. A spectrum of the crizzled glass fell in between the spectra for the hydrated glass and an anhydrous control, indicating that although a significant amount of the beta-hydroxyl was removed, a significant amount still remained after the crizzling was induced.

Infrared spectra of an autoclaved sample of XV (30 minutes at 121°C) were taken progressively as the hydrated surfaces were polished away. By this means it was possible to estimate that this particular hydration process had hydrated this glass to a depth of approximately 20 μm, somewhat less than the thicknesses of the crizzled layer on early glasses.

Further infrared work is being conducted in an attempt to identify the different states of binding of water within the hydrated glasses [7].

7. HYDRATION—DEHYDRATION EXPERIMENTS

Several experiments have been carried out with a view to duplicating crizzling in the laboratory. Among these were preliminary experiments which demonstrated that by heating certain types of actual historic glasses (but not all types) to temperatures between 100° and 150°C, severe surface crizzling can be produced. These glasses were of diverse origins, including Roman glass from Karanis, some specimens of mediaeval stained glasses and eighteenth century vessel fragments. Other investigators have had similar experiences [8]. With this in mind, several pieces of synthetic glasses having corrosible compositions were held over water or immersed in water at 85°C for varying times and then dehydrated. It was found that the dehydration could be accomplished either by warming the glass to 50-65°C or by placing it in a desiccator. By various combinations of experimental conditions, several such glasses developed surface crizzling identical to that observed on early objects of crizzled glass. It might be added that some of the synthetic mediaeval stained glasses behaved similarly under these treatments.

We next set out to determine what levels of relative humidity, at room temperature, would inhibit the dehydration of hydrated glasses so as to arrest the development of crizzling. Experiments were carried out with the four synthetic glasses XS, XT, XU, and XV. In addition, two actual early objects were sacrificed for this

experiment. These experiments were carried out by M. L. Nelson and H. V. Walters. A similar series of experiments was conducted by the author in the Museum.

Small polished plates of the four synthetic glasses were hydrated by autoclaving at 121°C and 15 psi with total immersion in water. Various autoclaving times were used. After drying in air, the hydrated glasses were placed in glass chambers (actually desiccator jars) which maintained constant internal relative humidities established by saturated salt solutions in the bottoms of the chambers. The relative humidities were monitored with an electric hygrometer. The humidities were: 1%, 25-30% (ambient laboratory conditions), 40%, 72%, and 100%. (The samples in the 100% chamber soon became covered with droplets of condensed water.) Although the samples selected for the experiment were autoclaved for different times, all were similar in that after the autoclaving they showed no surface damage detectable by the unaided eye. After varying intervals of time, extending from a few days up to several weeks, many of the glasses developed crizzling. At the time of writing (March 1975), some samples still have not crizzled. The results are summarized in Table 5. .

Table 5. Effect of storage conditions on hydrated glasses

Glass	Percentage of glasses which ultimately crizzled*				
	1%RH	25-35%RH	40%RH	72%RH	100%RH
XS	100%	17%**	0	0	0
XT	100	40	40	0	0
XU	100	100	100***	50***	0
XV	100	100	12	0	0
% crizzled irrespective of composition	100%	65	38	12	0

Duration of experiment to date: 11 Sept. 1974 — 17 Jan. 1975
Total number of samples used: ≈110

* The times required to develop crizzling varied widely. Some samples crizzled within a few days, others required several weeks.
** Of the balance, they might not all have been hydrated.
*** Hydration might have been excessive.

Some other experiments		
Glass	Treatments	Results
XS	1. Imm. water, 85°C, 78 hrs	Little surface change
	2. Storage at: 0%RH	Crizz. after few days
	31%	No change after 35 mos.
	75%	No change after 35 mos.
	100%	No change after 35 mos.
	3. Storage at: 0%	All show crizz. after 9 hrs
XS, XT, XU, XV	1. Imm. water, rm temp., 35 mos.	XS, XU — Incip. crizz.
		XT, XV — No change
	2. Storage at: 0%RH	XS, XU, XV — Crizz. after 9 hrs
		XT — Start crizz.(?) after 2 wks
1823	1. Imm. water, rm temp., 35 mos.	No change
	2. Storage at: 0%RH	Start crizz. after 90 min.
		Crizz. after 16 hrs
	12%RH	Start crizz.(?) after 2 wks
1823	1. Storage at: 100%RH	No change
	Rm temp., 35 mos.	
	2. Second storage at: 0%	Crizz. after 16 hrs
4011	1. No laboratory hydration	
	2. Storage at: 0%RH	Crizz. within 24 hrs
	12%	Start crizz.(?) after about 4 wks
	21%, 34%, 52%,	
	70%, 100%	No change yet after 11 wks

