



THIS ISSUE CONTAINS ARTICLES ON:
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CE NUMERO CONTIENT DES ARTICLES SUR:

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1 generalities

1.1 Editorship of the News Letter

There were unexpectedly long delays in the publication of News Letter No.27 and in the preparation of No.28, which will now be the last issue to appear in 1978, and under the general editorship of Professor Roy Newton. At the meeting of the Comité Technique of the Corpus Vitrearum, held in Paris in the middle of June, it was decided that the Editor should be changed annually and that Dr Bruno Mühlethaler, of the Schweizerisches Landesmuseum, Postfach 3263, CH-8031 Zurich -23, should be the general editor in 1979.

It was also decided that, in future years, there should be only two issues of the News Letter per year. The subscription rate for these years has yet to be decided but, assuming that only three issues will appear in 1978 (Nos. 26, 27 and 28) instead of the intended four issues, there will be a credit of 25% of the 1978 subscription for all existing subscribers.

1.2 Projektgruppe "Glas" meeting, held in Bonn on 13 March 1978

Brief mention of this meeting, and of the papers read at the meeting, was made in Section 1.3 of N.L. No.27. The abstracts of these papers are now included as Abstracts Nos 334-339 in Section 7 of this News Letter.

At the meeting it was agreed that the scientific discussions which had taken place during the first (Würzburg, 14th September 1977) meeting had been very fruitful, nevertheless it would be desirable for all concerned that closer contacts should be made with art-historians, restorers and glass technologists during all future meetings (the third meeting is expected to take place in Zürich between 13th and 16th March 1979).

1.3 Silicone adhesives; some second thoughts

In four earlier News Letters there was some discussion of silicone sealants. Those which release acetic acid during their hardening may occasionally attack either the leads (N.L. No.18, Section 3.8) or, apparently, some medieval glass (N.L. No.25, Section 1.5). Oxime-curing sealants were therefore recommended as a replacement (N.L. No.20, Section 1.2; and N.L. No.22,

Section-1.4). Some time has passed since these discussions took place and no more examples of difficulties have been reported. However, it seems that some oxime-curing silicones harden rather slowly, and this can be a distinct disadvantage. All in all, therefore, it seems that the advantages of acetic-acid curing silicones can outweigh the occasional disadvantages.

1.4 Price reduction on certain Corpus Volumes

An important price-concession to Members of the Corpus Vitrearum is set out in Section 6.6.

2 external protective glazing

A general discussion of the scientific aspects of external protective glazing (Aussenschutzverglasung) - by Roy Newton

2.1 INTRODUCTION

Experiments are in progress in various countries (certainly in Austria, Britain and Germany, and no doubt elsewhere also) to test external protective glazing systems. Some of the experiments (such as those on the south-west transept window at Canterbury Cathedral) are concerned with the important problem of the visual appearance of the external window, as seen both from the outside and from the inside, but these aesthetic problems, and also those concerning the width of the space between the windows, will not be discussed here.

We do not yet know enough about the best way to instal such windows, and especially about the best way to ventilate the cavity. Moreover, some of the experimental results appear to lead to opposite conclusions and this article has been written in an attempt to clarify the situation.

The obvious reason for installing an outer window of modern glass is to assist in protecting the medieval stained glass against the corrosive attack by the weather, especially the moisture resulting from rainfall, and from materials such as pigeon dung, lichens and the general dirt in the air. A second reason is to protect the stained glass from damage by stones and other hard objects. A third reason is to

keep the stained glass warmer by protecting it from the very cold air of winter nights. A fourth reason which is put forward in some quarters⁽¹⁾ is that the outer window can reduce the attack on the medieval glass by sulphur dioxide and the oxides of nitrogen, apparently by reacting with those gases (especially if an absorbing medium is introduced), but the evidence for this belief has not yet been published.

There seems to be little doubt that an external window can afford great protection to medieval glass because the glass in the little German church at Lindena has had external protection since 1897 and the protected glass is said to be in a better state than any other 13th century glass in the D.D.R.⁽²⁾

The next question concerns the occurrence of condensation in the cavity, or the entry of driving rain. An ideal situation would involve complete (hermetic) sealing of the space between the two windows, and there have even been suggestions that the space should be filled with a dry inert gas. However, practical experience with cathedral windows has demonstrated that such hermetic sealing is probably impossible. The cement which holds the window in its leads will crack, movements of the stonework occur, and strong winds buffet the outer window so that it becomes leaky. Experiments at York Minster using smoke generators⁽³⁾ have shown that smoke can enter every window tested. Thus it must be assumed that rain will sometimes get into the cavity and hence the space should be ventilated so that moisture in the cavity can dry out. The window at Lindena was not deliberately ventilated but Dr Maercker's report⁽²⁾ shows that enough exchange of air is likely to occur through the cracks which have developed.

