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Characterization of corrosion products on old protective glass, especially daguerreotype cover glasses

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The method of casing objects using a protective cover glass bound to the object using a tape or frame promotes glass corrosion on the inside surface of the cover glass in preference to the outside surface. The characterization of some of the corrosion products found on these glasses is discussed especially as it applied to cased daguerreotypes. The geometry of these packages is responsible for the corrosion phenomenon. The types of corrosion products and the severity of the corrosion is a function of the bulk composition of individual cover glasses.

1. Introduction

The problems of deterioration and corrosion of glass artifacts dating from antiquity and later have been studied and addressed in some detail. The composition and manufacturing methods for these types of glass artifacts have been investigated by many workers using many different analytical techniques [1–6]. In more recent times, the storage and display of all types of glass has been of great concern because of the new efforts to preserve these items from long term decay and deterioration [7, 8]. From another standpoint, the long term durability of antique glasses has also been of interest as a natural analogue for glass containment of high level nuclear waste [9–13].

The paper addresses the specific problems of corrosion of glasses used in protective casings for other objects. In this instance, the glass is merely there to protect objects from dust and debris, from chemical and atmospheric attack, or from mechanical damage. These protective glazings are usually put together in a package made up of the glass, a spacer, and the object. This package is then held together in a variety of ways – by a frame, a tape or metal seal, an adhesive seal, or some combination of these materials. This method of casing can cause moisture to be trapped inside the package which can help to initiate corrosion of the glass. The initial environment of the package may be controlled by the atmosphere at the time the package was sealed. In turn, the corroding glass can produce materials that may act to degrade the object the glass is meant to protect.

This paper describes the characterization of some glass decomposition products and the forces which drive their formation. Specifically, it is concerned with this phenomenon as it applies to cased daguerreotypes. Other similar results found are on optical lenses bound together by brass rings. Cased ivory miniature portraits will also be considered.

Daguerreotypes were the earliest common photographs. They were popular from 1839 until the end of the 1850s. Essentially, the daguerreotype is an image produced on highly polished silver plate. The appearance of the image is the result of differing amounts of light scatter from small crystalline image particles (~ 0.1–$1\,\mu$m in diameter) on the surface of the silver plate and specular reflectance away from the viewer on non-image areas of the plate. The material properties and deterioration of daguerreotypes have been studied extensively and are described elsewhere [14–17].

Daguerreotypes are mechanically fragile because the substrate silver is relatively soft and easily scratched. The practice of casing these objects was typical of the traditional way in which miniature portraits were displayed and stored in the eighteenth and nineteenth centuries. The usual daguerreotype case was made up of the daguerreotype, a mat (usually made of stamped brass), and the cover glass. These components were bound together with a paper tape and some sort of adhesive. The tapes were often covered with a decorative brass foil tape called a "preserver". This entire package was placed in a small case made of leather and wood, *papier maché*, or moulded plastic. These cases were hinged with clasps and usually had some sort of cloth pad inside the cover portion of the case. A typical case and daguerreotype is shown in Fig. 1. In some instances, daguerreotypes were sealed to a glass and placed in *passe partout* type frames for hanging or other types of display.

These methods of casing are an effective means of preserving the daguerreotype because the package acts as a corrosion barrier, However, it has been observed that the interior surfaces of many cover glasses dating

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Figure 1 A cased daguerreotype showing the daguerreotype, mat, cover glass, and case.

from the nineteenth century become dusty and dirty with age. The glasses are said to "weep" and to become "greasy" over time. The debris seen on the glass in Fig. 2 is typical of the appearance of aged nineteenth century daguerreotype cover glasses. Other commonly observed problems with these glasses are the appearance of patchy areas of discoloration, or discrete spots or clumps or amber coloured "crystals", and of "mould growths". There were also nineteenth century reports of the presence of mites and their "excrementious matter" on cover glasses [18].

Similar kinds of problems are found on some cased optical lenses. The common occurrence of mould-like growths on these materials when sent to the tropics during World War II, led to an intensive study of the problem. These studies on "fungus fouling" of lenses were carried out by about two hundred investigators working at Bausch and Lomb (Rochester, NY), the Navy's Ordnance Research Laboratory, Frankfurt Arsenal (Phildelphia, PA), the University of Pennsylvania (Philadelphia), University of Pittsburgh (PA), and the Tropical Research Laboratories (Panama) [19–22]. There were similar groups working on the same problem among the British during the same period [23].

2. Historic pane glasses

Generally, when glass is chosen to put over a picture or other object for protective glazing, it is not chosen because of its specific durability or corrosion-resistant characteristics. With the current increasing interest in the preservation of cultural artifacts, there may be some thought given to the radiation filtering properties or the specular reflectance of the glass surface, but long term chemical durability is not likely to be a factor in the choice of any particular glass used for glazing an object, even in a museum setting. In museums, glass is very often continually washed and re-used as needed. There is no evidence to suggest that glasses used for casing were chosen any more carefully in the past, than is now the case. Easy availability is (and was) most likely the main factor in the choice of glazing materials. Certain special fashions, such as domed glazing and bevelling, play a role in selection of casing materials, but these factors have little or no direct bearing on the ultimate chemical durability of the cover glass.

To test this idea, a collection of some two hundred cover glasses from daguerreotypes was assembled. These cover glasses were gathered from a large number of sources and represented a variety of source

Figure 2 A daguerreotype with a 'dusty' cover glass – the typical sign of glass corrosion in these packages.

conditions and ages. Some were removed directly from daguerreotypes with intact nineteenth century seals. Some were from daguerreotypes that had been cleaned, resealed, and re-cased in the more recent past using a new (modern) or cleaned (vintage) glass. Some glasses came from stockpiles of vintage daguerreotype cover glasses that had been removed from daguerreotypes either in a museum setting or by private collectors and stored for re-use at some future date. The cover glasses came from a random and wide reaching assortment of geographic locations. There is little likelihood that the samples could have come from the same glass houses.

Glazed and sealed daguerreotypes were kept as received until the seals were broken directly before the characterizations described. The procedure was to prevent any loss of the corrosion products found on the inside surfaces of the glasses through drying or accidental removal.

Several lenses from the World War II fungus fouling experiments were also used in the study. These were obtained from one of the workers (Wilman Spawn) who was involved in this work at the Frankfurt Arsenal. These lenses had been stored during the intervening years in a Philadelphia basement. Some other lenses with similar deterioration were also examined.

3. Experimental methods

Glass durability is dependent upon many factors. Those items specific to the glass itself are its bulk composition, its thermal history, the homogeneity of the glass, surface treatments and characteristics (roughness and surface composition), and the previous corrosion history of the glass. Further, durability is complicated by the separate history dependence of the glass surface which is also affected by annealing temperature and atmosphere, surface preparation, storage conditions before and after the glass was put to use, and its cleaning and corrosion history. This study examined both the bulk characteristics of pane glass and the typical surface features that develop when these pane glasses are used for protective glazing.

The bulk composition of ten of the cover glasses collected for the study was determined using atomic absorption and atomic emission spectroscopy from lithium metaborate fusions of the powdered glass.

There were no bulk analyses for any of the lenses in the study because all of the lenses were loaned for examination.

All of the glasses were examined using a petrographic microscope to look for evidence of devitrification and phase separation during glass manufacture. Optical microscopy was also used to examine surface films on the glasses.