A similar set of hydration — dehydration experiments was started in 1971, but most of the apparatus, glasses, and records were destroyed in the flood which struck the Museum in June 1972. Fortunately, there were some survivals which now show interesting results. Samples of glass XS were hydrated by immersion in water at 85°C

for 78 hours. The samples showed little change after the hydration step. They were then stored for eleven days at humidities of 0%, 31%, 75%, and 100%. The piece stored at near-zero percent crizzled severely; the others did not show much change. They were left in the same chambers for 35 months and little further damage occurred. They were then transferred to a near-zero humidity chamber and within nine hours all developed crizzling.

In another experiment, pieces of glasses XS, XT, XU, and XV were given no high temperature hydration, but just left to hydrate in distilled water at room temperature for 35 months. XS and XU developed some chemical cracking and incipient crizzling, respectively; but XT and XV showed no surface alteration at all. However, when placed in a near-zero humidity, all except XT developed severe crizzling within nine hours. (XT again proved to be surprisingly durable, as it did in certain other experiments.)

The experiments carried out on the two early glasses, nos. 1823 and 4011, offer a different approach to the problem and avoid the difficulties posed by the use of autoclaving to hydrate the glasses.

Glass no. 4011 is an engraved Silesian goblet made in about 1710-30. The piece shows typical incipient crizzling (Figure 3). The foot of the goblet had been broken in the distant past, and the piece was not considered to be of outstanding historical importance. Therefore, Mr Jerome Strauss, who owned the object for some years, donated it to the Museum for use in our experiments, feeling that the information to be gained from sacrificing parts of the glass would prove to be more valuable than the glass itself. Samples were sawed from the rim above the engraving. They were carefully photographed under reproducible lighting conditions, and photomicrographs were taken to record the original state of the incipient crizzling. One small piece was used for chemical analysis, and several of the others were placed in chambers for storage at known humidities.

Once again the humidities of the chambers were controlled by saturated salt solutions, except for a desiccating chamber employing silica gel for a near-zero humidity, and one containing distilled water for 100% humidity. No attempt was made to control the temperature. Instead, ambient room temperatures prevailed. The humidities, as measured with an electric hygrometer, are: ≈0%, 12%, 21%, 34%, 52%, 70%, and 100%.

It was found that the piece of object no. 4011 placed in the chamber at near-zero humidity became severely crizzled within 24 hours (Figures 4 and 5). The piece in the chamber at 12% seems to have begun to show signs of developing crizzling at the time of writing, which corresponds to an elapsed time of about four weeks at 12%. None of the samples at other humidities have changed.

Glass no. 1823 is a small green bottle made in 1971 at the Jamestown, Virginia, factory. It was sent to the author for examination because it developed a slippery surface feeling shortly after manufacture. After a chemical analysis showed an excessive alkali content to be the cause, parts of this bottle were also sacrificed for hydration—dehydration experimentation. Fragments were stored for four months at ambient conditions in Corning and then stored in a 100% humidity chamber for 35 months. Another fragment of the same glass was immersed in distilled water for 35 months. Neither glass showed any visible signs of surface deterioration at the end of these hydration steps. Samples of these same fragments were then placed in a near-zero humidity chamber, and others in a 12% chamber. Within 90 minutes of being placed in the near-zero chamber, the samples showed beginning stages of crizzling. They were left overnight in the chamber and had become severely crizzled by the next morning after a total of 16 hours at near-zero humidity. One of the samples in the 12% chamber appears to be developing slight crizzling after about two weeks, at the time of writing.