If the cavity is ventilated, either to the inside of the building or to the outside air, there will be some occasions when condensation will occur in the space between the glazings (see below). Here it should be pointed out that there is as yet no unambiguous evidence about the effect which repeated condensation may have on medieval stained glass. Until recently it was argued on theoretical grounds that repeated condensation would be particularly damaging to medieval glass; the assumption was that each droplet of water would produce some alkali extraction; the alkali would attack the glass as it became more concentrated when the water dried out; the next occasion for condensation would produce droplets on the same places as before because nucleation would occur there; more alkali would then be extracted, etc. etc. Thus condensation had been feared as being a particularly dangerous source of attack on medieval glass⁽⁴⁾ but recent experimental work has either failed to reveal this expected attack⁽⁵⁾ or has shown that it may be less severe than the attack by high humidity⁽⁶⁾.

However, it should at present be assumed that the presence of condensation is likely to be more harmful than the absence of condensation and external glazing systems should be designed to have as little condensation as possible. Recent arguments have been concerned with whether it is better to ventilate the cavity to the outside air or to the inside of the building, or even to install heating wires in the cavity⁽⁷⁾ but it is first necessary to define the double-window situation more precisely.

2.2 PLACES WHERE CONDENSATION CAN OCCUR

In a doubled window there are four air-glass interfaces to be considered. Counting from the outside they are:-

- Face 1 = the outer face of the external glazing
- Face 2 = the inner face of the external glazing
- Face 3 = the outer face of the medieval glass
- Face 4 = the inner face of the medieval glass

We can ignore Face 1 because it will often be wet, being exposed to rain, fog, snow, etc. and is made of modern glass. Face 4 will no doubt be the one which could suffer most from condensation because it is the one which bears most, or all, of the painted decoration, but it is not actually in the cavity, so the requirements will be somewhat different from Faces 2 and 3.

Face 3 is probably next in importance because it often bears some painted decoration, especially in Austria. Even if there are no trace lines on Face 3 there may well be some matting which could be damaged by condensation.

Face 2 is probably the least important because it consists of modern glass and is consequently more durable; moreover it can be replaced if it does become damaged. The presence of condensation on Face 2 means that there is some water in the cavity, thus increasing the humidity of the air, but the effect of this increase in humidity on the medieval glass is not clear. Here mention should be made of a domestic situation which could cause misunderstandings in the discussion. In domestic double-glazing, if there is a break in the seal towards the inside of the house condensation will form on Face 2 during cold weather. This is a nuisance to the people in the house because it interferes with their view to the outside! Thus, in the home, condensation on Face 2 causes the most trouble but this would not be true in a cathedral (the domestic problem can be solved⁽⁸⁾ by drilling holes from the cavity to the outside air because the outside air generally contains less water than the inside air).

In conclusion, therefore, condensation on Face 4 is the worst case, followed by condensation on Face 3. Such condensation will form when the temperature of the glass falls below the dew point of the air in contact with it. In the case of Face 4 this air is always the air in the cathedral (but see note⁽¹¹⁾). In the case of Face 3 the air under consideration is that which is in the cavity; it may have come from the cathedral (internal ventilation) or it may have come from outside the building (external ventilation); in either case the humidity may have been increased if there is already some condensation on Face 2.

2.3 HUMIDITY AND TEMPERATURE OF THE AIR

It is important to distinguish between the humidity of the air and its water content. The water content of the air is the amount of water actually present, measured either by its weight

(as grams of water per cubic metre of air, e.g. 10g/m^3) or by its vapour pressure in millibars (e.g. 10g/m^3 is equivalent to $13\frac{1}{2}\text{mb}$). The relative humidity (RH) of the air is the ratio of the weight of water which is present, compared with the weight of water which the air could hold at that temperature if it were fully saturated with water. Thus air which contains 10g/m^3 would have a RH value of 100% at 11°C (its dew point); 78% at 15°C ; 57% at 20°C ; and 43% at 25°C . The RH value is the one which is usually quoted but it can be misleading because air outside a building during the winter could have an RH value of 100% at 0°C but its water content would be 5g/m^3 , only half the water content of the air described above which has 57% RH at 20°C . Thus we have the paradox that the outside air can have nearly twice the relative humidity of the air inside the building (and thus seems to be the wetter) yet the inside air would have twice the water content of the outside air (and is actually much better)! The dew points of the two lots of air are: inside air, 11°C ; outside air, 0°C ; hence Face 4 would form condensation if it were cooled to 11°C but an externally-ventilated cavity would not contain any condensation (Faces 2 and 3) unless it were cooled to 0°C .