Much of the surface characterizations described below were obtained using a scanning electron microscope (SEM) with an energy dispersive X-ray spectrometer (EDX). All glass samples examined by SEM were coated with carbon. When glasses were still sealed to their daguerrotypes, the seal was broken and the cover glass was coated with carbon immediately prior to SEM examination. This approach was to prevent loss of water or other volatile components and drying of the interior surface. Of course, some loss of volatiles is inevitable because of the carbon coating procedures and the vacuum in the SEM sample chamber.

Surface deterioration products and debris were also analysed using X-ray diffraction (XRD) and a Gandolfi camera for microsamples. The microsamples were all obtained by scrapping or by lifting these products from the interior surfaces of the cover glasses under a binocular microscope. The corrosion products on the lenses in the sample were also analysed in this way. In addition, the inside and outside surfaces of the glasses were analysed using secondary ion mass spectroscopy (SIMS) and also microfocus Raman spectroscopy. The results presented here are based primarily on the data from SEM, EDX, and XRD examinations.

4. Results and discussion

4.1. Bulk compositions and characteristics of the cover glasses

The results of the bulk composition analyses are given in Table I and shown graphically in Fig. 3. It was

TABLE I Quantitative chemical analysis of various daguerreotype cover glasses

Oxide	19-76	19-XXX	19-V	19-77	19-18	19-37	19-XIV	19-VIII	19-VI	19-XXXI
SiO_2	56.3	72.2	65.9	66.4	66.1	72.2	70.2	70.2	71.9	71.5
Al_2O_3	0.68	1.89	1.47	1.06	0.97	1.93	0.84	2.32	1.21	1.83
TiO_2	0.04	0.04	0.05	0.05	0.06	0.05	0.05	0.05	0.04	0.06
Fe_2O_3	< 0.02	0.04	0.05	0.05	0.03	< 0.02	< 0.02	< 0.02	0.19	0.26
MgO	0.01	0.08	0.07	0.08	0.22	0.05	0.06	0.06	0.07	0.08
CaO	< 0.05	5.10	10.7	10.1	8.57	6.39	6.77	6.56	13.7	13.5
MnO	0.03	< 0.01	0.18	0.16	0.22	< 0.01	< 0.01	< 0.01	0.4	0.32
SrO	< 0.01	< 0.01	0.03	0.03	< 0.01	< 0.01	< 0.01	< 0.01	0.02	0.02
BaO	< 0.01	< 0.01	0.01	< 0.01	0.02	< 0.01	< 0.01	< 0.01	0.01	0.01
Na_2O	2.30	13.8	1.73	1.61	0.87	14.8	16.6	16.4	12.2	11.8
K_2O	7.67	2.52	19.2	19.2	21.1	3.32	2.56	2.43	0.09	0.14
P_2O_5	0.04	0.05	0.09	0.14	0.12	0.04	0.06	0.04	0.05	0.06
SO_3	0.03	0.33	0.31	0.30	0.24	0.24	0.61	0.59	0.49	0.45
PbO	29.4	3.10	0.15	0.37	0.24	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05
Sb_2O_3	0.13	< 0.10	0.59	0.64	0.51	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10
As_2O_3	0.07	0.29	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	0.13	0.11
TOTALS	96.70	99.49	100.53	100.2	99.27	99.04	97.75	98.65	100.51	100.14

*Performed by H. Gong, Mineral Constitution Laboratory, The Pennsylvania State University. All results given as weight percent oxide.

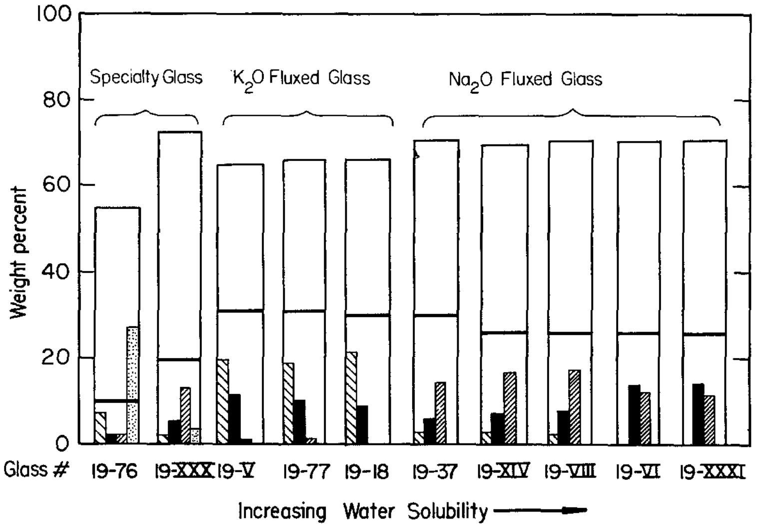

Figure 3 Graph showing the results of bulk analysis of typical daguerreotype cover glasses. The heavy line in each histogram indicates the total percentage of flux. (□ SiO_2, ▧ K_2O, ▩ PbO, ■ CaO, ▨ Na_2O)

found that the collected glasses could be grouped using a hand-held ultraviolet lamp on the basis of their characteristic luminesence colours – a yellow–orange, and orange–magenta, and a blue. The glasses chosen for bulk analyses were picked on the percentage of the total glass sample with similar luminesence colours. Thus, the largest percentage of the glasses were primarily soda fluxed and had a common yellow–orange luminesence. The next largest group was made up of soda-lime fluxed glasses with a common orange–magneta luminesence. There was a small percentage of lead glasses which had blue luminesence under the UV lamp. The lead glasses represented only about 5% of the total, however, their blue luminesence was so striking that two of those samples were analysed.

It can be seen from the bulk compositions that the formulae of the glasses within the groups are remarkably similar. They all have unexpectedly high levels of total flux, as can be seen by the heavy line in each of the histograms found in Fig. 3. The glasses in Fig. 3 are arranged in order of increasing water solubility. This solubility, of course, is one indication of the long term durability of glasses. Pane glass made with lead is fairly unusual because of the comparatively high cost. For that reason, it is thought that these glasses may have been mirror glass or some other specialty glass, or that the lead may have been derived from lead glass cullet used in the glass melt. These results, in general, support the idea that these glasses were not chosen for any reason other than easy availability.

Optical microscopy was used to check for the presence of glass stones (crystals), seeds (bubbles), and bits of refractory debris. This information reflects the melt history of the glass, its degree of homogeneity, and is indicative of the ultimate stability of a particular glass. In order of decreasing prevalence, the following glass stones were commonly found in the nineteenth century glasses: devitrite, alpha and beta wollastonite, diopside, cordierite, and quartz (unmelted sand). None of these stones are unusual given the bulk chemical compositions listed above. Unmelted refractory brick and sand and seeds were also present in most of the glasses. Glasses that appeared to be of more recent manufacture had fewer or no discernible glass stones.

A wide variety of body colours was found in the sample. These body colours are merely indicative of the presence of very minor constituents, however, the variety suggests the random assortment of the glasses used in the study. The colours ran from clear or colourless to various greens and blue–greens to purple and pink casts.

4.2. Surface composition and characteristics

The degradation of glass surfaces is usually first noted visually by the appearance of a faint haze or clouding of the surface when viewed in transmitted light. This haze is called "weathering". Weathering phenomena, unlike aqueous corrosion of glass, are the result of atmospheric interaction of water vapour and other airborne gases with the glass surface. There are two types of weathering: Type I where sufficient moisture collects on a surface so that it periodically runs off and carries away reaction products and Type II where moisture evaporates before run off can occur. Type I weathering usually is characterized by localized areas of total glass breakdown which leaves a roughened and pitted glass surface. The presence of surface reaction products (salts and leached residues) is usually indicative of Type II weathering [24].