It is conceded that the logic which is about to be followed is weakened by a few significant defects, but even with these in mind it is worth pursuing. In some of the experiments outlined above, the hydration conditions were chosen arbitrarily and were not always the same for each glass, so care must be exercised in comparing the behaviour of one glass with another. Moreover, the autoclaving used to hydrate the glasses was a rather drastic treatment. It can be argued that the hydrated state induced by autoclaving might not be the same as that brought about by the slower 'natural' hydration produced by the action of atmospheric water vapour over centuries at room temperature. But nonetheless, these are the only data we have, and in effect this same defect marks the interpretation of any accelerated ageing test, so it is familiar to all conservators.

From the results in the first part of Table 5, it could be concluded that hydrated glasses of this type will crizzle rapidly if stored at near-zero humidity, but will not dehydrate (not rapidly) at humidities of about 70% or greater. In the range of 25-40%, many such glasses will crizzle; between about 40-70%, some glasses will crizzle.

The findings presented in the second part of Table 5 represent longer term experiments and different hydration processes, some of which eliminate the onus of accelerated ageing. From the results of these experiments, it can be inferred that glasses hydrated by exposure either to hot water for short times or to cool water for a matter of years will retain their moisture for long periods when stored at humidities between 30-100%, but that they rapidly give up that moisture and become severely crizzled if transferred to a near-zero humidity environment.

The experiment most closely simulating actual museum conditions, that involving the Silesian goblet, demonstrated unequivocally that storage of a glass showing incipient crizzling at a near-zero humidity will provoke severe crizzling within a matter of hours. The data on the Jamestown glass substantiate this finding. It remains to be seen whether relatively rapid crizzling can also develop on susceptible glasses in the range of about 25-40% relative humidity, and we have set up long-term experiments to answer this question.

8. STORAGE CONDITIONS AND CASE DESIGN

From all of the foregoing, it is apparent that dehydration is the cause of the advancement of incipient crizzling into full crizzling, and it is obvious that very low humidity conditions must be avoided if susceptible glasses are to be protected. The next point to be established is just what constitutes an optimum range for safe storage.

It is somewhat disquieting that dehydration occurs at relative humidities as high as 40-60% and that only levels

of 70% or greater appear to hold hydration water in the experimental glasses. It is likely, however, that this is because the water had been driven into the glasses under rather drastic conditions. It is doubtful that early glasses with incipient crizzling dehydrate significantly in the 40-60% range. After all, such glasses must already have spent much of their existence in humidities within that range and have not gone over to full crizzling. We are prepared to assume, then, that the 40-60% range is safe.

Storage at very high humidities with a view towards keeping water in might then accelerate the hydration of the glasses and contribute to their ultimate deterioration, to say nothing of the impracticalities posed by possible mould growth, condensation, etc. We conclude, therefore, that from the viewpoint of protection against dehydration:

1. The 70-100% range is unnecessarily high and undesirable.
2. The 40-60% range is safe.
3. The 25-40% range remains open to question and should be studied in terms of years-long storage experiments on actual early glasses.
4. The 0-25% range is dangerous, in fact very dangerous at the lower end.

The situation, then, can be reduced to questioning whether there is anything else that can go wrong in the 40-60% range.

In 1959 Organ and Bimson [9] dealt with a related — but not identical — problem to that being discussed here. They recommended that for safe storage unstable glasses should be kept dry, specifying that by dry they meant at a relative humidity below 42%. The reasoning was that at humidities below 42%, potassium carbonate (the ultimate form of alkali leached out of potassium glasses) is not hygroscopic. This reasoning is certainly sound for the types of glasses they were considering, that is, 'weeping' or 'sweating' glasses, and the validity of their recommendation seems to have been borne out by actual experience. In the intervening years, large numbers of 'weeping' glasses from the collections of the British Museum were stored in cases where the humidity was kept at or below 42%. In a recent visit to the British Museum, the author accompanied Ms Bimson and Mr Hugh Tait on an inspection of the glass involved. It was found that few of the glasses in the cases had the slipperiness to touch which characterizes 'weeping' glasses. (Those examples which were found to be somewhat slippery were Venetian glasses which might have been soda glasses instead of potash glasses.)