Thus in this case, and also in general (see (9)), condensation in the cavity is likely to occur less frequently when the cavity is ventilated to the outside. Nevertheless, the important laboratory experiments carried out in Vienna, and reported in Section 3 (pages 6-8 of CV News Letter No.27) led to the opposite conclusion, that condensation occurs more frequently when the ventilation air is taken from outside the building. This unexpected result requires further consideration.

2.4 COMMENTS ON THE AUSTRIAN LABORATORY EXPERIMENTS

In this Austrian work, experiments Nos 1-4 used temperatures for the outside air which were representative of a very cold winter, i.e. -15°C , and these extreme conditions clearly create difficulties because the cold outside air can make the stained glass rather cold. The work at York Minster, using variable apertures on an externally ventilated window, showed that the ventilation openings should be made as small as possible, preferably less than 1mm wide⁽¹⁰⁾. In the Austrian experiment with external ventilation the openings for the air flow consisted of two slots, each 170mm long and 5mm wide, and five holes 6mm in diameter; the resultant air stream passing up the cavity had a velocity of about 25cm/s with the result that the stained glass at the bottom of the window became very cold, for example -1.2°C when the air "in the building" was 20°C , and -8.7°C when the "internal air" was 2.2°C . (All of these temperatures were below the dew point of the "internal air" and hence condensation occurred on this part of Face 4.)

As the air passed up the window, however, it rapidly became warmer so that the stained glass temperatures at the top of the window were of the order of 8 degC warmer than those at the bottom. A slower air stream would certainly have produced relatively less chilling at the bottom of the window; only a guess can at

present be made about the temperature of the glass if the ventilation slots were made very small, but it would probably be reasonable (for purposes of this discussion) to suppose that all the temperatures might at least be as high as those measured at the top of the window. The temperatures at the top were: 9.1°C in Experiment 1, when the "cathedral air" temperature was 20.0°C ; 5.0°C in Experiment 2 ("internal air" = 15.9°C); 1.0°C in Experiment 3 ("inside air" = 9.7°C); and 4.0°C in Experiment 4 ("inside air" = 2.2°C); in all these cases except the last, Face 4 would be above the dew point of the "cathedral air" (4.0°C for Experiments 1-3 and -1.2°C for Experiment 4). (Here I would ask the question whether cathedral services can be held when the air temperature is only 2.2°C , or whether this is too cold for the congregation.)

The second general observation on the Austrian laboratory experiments is that they were not able to reproduce the important effects of solar radiation. At both Canterbury and York, when the sun is shining the temperature of the air in the space between the windows can, not infrequently, exceed 40°C (on 13 occasions at York and 15 occasions at Canterbury, in the 4 months of February-May 1978). But even when the sun is not shining (no sunshine recorded at the weather station) increases of 4 degC to 6 degC are not unusual. All these temperatures would ensure that any condensation at night would be evaporated during the day. Thus there seems to be little risk of condensation on Face 4 during daylight hours and we need to worry only about what occurs during the night.

An extremely interesting feature of the records at present being made at Canterbury and York is the discovery that these massive stone buildings are wrapped in a "skin" of warm air, even during the coldest nights. The air temperatures measured on the sill of a south-facing window (close to the stonework at the point whence the current of air would be drawn for the external ventilation) remain distinctly warmer than the true air temperatures (as measured in a Stevenson Screen in an open field 3km from York Minster). The average increase in temperature (about 100 measurements) has been 3.3 degC although some cases have occurred where the "stonework air" is 6 degC warmer, even in the middle of a cold winter night when the true air temperature has been -7°C .

Presumably the reason for this increase in temperature is that the massive stonework is warmed up during the day by solar radiation (even when the sun is not shining) and it gives up some of its heat again during the night, warming up a thin layer of air which envelops the stonework. However it is not yet understood why the temperature difference is sometimes as high as 6 degC but further study of the data will take into account the solar flux over the previous day (or days); the presence of a "radiation night"; the wind speed, etc. It should also be remarked that these measurements at York Minster were made on the south side and it is not yet known what temperature differences will be found when the recording equipment is transferred to windows on the north side, during the winter of 1978/79.