The severity of surface corrosion is also controlled by the geometrical configuration of the glass surface. For instance, corrosion on the interior and exterior surfaces of a empty glass container proceeds at a similar rate if the opening of the container is very large so that all surfaces are exposed to the "same" environment. However, as the opening of the container decreased, the corrosion on the interior surface will increase in a way that is inversely proportional to the size of the opening [25]. This pattern evolves because as the opening becomes smaller and smaller, the environment of the two glass surfaces becomes very different.

Water or moisture is easily trapped inside an empty container with a small opening. Air exchange within the container may be dominated by barometric variations or similar mechanisms and the possibility of dilution from the ambient environment is diminished along with the closure of the container. If the external environment is static and there is little or no air exchange through the container opening, once the glass corrosion cycle begins, corrosion products are trapped and contaminate the interior environment and surfaces of the container. Trapped condensate initially allows for selective dissolution of sodium from the glass surface. This reaction leaves a hydrated silica-rich layer on the surface along with sodium hydroxide. Over time, the effective pH of the condensate rises as more and more sodium hydroxide is formed. As the pH rises, there is also increased dissolution of the glass surface resulting in pitting and the formation of various dissolution products. Thus, the geometry of the container itself can promote the evolution of a potentially hostile interior environment that actually increases the rate of glass corrosion [26–30].

Similarly, stacked panes of glass also exhibit weathering that is increasingly more severe as the separation distance between the panes is decreased, especially in environments with high relative humidities. In this case, the amount of collected and trapped condensate can be extremely high relative to the exposed glass surface and the possibility of removal of this moisture is very low. Because there are no buffers present, the pH of the trapped condensate rises uncontrollably as sodium ions migrate out from the glass surface. Again, there is total breakdown of the glass surface. As long as the pH remains high ($\geqslant 9$), glass breakdown will be the dominant reaction. Whereas, sodium leaching and hydroxylation of the corroding glass surface dominate at surface pH values $\leqslant 9$.

The deterioration products found on these cover glasses fall into four categories: amorphous gels, crystals found in these gels, products formed by gel interaction with the surface of the daguerreotype plate or its brass mat, and other products. These products will be discussed in some detail below. The chemical species found on the glasses are summarized in Table II. Recurring, but unidentified corrosion products have been given letter names and their XRD data (intensities and d spacings) are given in the appendix. Elemental data on these unidentified phases derived from EDX are also given in Table II. XRD and SEM were also used to identify corrosion products and to look at the similarity of debris found on interior glass surfaces and their corresponding daguerreotype surfaces.

4.3. Amorphous gels

The inside surfaces of the cover glasses usually could be identified by examination under the optical microscope because that surface was always more seriously degraded than the outside surface. This difference was even true of cover glasses that had long since been removed from daguerreotype packages. The different surfaces of cover glasses that had been cleaned for re-use could also be identified in petrographic examination, albeit with more difficulty.

The inner surface of cover glasses is often covered with sticky droplets commonly referred to as "weeping" glass. These droplets are primarily composed of amorphous sodium silicate or water glass. The exact composition of these gels varies according to the bulk compositions of the glasses from which they are derived. Qualitative pH measurements of these droplets made by burnishing pH paper over the interior surface of freshly uncased cover glasses, show that the pH of these interior surfaces ranges from 10–14. Soda fluxed glasses always show signs of this weeping phenomenon – either because there are visible droplets or because the interior surface of the glass has a dried, cloudy frosting. The interior glass surface from freshly uncased daguerreotypes with wet droplets usually feels "greasy" or "soapy' to the touch.

The location of these gel droplets appears to be controlled by the geometry of the package or by the location of defects (stones, seeds, refractory, and chemical inhomogeneity) in the glass itself. It is rare to see patches of weeping glass in the areas directly above the mat in a cased daguerreotype, although the effects of glass corrosion can be seen on mats. It is more common to see clusters of droplets in the more central portions of the cover glasses where there is a space between the glass and the daguerreotype. Some corrosion products seem to congregate at the mat edge, but this weeping phenomenon tends to be general.

Typically, the most severe weeping was associated with cover glasses from the soda fluxed bulk composition group which had intact nineteenth century seals*. Among the soda–lime fluxed glasses, "weeping" is less pronounced, Severe weeping is rarely observed among the lead glasses, except in cases like Glass 19-XXX (Table I and Fig. 3) which appear to be soda or soda–lime fluxed glasses manufactured with lead glass cullet. Evidence of weeping is not solely confined to nineteenth century cover glasses of poor composition. This phenomena has also been observed on daguerreotypes that were re-sealed and glazed with more durable, "modern" glasses 30–40 years ago.

4.4. Crystal products in the gels

The secondary electron micrograph shown in Fig. 4 shows the inside surface of a typical daguerreotype cover glass. The micrograph covers an area aproximately 3 mm^2. On simple visual examination, the rounded patches are seen as droplets of "weeping glass" and the spikey bundles are seen as dust. The cracked material in the surface shown in Fig. 4 is the hydrated silica layer formed during the process of sodium leaching. Once this layer is cracked, it can spall off the glass surface onto the underlying daguerreotype. The crystalline features on the interior glass surface grown from the gels formed during the weathering cycle. They typically are needle-like crystals that can form in sheaves or spikey balls (as in Fig. 4), laths, dendritic crystals, cubes, weakly crystalline silicate fibrils, and occasionally, spherical balls. The chemistries of these crystals closely follow the chemistry of the glasses from which they are derived. They typically contain silica, sodium, calcium, potassium, phosphorus, aluminium, etc. Crystals similar to those

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* It should be noted that the presence of a nineteenth century seal is no guarantee that the cover glass is original to a particular daguerreotype. It is only indicative that the seal was made sometime in the past.