A troublesome question then arises as to whether the dehydration rate of glasses with incipient crizzling might become fast enough to provoke full crizzling if they are stored at humidities below 42%; or, indeed, could the same thing happen to 'weeping' glasses? It is probably artificial to treat these as two entirely different kinds of glasses. Mr Tait and Ms Bimson did not recognize among the glasses in the British Museum cases any which they could say had become more deteriorated during the years of storage in those cases. However, since so many glasses were involved, and since no photographic records of the original states of the objects were at hand, it could not be determined with certainty whether or not any of these glasses had become more crizzled.

With this in mind, we can turn to the practical problem faced by The Corning Museum of Glass, the protection of glasses which show incipient crizzling. There are perhaps 50 such objects in our collections. Our primary object is to arrest any further deterioration brought on by dehydration and, if possible, to minimize the continued uptake of moisture. (It is recognized that improving storage conditions will not correct the damage already inflicted upon the glass.) Ideally, one would assume the safest condition to be a humidity level where a steady state could be established under which neither the hydration nor dehydration reactions would progress. Since it is not likely that we could now arrive at a single level which would satisfy steady-state conditions for so many different glasses, we have elected to err on the side of hydration, feeling that this offers less hazard to the glasses than dehydration. It might further be guessed that, to ensure that dehydration will not occur, the humidity should be in approximately the range to which the glasses had become accustomed in their early histories.

For these reasons, we have decided to aim initially for case control at the 45-55% relative humidity range, with provisions for sufficient adaptability to allow the humidity level to be shifted somewhat in either direction. (For example, if persistent slipperiness developed upon the surfaces, we might want to drop slightly below the 42% level.)

A committee of conservators was convened to offer advice on our system design and case construction. The committee consists of Robert Feller, Lawrence Majewski, Susanne Sack, and Nathan Stolow. The designs have not yet been completed, but several pivotal decisions have been made. The resultant system contains three main components: the cases, controlling devices, and a regenerating unit.

The cases themselves will be sealed, with access through one door. One face, at least, will be glass or plexiglas for exhibition purposes. Proper gasketing will be very important. The case will contain some humidity-buffering material to offset variation caused by changes in temperature. Since the temperature of our galleries can be controlled, no special temperature control will be introduced in the cases.

Special care will be given to lighting the cases. The lighting will be external and properly situated so as not to cause a heat build-up, and infrared absorbing shields will be used. The deleterious effects of spotlighting objects for dramatic exhibition are appreciated by conservators but not by all curators or collectors. The effects of heat build-up can be very serious on certain types of glass, for example, glasses with incipient crizzling, painted surfaces, or weathering products. In an experiment conducted in our museum, flat plates of glass were placed on a wooden pedestal painted black and lit with two 12-volt automobile lamps at a distance of about one metre. The temperatures of the glasses were measured by thermistor probes placed in hollowed-out depressions in the glasses. At one point within a piece of glass, a temperature of 67°C was measured. Temperatures of this level could seriously endanger glasses of the sorts mentioned and should never be tolerated.

The cases will be connected to controlling units containing trays of silica gel which will have been equilibrated previously to the target relative humidity, perhaps 45% to start with. It was decided that silica gel would be used

as the controlling medium because of its inertness, low sensitivity to temperature change, regenerative qualities, and adaptability to different levels of humidity control. Circulating devices with proper safety controls will be used to assure adequate circulation between the control units and the cases. A remote recording thermohygrograph will monitor the relative humidity and temperature through sensing probes. A separate re-equilibrating unit in our workroom will be used to regenerate the silica gel as required.

It is expected that, if the sealants are good and the cases are not opened frequently, the system will remain stable for some months at a time. One of our major goals is to install a system which will operate with a minimum of maintenance and will be as free as possible of annoyances caused by failures of mechanical or electrical parts. For this reason, which may appear paradoxical to some readers, the Museum has elected not to install a fully-automated system. Our belief is that the more elaborate a system becomes mechanically, the more things there are to go wrong.

It is hoped that, through proper design and construction of these cases, our glass with incipient crizzling will be safely preserved throughout the coming years while we attempt to devise treatments which will restore chemical stability to these glasses, instead of just maintaining a delicately-balanced metastable state.