However, for purposes of the present discussion, I shall use the average temperature increase found at York (3.3 degC) and apply it to the Austrian data. In their Experiment No.4 I have assumed that, if the flow of ventilation air was very slow, the temperature of Face 4 might be -4.0°C; if the temperature of the incoming air were then raised by 3.3 degC (the "stonework effect") the temperature of Face 4 (in a large cathedral) might be as high as -4.0 + 3.3 = -0.7°C, i.e. just above the dew point of the "cathedral air" (-1.2°C). There is, of course, much speculation about my assumptions concerning the effects of a very low flow rate for the air and the "stonework effect" but there is at least a potentially interesting situation to be explored in the next series of studies.

The Austrian workers also found condensation on Face 4 in their Experiments Nos 5-7, when the dew point of the "cathedral air" was about 8.5°C and the temperature of the "outside air" was 0.5°C to 2°C. If the same assumptions are made about the effects of a very slow air stream and the warm stonework, then no condensation would occur on Face 4, except in Experiment No.7, where the outside temperature was 0.5°C and the cathedral air was 9.0°C (with a dew point of 7.7°C), where the temperature of Face 4 might have been 2.8°C + 3.3 = 6.1°C, still 1.6 degC below the dew point.

Some condensation was recorded in Experiments 10-13 when the dew points of the "outside air" were 17-22°C and the "internal air" temperatures were only 10-17°C but these conditions must have been extremely uncomfortable ones, even with a mist inside the "cathedral". I should like to know how often such conditions actually occur.

2.5 CONCLUSIONS

This laboratory experiment has been extremely profitable and stimulating, and I am glad that the MBVA and the Bundesdenkmalamt undertook it, if only because it has helped to clarify my own ideas. It has raised some important questions which will require (and are receiving) fuller consideration in England by some of those who are concerned with the problem.

It seems that Face 2 is likely to have condensation on it more frequently when internal ventilation is used because the dew point of the cathedral air in the winter is nearly always higher than that of the outside air⁽⁹⁾ and this raises the question of what effect this might have on the humidity of the air in the cavity.

Face 4, which is always exposed to the cathedral air (unless, as is not unknown in England⁽¹¹⁾ there is also some internal protective glazing) is somewhat more likely to have condensation on it when external ventilation is used because the glass is likely to be colder when outside air is admitted to the cavity although, at least in England where the winters are generally not severe, this chilling effect may only be about 1.6 degC when the ventilation slots are very narrow⁽¹⁰⁾.

It seems that Face 3 is not likely to have condensation on it during the winter because the glass is almost always warmer than the outside air, and hence will be above its dew point. There will be occasional situations where a "warm front" follows a period of sub-zero weather⁽¹²⁾. The data being collected at Canterbury and York will help to show how often this occurs.

NOTES

- (1) Private communication from J.C. Ferrazzini.
- (2) H.J. Maercker, see Section 3.4 of CVMA News Letter No.7, p.8.
- (3) See CVMA News Letter No.15, Section 2.2, p.7.
- (4) I have been responsible for making a theoretical statement of this kind, without enough evidence, see the third paragraph on page i of "The deterioration and conservation of painted glass; a critical bibliography", British Academy Occasional Papers I (1974).
- (5) See CV News Letter No.22, Section 6, pp.9-10.
- (6) See CV News Letter No.24, Section 4.3, p.10, and No.25, abstract No.268 (end of the abstract, in the middle of col.1, p.10).
- (7) The use of electrically heated wires, strung in the cavity, to prevent condensation occurring has been suggested by G. Frenzel, see CV News Letter No.24, abstract No.251 (col.2 on p.13).
- (8) See the discussion on p.60 of R.M.E. Diamant, The Internal Environment of Dwellings, Hutchinson London (1971).
- (9) R.E. Lacy has calculated the frequency of condensation occurring under four different conditions and his figures are given on p.6 of CVMA News Letter No.7; some data for York Minster are given in CV News Letter No.21, Section 3.2.2; and summarised data for Freiburg Minster are in CV News Letter No.24, Section 4.2.
- (10) This conclusion is based on Table I of CVMA News Letter No.16, Section 2.1.5, p.7.
- (11) For example in Bardwell Church in Suffolk. England, there is internal protective glazing on the East Window.
- (12) See the discussion in CV News Letter No.21, Section 3.2.3 (col.1, on p.7).