TABLE II Identification of corrosion products

Identification	XRD	Crystallinity	EDX Data	Sample #	Description
Silver	X	good	Ag, Cl (Cu, Na/Si)	19-120-1	Found w/AgCl + Phase X
	X	good	Ag, Cl	19-120-2	Found w/AgCl
	X	good	Ag, Cl (Cu, Na/Si)	19-120-4	Found w/AgCl + Phase I
	X	good	–	19-121-1	Found w/AgCl
Silver chloride	X	good	See above	19-120-1	Found w/Ag + Phase X
	X	good	See above	19-120-1	
	X	good	See above	19-120-2	
	X	good	See above	19-120-4	
	X	good	See above	19-121-1	
	X	good	–	19-125-1	Found w/Phase M
Silver phosphate	X	good	Ba, S, Ag, P, Si, Na		Found w/$BaSO_4$ + Phase Q
Cuprite (Copper (I) oxide)	X	v good	–	19-122-1	Found w/NH_4Br
Ammonium bromide	X	v good	–	19-122-1	Found w/cuprite
Barium sulphate	X	good	Ba, S, Ag, P, Si, Na	19-120-3	Found w/Ag_3PO_4 + Phase Q
Sodium sulphate	X	v good	Na, S, Si, K	19-113-3	
Sodium formate	X	good	–	19-26-6	Surface scrapings
	X	v good	Na, Ca, S, K, Si, Cl, Ba	19-67-1	Bug
	X	good	–	19-113-10	Orange spot
	X	v good	–	19-113-12	Orange spot
Amorphous material	X	no	Si, Na, Ca, Al, K, Cu, Sn	19-31-6	Red fibrils
	X	no	Si, Na, Ca, Al, K, Cu, Sn	19-31-7	Yellow crust
	X	no	Si, Na	16-67-3	Mould-like mass
	X	no	–	19-113-7	Mould-like mass
Mould-like masses	X	no	–	19-113-8	White spots
	X	weak	Si, Na	19-113-3	Mould-like mass
	X	broad/fair	Si, Na	19-113-4	Mould-like mass
	X	broad/fair	–	19-122-4	Bolder blisters
	X	fair	Na, Si, Ca, K, Al, Cl, S	WS-BR-composite	Fibrils
	X	poor	Si, Na, Ca, K	glass UK-LK-2	Fibrils
	X	fair	Si, Na, Ca	glass UK-LK-1	Brown spots
Phase A	X	weak	Na, Si, S, Cl, Ca, Cu	19-31-4	Red-orange blisters
	X	good	S, K, Ca	19-67-4	Brick red crystal
	X	weak	Si, Na	19-113-11	Colourless spot
Phase B	X	v good	Na, K, Cu, (Al, Si, P, S, Cl)	19-31-1	Yellow bug
	X	good	Si, Ca, Na, K (P)	19-31-2	Red spot w/fine crystals
	X	weak	Si, Ca, Na, K (P)	19-31-3	Orange waxy spot
	X	good	–	19-113-9	Yellow orange spot
	X	v good	Si, S, Ca, Cu, Zn	16-67-2	Yellow waxy spot
	X	good	Ca, K, (Na, Si, S, Cl)	19-118-2	White crystals with black spots found with alizarin
	X	good	Ca, K, Si (Na, S, Cl)	19-118-4	Smooth rough blisters found w/phase H
	X	good	Ca, K, Si (Na, S, Cl)	19-118-5	Cores of rough blisters, found w/phase H
	X	good	Na, K, Ca (Si, S, Cl)	19-118-6	Decomposed bug, found with phase F
Phase C	X	weak	Si, Ca (Na)	19-26-2	Silvery brown blisters
	X	weak	Na, Si, S, Cl, KCa, Fe, Cu, Zn	19-26-3	Silvery brown needles
Phase D	X	weak		19-31-8	Yellow–green mass
Phase E	X	v good	S, (Si, Na, K, Ca)	19-115-2	Blisters
Phase F	X	weak	Ca, Si, Na	19-118-1	Orange red spot
Phase G	X	weak	(Ca, K, Na, Si, Al, S)	19-118-3	Fibrous mass (paper?)
Phase H	X		See above	19-118-4	Found with Phase B
	X		See above	19-118-5	Found with Phase B
	X		See above	19-118-6	Found with Phase B
Phase I	X		See above	19-120-4	Found w/phase X, Ag, AgCl
Phase J	X	fair	–	19-122-2	Lime green crystal
Phase K	X	good	–	19-122-3	White balls
Phase L	X	good	–	19-122-5	Golden rod
Phase M	X	good	–	19-125-1	Yellow green crystals/found w/AgCl
Phase N	X	good	–	19-125-2	White microcrystals
Phase O	X	good	–	19-1253	White shard
Phase P	X	weak	–	19-125-4	Black scale
Phase Q	X	good	Ba, S, Ag, P, Si, Na	19-120-3	Found w/$BaSO_4$ + Ag_3PO_4
Phase X	X	good	Ag, Cl, Cu, Na, Si	19-120-1	Found w/Ag + AgCl
	X	good	Ag, Cl, Cu, Na, Si	19-120-4	Found W/Ag + AgCl + Phase I
Phase R	X	good	Si, Na, Ca, K, Al, Cl, S	WS-BR-3(lens)	Yellow masses

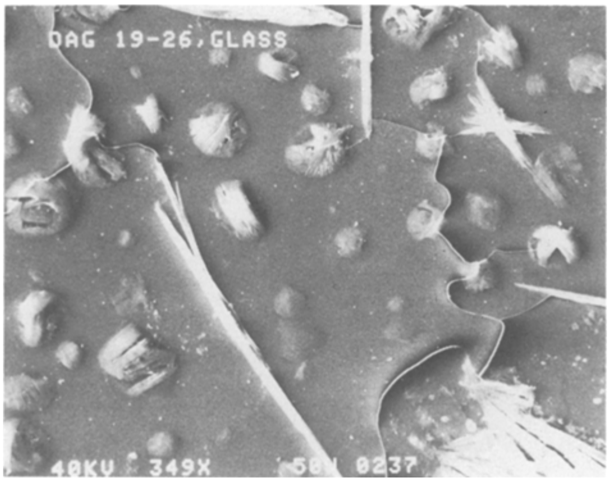

Figure 4 Secondary electron image showing the inside surface of a daguerreotype cover glass with moderate corrosion. The scale bar is equal to 50 μm.

found on the cover glasses were also found on the lenses in the study. The same types of crystals and morphologies on weathered glass surfaces have been reported by other workers [31, 32].

In only a few cases, was it possible to obtain good XRD pattens from the crystals found in the surface gels. This success rate was true of crystals on both the cover glasses and the lenses. EDX always showed that these crystals have different compositions than the underlying glass surfaces or surrounding gels. Many of the crystals appear to be various calcium silicates based on both crystal habit and EDX data.

For instance, the EDX spectra shown in Fig. 5 are for the glass surface shown in Fig. 6. The spectrum with the broken line is from the large group of crystals on the left-hand side of the micrograph; the spectrum with the solid line is from the darker background area. The XRD samples identified as 19-26-2 and 19-26-3 (Table II) are for crystals similar to those in the micrograph taken from the same sample. These two XRD samples produced the same unidentified, weakly crystalline patterns. Many of the silicate crystalline products identified by SEM and EDX produced XRD results that added very little to the specific identification of these compounds.

Some glasses develop blister-like crystal growths that appear to have a small darker coloured core (Fig. 7). Usually these blister-like crystals are sulphates – sodium sulphate or barium sulphate. These sulphates are more likely derived from the presence of sulphur dioxide in the furnace gases during glass melting or from the intentional use of sulphur dioxide atmospheres during the annealing process. Since the 1920s, it has been known that such treatments improves the chemical durability of pane glasses. Adsorbed sulphur dioxide and water act like a sink for migrating sodium ions leaving a dealkalized surface layer on the glass. This treatment subsequently retards the formation of surface sodium hydroxide during weathering [33].

Carbonates can be formed by the interaction of carbon dioxide and water from the air with various products of the glass dissolution reactions. The carbonates and bicarbonates of sodium, potassium, and calcium have been found on weathered glass surfaces by us and other workers. These compounds were expected, but none were identified in this study of cover glasses.