ACKNOWLEDGEMENTS

REFERENCES

1. There are numerous accounts of Ravenscroft's early experimentation. One is: Hartshorne, A., 'Antique Drinking Glasses', Brussel and Brussel, New York, 1968, pp.240-241. The term 'crizzle' was applied to glasses as early as Ravenscroft's time. The common usage of the word was to describe roughening of surfaces, or the crackling of sunburnt skin on the face or hands, an apt parallel to the appearance of these glasses.

2. Hedvall, J. A., Jagitsch, R. and Olson, G., Uber das Problem der Zer-Störung antiker Gläser, 'Transactions of Chalmers University of Technology' No.118, Gothenburg, Sweden, 1951. We are not attempting here to compile a complete bibliography on this subject.

3. Brill, R. H., The scientific investigation of ancient glasses, in 'Proceedings of the Eighth International Congress on Glass', London, 1968, pp.47-68; Incipient crizzling in some early glasses, 'Bulletin of the American Group of the International Institute for Conservation of Historic and Artistic Works', 12 (1972).

4. There are many editions of Antonio Neri's 'L'Art Vetraria'. The first edition was printed in Florence in 1612; the first English translation, by Merrit, was in 1662. R. M. Organ has also described this chemical effect [9].

5. Brill, R. H., Scientific studies of stained glass, 'Journal of Glass Studies', 12 (1970), 185-192.

6. Adams, P. B., Crack propagation of annealed glass during exposure to water, in 'Tenth International Congress on Glass', No. 11, The Ceramic Society of Japan, Kyoto, 1974, pp.16-23.

7. Other experiments have also been attempted or are as yet incomplete, so they are not discussed here. These include various approaches to determining water contents, and electron microscopy.

8. Bimson, M. and Werner, A. E., The danger of heating glass objects, 'Journal of Glass Studies', 6 (1964), pp.148-150.

9. Bimson, M. and Organ, R. M., The safe storage of unstable glass, 'Museum News', 46 (1968), pp.39-47.

APPENDIX: CATALOGUE OF SAMPLES

449 Wineglass, French, c. 1750.
Colourless glass, pink surface, heavily crizzled.

457 Beaker, Venetian(?), c. 1709.
Colourless glass, heavily crizzled.
Donated by Gudmund Boesen; Rosenborg Collection, Inv. no. 109.

461 Cut pendant from candelabrum, Venetian(?), c. 1709.
Colourless glass, heavily crizzled.
Donated by Gudmund Boesen; Rosenborg Collection, Inv. no. 27-43.

1050 Wineglass, French, 1600-50.
Grayish glass, heavily crizzled.
Donated by William J. Young.

1487 Pane in bookcase, American, 1790-1810.
Colourless glass, heavily crizzled.
Donated by Dwight Lanmon.

1488 Pane from frame of painting, American, nineteenth century.
Colourless glass, heavily crizzled.
Donated by the Henry Francis duPont Winterthur Museum.

1498 Wineglass, French, 1725-50.
Colourless glass, pink surface, heavily crizzled.
Donated by the Henry Francis duPont Winterthur Museum.
(Figure 1 in text.)

1630 Rim fragment, petal and loop design, American, late nineteenth century.
Light blue, heavily crizzled.

1823 Reproduction of early bottle, Jamestown, Virginia, 1971.
Green glass, 'weeping'.
Donated by James Haskett.

4011 Engraved goblet, Silesian, 1710-30.
Colourless glass, incipient crizzling.
Donated by Jerome Strauss. (His no. S538)
(Figures 3, 4, and 5 in text.)

Figure 1.

Figure 1. Typical example of early crizzled glass. French, 1725-50, no. 1498 in this study.