4.5. Interaction of glass corrosion products and underlying surfaces

The various dissolution products and crystals formed on the cover glass can dry up and spall off the glass surface onto the underlying surfaces as result of seasonal cycling or some similar change in the ambient humidity. This debris can be found littering the daguerreotype surface when these objects are examined by scanning electron microscopy. In some cases, these products act as transfer media to carry metal and metal salts from the daguerreotype or brass mat back to the glass surface. The silver, silver phosphate, and silver chloride identified on Glass 19-120 (see Table II) are clearly derived from this kind of interaction. The secondary electron image shown in Fig. 8 shows some unidentified copper bearing crystals that are most likely derived from copper found in the brass mat

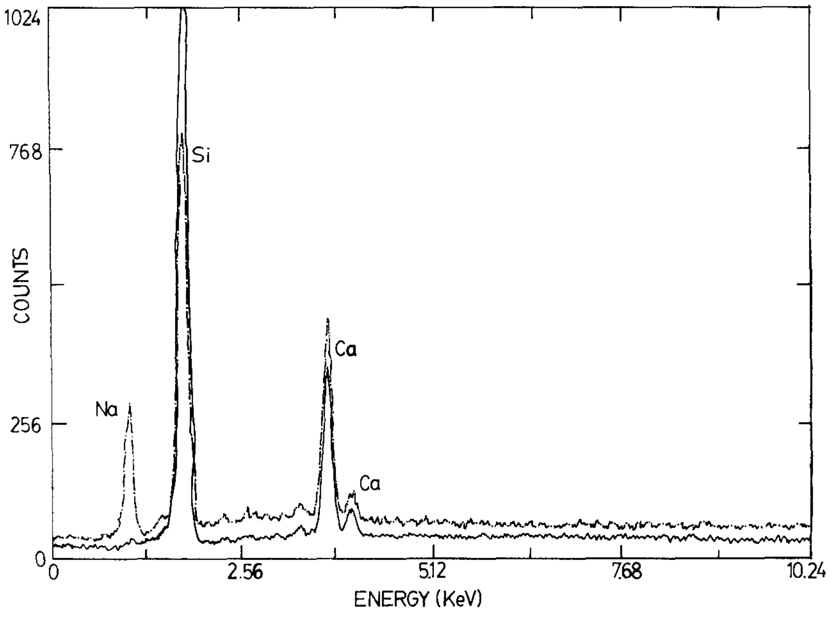

Figure 5 EDX spectra of the interior cover glass (glass 19–26) surface shown in the secondary electron image shown in Fig. 6. The solid line is the spectrum for the darker background area in the micrograph. The broken line, for the large mass of surface crystals to the left of the micrograph.

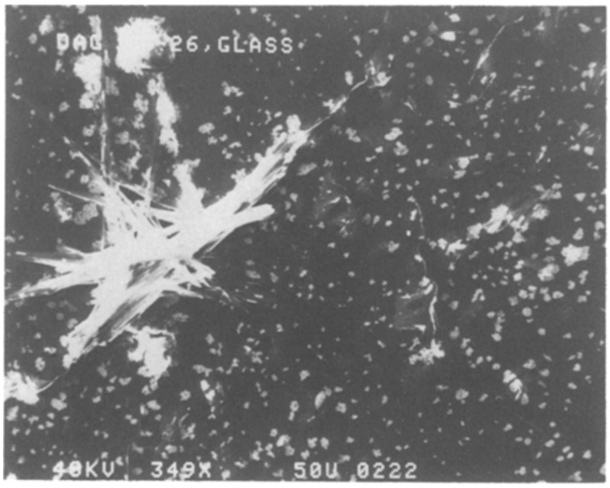

Figure 6 Secondary electron image of the interior surface of a daguerreotype cover glass (see Fig. 5). The scale bar is equal to 50 μm.

(rather than copper from the daguerreotype plate itself). EDX data on the corrosion products often shows traces of silver, copper, zinc, and sometimes tin.

The most surprising silicates that appear on both daguerreotype cover glasses and on daguerreotypes are mould-like masses like that shown in the composite secondary electron image in Fig. 9. The underlying surface in the micrograph is the silver surface of a daguerreotype. It can be seen in the figure that the mould-like mass is clearly related to the white shard that has fallen from this daguerreotype's cover glass. These masses have been identified as mould by other workers on the basis of morphology [34]. These masses also appear to be related to materials identified as "fungus" during the World War II fungus fouling studies [21].

The masses resemble the morphology of Candida, a very common yeast-like fungus. However, these masses are consistently composed of silicon and sodium with smaller amounts of potassium and calcium. Similar chemical compositions determined on the basis of EDX data were reported by the Swan, Fiori, and Heinrich study [34]. Attempts were made in the present study to culture these masses with no success. The bead-like portions of the masses were examined by scanning electron microscopy to check for any evidence of spores, with no success. There was no evidence of the presence of either DNA or RNA. A similar testing regime was used during the World War II Fungus Fouling studies. In spite of some success at culturing and positive identification of various fungi, it was acknowledged that in spite of morphological appearances, not all of the growths on "fouled" lenses appeared to be related to fungal attack [35].

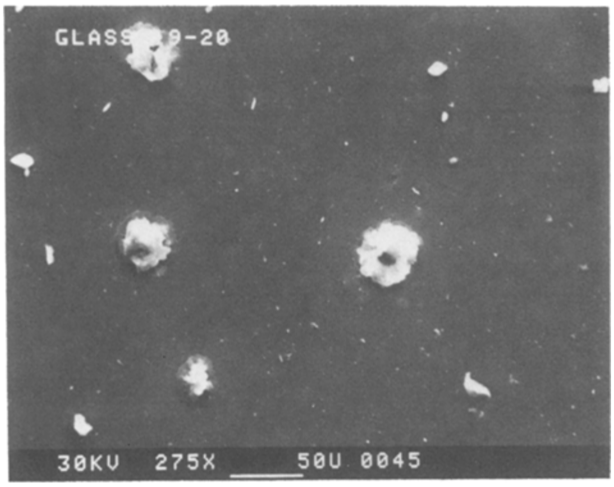

Figure 7 Secondary electron image of sodium sulphate blisters on the interior surface of a daguerreotype cover glass. The scale bar is equal to 50 μm.

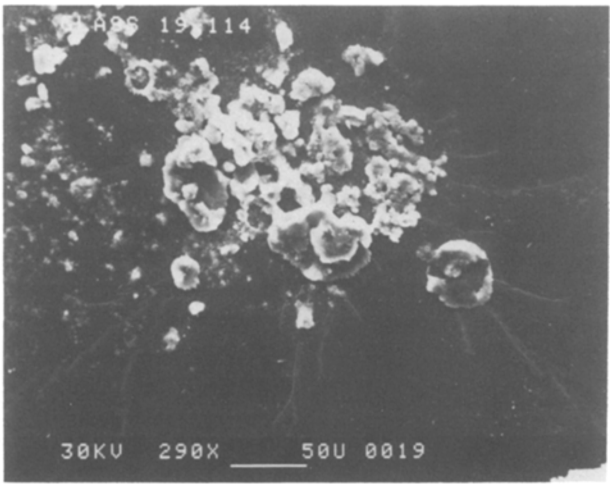

Figure 8 Secondary electron image of copper-bearing crystal on the interior surface of a corroded daguerreotype cover glass. The scale bar is equal to 50 μm.

The evidence in the present study supported the idea that these mould-like masses were clearly inorganic material, probably crystalline, which grows by some inorganic growth mechanism, which is still undetermined. These growths occur only in those cover glass-daguerreotype packages that have the least durable glasses, i.e., the high soda glasses particularly those which have yellow–orange florescence under a ultraviolet lamp. There must be some transfer of silica gels from the corroding glass surface to the metal daguerreotype surface for the masses to occur (see Fig. 9). The tangled masses of these silicates suggest rapid growth once the necessary conditions for growth are met. There are deep dendritic fissures in the daguerreotype surfaces where these masses have grown. The measured pH of the glass surface gels is invariably in the range of 11–14. All silicate growth of this type found in daguerreotype packages have the same "bead and thread" morphology, even if their exact chemistries vary slightly from sample to sample.