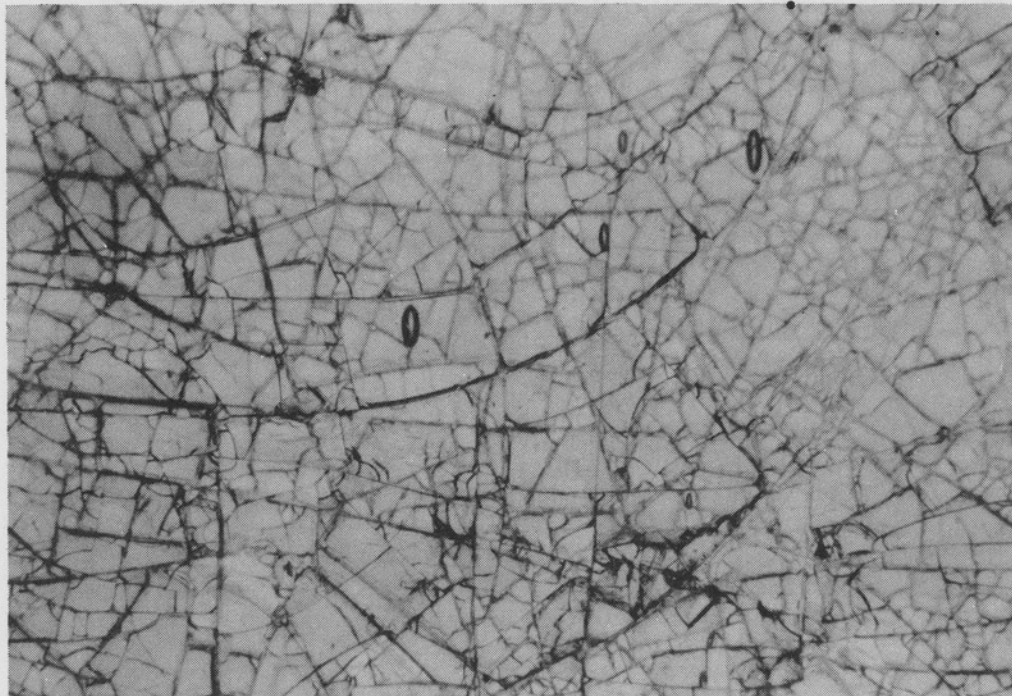Figure 2. Photomicrograph of surface of wineglass in Figure 1. Magnification approx. 6X.

Figure 2.

Figure 3. Typical example of glass with incipient crizzling. Silesian, 1710-30, no. 4011 in this study. Donated by Mr Jerome Strauss for experimentation.

Figure 4. Rim sample of glass in Figure 3. No hydration treatment. Traces of incipient crizzling can be seen along lower left edge.

Figure 5. Same sample as in Figure 4. Severe crizzling was produced by room-temperature storage at near-zero RH within 24 hours.
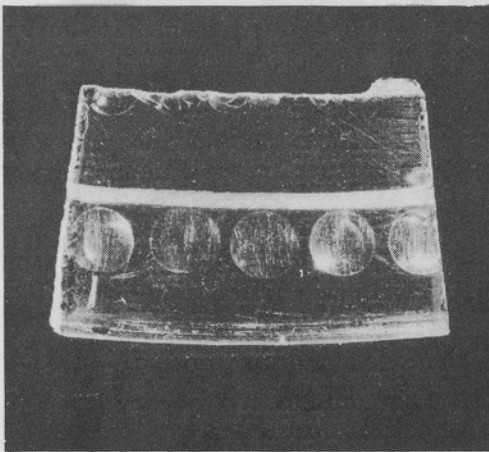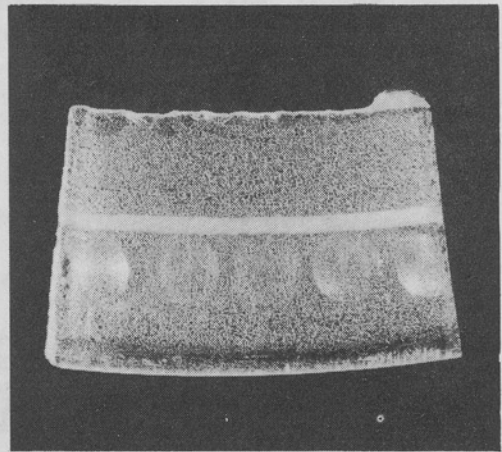
Figure 3.

Figure 4.

Figure 5.