The mould-like masses found in daguerreotype packages have twisted thread morphologies that resemble the Induced Morphology Crystal Aggregate (IMCA) alkaline-earth carbonates studied by Garcia-Ruiz and his coworkers [38–40]. The pH range of the silica gels from corroding cover glasses is easily above where silver hydroxide would be precipitated and, indeed, silver hydroxide has never been identified in any of the masses. There is, however, scant evidence for the presence of two-dimensional membrane in these masses.

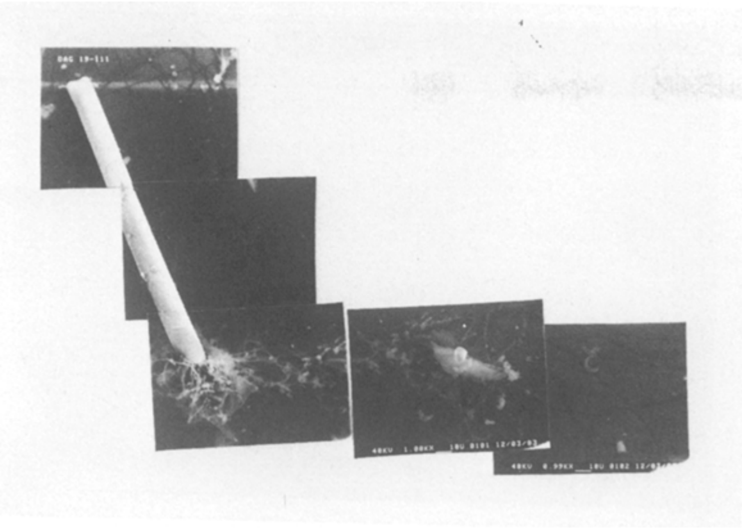

Figure 9 Composite secondary electron image showing mould-like masses of silicates formed by the interaction of glass corrosion debris and the daguerreotype surface. The dark background is the silver surface of a daguerreotype. The scale bar is equal to 10 μm.

It is possible to produce similar mould-like masses in the laboratory by 1) placing a drop of sodium silicate gel (pH 12–13) on a glass slide and placing a small silver nitrate crystal in the drop or by 2) placing a drop of sodium silicate on a daguerreotype plate. When observed by optical microscopy, very similar bead and thread silicate growths appear in a matter of minutes to an hour. By SEM, the resemblance of these growths to those actually found in deteriorated daguerreotype packages is even more striking. The growths produced in the laboratory are much more regular and clean, but the morphologies are the same. The samples produced using silver nitrate crystals have a characteristic red ring which appears to be the membrane. The red colour is from colloidal Carey Lea silver that is typically made by precipitation at high pH.

Similar mould-like masses have also been observed on the surface of eighteenth and early nineteenth century painted miniatures with corroding cover glasses. In the case of the miniatures, several different mass morphologies were found. These seemed to be related to different metals present in various pigments used in the paints. Other than optical microscopy, no other characterizations have been undertaken on these crystal aggregates.

4.6. Other products found on cover glasses

Another crystalline species found on the inside of daguerreotype cover glasses is sodium formate. Other workers have also found this product on daguerreotype cover glases [41] and on cover glasses from other case artifacts [42, 43]. Along with formic acid and sodium formate, various formates and acetates have been commonly reported corrosion products found on many types of objects encased in glazed vitrines [44] and on deteriorating building stones [45]. Formic acid and formate salts have also been identified as factors in the corrosion of optical glasses [46] and their presence has been noted as contaminants found on hydrogen electrodes [47].

The widespread instances of formic acid and formate salts on enclosed glass surfaces indicates that these species should be expected as easily formed corrosion by-products which occur during the ageing of these materials under common physical conditions. There is some argument over how these products are formed and over how to control or prevent their formation.

When formates and formic acid are found on stored or displayed artifacts or their casing materials, the prevailing assumption within the conservation community is that these products are derived from organic gas or vapours given off by paints, varnishes, adhesives, and wood products used to make the storage enclosures, display vitrines, and frames [42–49]. Experiments with many modern (and old) paints, varnishes, and adhesives have shown that short chained organic volatiles (such as C_1–C_4 acids) are given off during curing process. Likewise, many types of woods and wood products give off these corrosive materials. There is evidence that these materials continue to release these organic volatiles even many years after the curing or seasoning process would be considered ended [50–53]. Occasionally, the presence of formate salts has also been attributed to previous cleanings with formic acid [45].

In the case of the daguerreotype cover glasses and optical glasses, the quantities of formic acid and formate salts observed, their locations, and the frequency of their occurrence are greater than can be accounted for by a soley organic pathway. Often sodium formate is associated with the presence of mites or book lice on the cover glasses, however, it is not apparent that these creatures are the source of the formates (see below). The catalytic or electrochemical reduction of carbon oxides from the air is another, and far more likely, pathway.

Catalytic systems involving formic acid and formates have been well studied because they are used as model systems for the elucidation of the mechanisms of catalysis and they have been used to compare the activities of various catalysts [47, 54–55]. As can be seen in Table III, there is quite a variety of ways to obtain formic acid and formate salts from CO, CO_2, H_2, and H_2O under a wide variety of conditions using many different catalysts. In particular, silver and silver oxide provide excellent surfaces for oxidative catalytic reactions [56].

For the daguerreotype cover glass situation under discussion, there are several resonable pathways to

TABLE III Possible reactions leading to formic acid or formate species

Starting species	Conditions	Intermediate reactions	End reactions
CO_2, H_2	Cat†, T, P		$CO_2 + H_2 \rightarrow HCOOH$ [47]
CO_2, $H^{\cdot}$	Cat., HCOOH (g)		$CO_2 + H^{\cdot}$ cat./HCOOH(g)$H_2 + HCOO^-$ [55]
CO, H_2O	Cat., T, P		$CO + H_2O \rightarrow HCOOH$ [47]
CO_2, H_2H_2O	Cat., P	(a) $CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$ (b) $CH_3OH \rightarrow H_2CO + H_2O$	
CH_3OH, H_2O, CO_2	Cat., T	(a) $CH_3OH \rightarrow H_2CO + H_2$ (b) $CH_3OH + \frac{1}{2}O_2 \rightarrow H_2CO + H_2O$	$H_2CO + \frac{1}{2}O_2 \rightarrow HCOOH$
CO, H_2	AgO, T, P	$CO + H_2O \rightarrow H_2CO$	$2H_2CO + NaOH \rightarrow NaCOOH + CH_3OH$ (Cannizaro Reaction)
NaH, CO_2	s.t.p.		$NaH + CO_2 \rightarrow NaCOOH$
H_2, $NaCO_3H_{(aq)}$	Si gel supported cat. (Pd or W), s.t.p., pH 6.5–8.5	$H_2 + CO_2 \rightarrow NaOH$ $H_2CO_3 \rightarrow NaCO_3H + H_2O$ or $NaOH + CO_2 \rightarrow NaCO_3H$	$H_2 + NaCO_3H$ (aq) $\rightarrow NaCOOH + H_2O$ [60–62]

*Catalysts reported in the literature include: Hg, Pb, Cd, Sb, Zn, Au, Ag, various metal oxides, Ag–Hg compounds, W, Pd. Pt, In, SiO_2, various Si gels, Ru, TiO_2.

†Granular or particulate catalysts usually have noticeably lower activation energies of exchange and need significantly lower temperature for a given amount of reaction [63].

examine for the inorganic synthesis of formic acid and formate salts on the inner glass surface. According to the reactions listed in Table III, it should be fairly easy to form formic acid or formaldehyde at the silver/silver oxide daguerreotype surface by several of the reactions listed. These products, given off as volatiles, could then attack the inner glass surface, leaving sodium formate after subsequent reaction with sodium ions made available from the glass corrosion products. Silica gels formed on the corroding glass surfaces alone or with other corrosion products such as sodium hydroxide or sodium bicarbonate could act as catalytic or electrochemical cells promoting the formation of formic acid or formates directly at the glass surface. It should be noted here that for some glasses, corrosion by formic acid vapour requires both the presence of water vapour and a concentration of formic acid solution at the glass surface. As the same time, excess water-vapour can stop or reverse these reactions. Further, the relative vapour pressure of water vapour to formic acid vapour appears to be more significant in this corrosion reaction than the absolute vapour pressure of the whole system [46].

Whatever inorganic or organic reactions that produce formic acid or formaldehyde as starting materials, the ultimate appearance of formate salts on cover glasses or optical glasses is dependent upon the kind of silica gels that are formed by the corrosion of the bulk glasses.

(1) The surface features of a particular silica gel (or glass) control how formic acid is adsorbed to its surface, and this adsorption is required for the gel (or glass) to be catalytically active.

(2) Both silica gels and the glass from which they are derived may act as catalysts, but, each will have a characteristic disposition for different catalytic mechanisms. In general, surface OH^- usually act as centres for dehydration reactions. Certain modified Si–O–Si surface junctions, like Si–O–Al or Si–OH, can act as dehydrogenation centres.

(3) There are changes in the specific activity of catalytic gels due to changes in the porosity of the surface and the number of surface OH^- groups.

(4) Silica gels with large amounts of surface OH^- promote formic acid *decomposition* by both dehydrogenation and dehydration reactions. These gels also tend to be more active than silica gels without surface OH^- groups.

(5) Treating glasses that form catalytically active silica gels with different cleaners can dramatically alter gel activity with respect to formic acid decomposition. In particular, calcium hydroxide and potassium hydroxide cleaners leave modified surface layers (by adsorbed Ca^{2+} or substitued K in Si–OH chains) which alter the electronic properties of the surface gels. In the case of adsorbed calcium, the altered surface promotes the formation of formates [57].

These findings indicate that glasses which produce high calcium content gels on ageing or those with major portions of cations like lead which produce glasses with similar surface electronic properties to calcium glasses, may have a tendency form formate salts as part of their corrosion cycles if the glass is in an enclosed space and there is a source of formic acid. Indeed, all of the glasses in this study which formed sodium formate salts also had large amounts of calcium silicate gels on their inner surfaces, Further, the reported compositions of other cover glasses found with formate salts also appear to have surface films rich in calcium or they are glasses with a high lead content. This situation is also the case with reported compositions for optical glasses with formates [46]. Similarly, the majority of short chain organic acid–metal salt encrustations reported on encased objects occur on calcium rich materials like shells or eggs or on lead objects [43, 44].

Some cover glasses have small golden-yellow patches on their interior surfaces. These patches usually appear to be small, viscous spots but, with the aid of magnification, they may look like small bugs (arthropods).

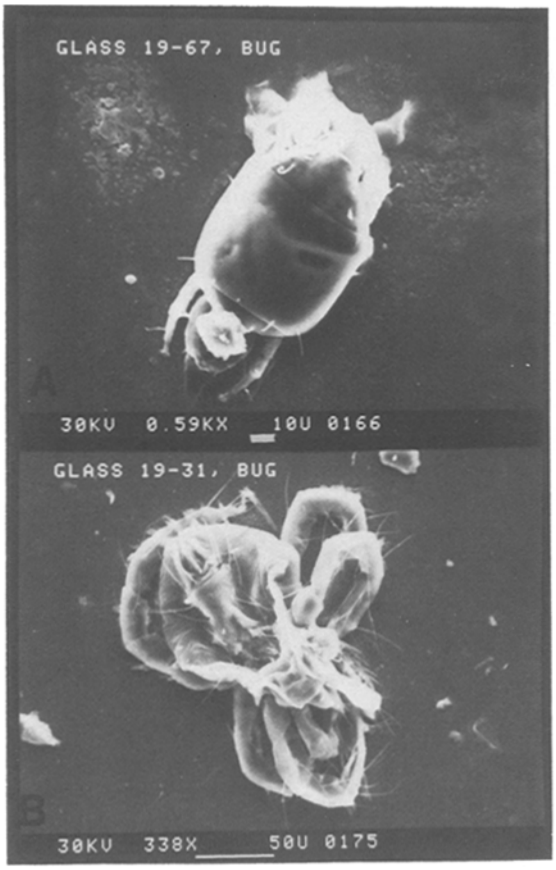

Figure 10 Secondary electron images of arthropods found on the interior surfaces of corroded daguerreotype cover glasses. (A) is a mite. The scale bar is equal to 10 μm. (B) is a book louse. The scale bar is equal to 50 μm.

Two types of arthropods were consistently found in various states of decomposition on the interior surface of these cover glasses. Fig. 10 shows mites (arachnid order *Acarina*) (a) and book lice (*Liposcelis divianatorius* and related genera of *Psocoptera*) (b) as are typically found in these packages. The World War II reports on fungus fouling of lenses also reported finding mites on deteriorated optical glasses [19]. These arthropods were identified using optical and scanning electron microscopy. Phase B in Table II (XRD pattern given in the Appendix) is usually found in conjunction with the arthropods. EDX data for Phase B varies, as indicated in Table II, according to the overall glass chemistry, but this phase is usually high in sodium, potassium, calcium, and sometimes, sulphur.

Although sodium formate is often found on glasses that also have mites or booklice, there is no evidence that the formation of formates is related to arthropods. Some arthropods, such as ants, produce venoms which are largely composed of formic acid. This production of formic acid is not the case with either mites or book lice. Some mites produce aggregation and alarm pheromones which are formate salts of complicated terpines, but it is unlikely that these compounds would produce the amounts of sodium formate during deterioration as is found on some of the cover glasses [58]. In the case of the mite found on Glass 19-67 which produced an X-ray diffraction pattern identified as sodium formate, EDX on the same sample also showed the presence of sodium, calcium, sulphur, potassium, silicon, chlorine, and some copper.

It is unlikely that these arthropods have anything to do with causing or initiating the glass corrosion cycle, however, they do get caught up in the cycle. Mites make up a large portion of house dust and are commonly found pests in stored materials. Mite populations increase with increasing humidity. Book lice, too, are common pests found along with stored organic materials. These arthropods probably come into the package because they are initially attracted to the organic materials, like adhesives, cloth, and wood, in daguerreotype cases and sealing materials. They are further attracted into the package interior by the elevated relative humidity of the daguerreotype package. The silica gels on the inside surface of the cover glasses are very sticky and the arthropods become entrapped. While certain arthropods have been reported to tolerate living environments of up to pH 10, the entomological literature suggests that the intake of extremely alkaline nutrients ($>$ ph 10) causes such extreme cytological distress that the arthropods will not survive [59]. All of the arthropods found on the cover glasses in the sample were dead and had become silicified to some degree. Some had also become nucleation sites for further glass corrosion. There is no evidence to suggest that these small creatures initiate any of the problems associated with the overall deterioration cycle of the entire daguerrian package.

5. Conclusions

Protective cover glasses, because of the way they are placed to preserve objects, undergo very complex deterioration that is a function of both the geometry of the protective package and the composition of the glass itself. The geometry of the package promotes glass corrosion on the inside surface of the glass in preference to outside surface. This phenomenon occurs because there is little or no atmospheric interchange within the cover glass/object package, while there is continual change of the atmosphere outside the package. Water vapour and other atmospheric gases come into the package and react with the various components of the glass surface. In particular, sodium hydroxide is formed by the reaction of soda at the glass surface with water vapour. In the absence of any buffering agents in the glass composition, the surface pH of the glass rises uncontrollably and a self-promoting glass corrosion reaction results.

Corrosion products fall into roughly four groups: amorphous silica gels, crystals derived from these gels, products formed by the interaction of the various glass corrosion materials and the underlying artifact, and other products. These materials were identified and characterized primarily using a combination of optical and scanning electron microscopy, energy dispersive X-ray spectrometry, and X-ray diffraction. Identified crystalline species included sodium sulphate, barium sulphate, ammonium bromide, silver, silver chloride, silver phosphate, sodium formate and cuprite (copper (I) oxide). Recurrent, but unidentified phases were given letter names. Book lice and mites were also found on some glasses, although these arthropods are not invloved in the corrosion cycle for these cover glasses.

As these glasses age, a very hostile environment evolves within the cover glass/object package that can adversely affect the object that the glass is meant to protect. The types of products formed during these corrosion reactions offer indirect verification of the severity of the environment in the cover glass/object package. Corrosion products found on daguerreotypes themselves are often mineral-like species, but not analogues to mineral phases found directly in nature. Likewise, a highly reducing atmosphere is required in order for the formates found on the cover glasses to accumulate. The curious result of the common presence of formates suggests that usual organic hypothesis for their formation is not adequate. More likely, localized reactions in the cover glass/object package cause the catalytic reduction of carbon dioxide from the air, rather than oxidation which would leave carbonates as corrosion products.

This study concentrated on these types of interactions as they apply to protective cover glasses used for daguerreotypes. The same effects were also mentioned as they apply to encased optical lenses and cased painted miniatures. The geometry of these cover glass/object packages promotes glass corrosion, while this severity of corrosion and the types of corrosion products that result are determined by the bulk composition of the glass.

Acknowledgements

This work was supported by the Andrew W. Mellon Foundation.

Appendix: Diffraction patterns for selected phases found on daguerreotype cover glasses

PHASE B

19-31-1 Yellow bug		19-67-2 Yellow waxy spot		19-113-9 Yellow orange spot		19-118-2 Black core		19-118-5 Blisters + phase H		19-118-6 decomposed Bug + Phase H	
d	I	d	I	d	I	d	I	d	I	d	I
9.2	10	9.1	10								
8.3	100	8.3	80	8.35	100	8.35	100	8.35	100	8.4	100
6.5	50	6.55	30	6.50	50	6.55	40	6.50	50	6.55	50
5.25	2	5.3	5								
4.67	90			4.70	40	4.67	20				
4.05	10			4.05	10	4.02	10	4.02	20	4.04	30
3.85	10			3.88	10	3.86	5				
3.74	10										
3.66	5										
3.44	10	3.45	10	3.46	10	3.45	20	3.46	20	3.47	30
		3.35	5			3.35	10				
						3.24	10				
		3.20	50	3.19	5	3.21	5	3.20	10	3.20	30
								3.16	5		
3.09	25	3.09	40							3.09	30
		3.04	2			3.05	5				
2.90	50	2.90	40	2.91	75	2.90	90	2.90	90	2.91	100
										2.88	2
		2.85	10	2.84	50	2.84	10	2.85	5		
2.78	25	2.78	100	2.81	50	2.78	60	2.78	90	2.79	100
		2.72	10								
		2.65	50			2.65	5	2.66	10	2.66	10
2.54	25	2.54	10	2.54	50	2.53	5	2.53	30	2.54	50
						2.47	5	2.48	5	2.48	5
										2.46	5
		2.43	5			2.45	2	2.43	5	2.43	5
						2.40	5	2.40	5		
						2.37	2	2.37	5		
		2.33	40					2.33	5	2.34	10
		2.22	5			2.18	10	2.18	5	2.22	5
2.13	2					2.12	10	2.12	5	2.13	5
2.02	2			2.00	50	2.04	2	2.02	2	2.02	10
										1.96	2
		1.925	5					1.925	2	1.935	3
		1.898	5					1.899	2		
		1.870	50					1.868	20	1.875	20
										1.850	2
		1.808	10								
		1.765									
1.72	10			1.722	10	1.73	10	1.728	5	1.730	5
				1.718	10	1.714	20	1.712	20	1.720	20
1.57	10	1.560	20			1.577	10	1.570	5	1.518	5

Phase E 19-115-2		Phase F 19-118-1		Phase K 19-122-3		Phase R WS-BR-3	
d	I	d	I	d	I	d	I
9.8	100	9.5	5	3.82	10		
8.25	30	8.3	5	2.95	100	4.85	5
6.6	5	3.48	50	2.63	50		
4.68	10	3.33	100	2.29	90	4.32	50
4.30	60	2.93	50	2.02	2	3.90	5
4.08	10	2.93	50	1.97	2	3.46	50
3.85	10	2.80	20	1.92	5		
3.52	10	2.70	20	1.845	5	3.26	100
3.37	60	2.59	20	1.78	5		
3.18	20	2.47	20	1.716	10	3.12	20
3.03	50	2.39	20	1.630	20		
2.95	10	2.33	20	1.598	20	3.01	20
2.88	10	2.05	5	1.53	2	2.85	20
2.78	100	2.03	5				
2.65	20	1.88	5				
2.55	5	1.82	5			2.60	5
2.48	2	1.73	5			2.49	50
2.36	5	1.67	2			2.27	5
2.34	5	1.55	2			2.19	20
2.28	40	1.46	2			2.13	5
2.20	5	1.44	2			2.12	5
2.15	10	1.38	2			2.04	5
2.09	20	1.23	2			1.83	10
2.03	10					1.688	50
1.98	20					1.622	10
1.915	10						
1.865	20						
1.818	5						
1.720	5						
1.680	2						
1.645	2						
1.603	2						
1.552	2						

MOULD-LIKE MASSES

PHASE C

19-26-3		19-113-4 fibrils		WS-BR composite	
d	I	d	I	d	I
8.25	100	8.3	50	7.70	10
6.55	50	6.5	10		
3.43	100	3.19	10	4.40	10
2.91	50	3.08	10	4.30	50
2.89	75	2.90	10		
2.78	20	2.81	10	3.36	100
2.55	20	2.78	10	3.24	10
2.10	50	2.65	10	3.21	10
1.785	20	2.33	10		
1.715	20	2.00	10	3.09	50
		1.86	2		
				2.88	10
				2.80	5
				2.70	2

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