2.6 DISKUSSIONSBEITRAG ZUM THEMA AUSSENSCHUTZ-VERGLASUNG VON G. SCHUECKER, P.W. BAUER UND E. BACHER

Prof. R.G. Newton hat 1973 als erster mit theoretischen und experimentellen Untersuchungen über die Wirksamkeit von Aussenschutzverglasungen begonnen und seither dankenswerter Weise auch die Diskussion zu diesem Thema in Gang gehalten. Seine Anregung, zu seinem Beitrag "A general discussion of the scientific aspects of external protective glazing" (2.1-2.5, oben) Stellung zu nehmen, greifen wir gerne auf, um

im Anschluss an den Beitrag "Klimatechnische Versuche" (News Letter No.27, 3.1, Seite 6f.) folgendes festzuhalten:

2.7 Die Aussenschutzverglasung löst nicht das Problem der Konservierung mittelalterlicher Glasmalereien. Sie gewährt ausschliesslich eine erste Hilfe, die uns die Möglichkeit bietet, auf risikoreiche Konservierungsmassnahmen zu verzichten und im Laufe der Zeit vielleicht bessere Methoden zu entwickeln, um den Verfall mittelalterlicher Glasgemälde aufzuhalten. Wir dürfen uns von einer Aussenschutzverglasung nicht mehr erwarten, als sie zu leisten imstande ist, was allerdings nicht hindert, nach den praktikabelsten und wirksamsten Konstruktionssystemen zu suchen.

2.8 Die bisherigen Untersuchungsergebnisse zeigen, dass die verschiedenen Konstruktionssysteme (innenseitige bzw. aussenseitige Belüftung, geringer oder grösserer Abstand und Luftaustausch bzw. Heizung des Zwischenraumes, etc.) verschiedene Vor- und Nachteile besitzen, die es abzuwägen gilt. Die Diskussion dieser Fragen sollte unabhängig von dem Aspekt "to prove a system" das grundsätzliche Problem im Auge behalten.

2.9 Es ist offensichtlich, dass wir über die klimatische Situation mittelalterlicher Glasgemälde im Verband der Architektur noch viel zu wenig wissen, um alle Faktoren, die zur Korrosion beitragen, richtig einzuschätzen. Davon sind naturgemäss auch unsere Vorstellungen über die Wirksamkeit von Schutzverglasungen betroffen. (Die vor kurzem abgeschlossene Restaurierung der Glasgemälde von St. Erhard in der Breitenbau z.B. ergab für die Fenster nord II und süd II einen hochinteressanten, weil verschiedenen Befund des Schadensfalles, über den noch gesondert zu berichten sein wird: Die Fenster an der Nordseite wiesen zwar eine auffällige pulvrige Verwitterungsschicht auf, waren insgesamt aber weit weniger korrodiert als die Fenster an der Südseite, wo der Auflösungsprozess der Substanz weitaus stärker fortgeschritten war. Die Verwitterungsprodukte zeigten nach chemischen Untersuchungen von Dr. Bauer in der Röntgendiffraktionsanalyse dieselbe Zusammensetzung, für das unterschiedliche Ausmass der Korrosion der Aussenseite - an der Innenseite war der Zustand gleichwertig - kommen also nur "klimatische" Ursachen in Betracht, wie stärkerer Regen und Wind an der Nordseite, grössere Temperaturunterschiede an der Südseite, etc.)

2.10 Im Mittelpunkt der Diskussion der Aussenschutzverglasung stand in letzter Zeit immer wieder die Frage, welches Konstruktionssystem die Schutzfunktion am besten erfüllt (aussenseitige oder innenseitige Belüftung, Abstand der Schutzverglasung, Ausmass der Belüftung, etc.)

Dazu ist grundsätzlich festzuhalten: Die Tatsache, dass die mittelalterlichen Glasgemälde an der Aussenseite durchwegs viel stärker verwittert sind als an der Innenseite weist eindeutig in die Richtung, wo die Schutzmassnahme anzusetzen hat. Ursachen und Vorgang, die zum Zerfall der Gläser führen, sind sehr komplexer Natur. Wir wissen über diesen

Prozess zwar in grossen Zügen Bescheid, kennen aber kaum den Anteil der einzelnen Faktoren (Feuchtigkeit, Temperaturunterschiede, SO_2 -Gehalt der Luft, etc.), die dazu beitragen. Aus der bereits erwähnten Tatsache, dass die Korrosion in erster Linie die Aussenseiten der Gläser zerstört hat und die gegen das Innere gerichtete Seite immer viel besser erhalten ist, ergibt sich zwangsläufig, dass die Korrosion in erster Linie durch Angriffe von aussen, durch den Kontakt mit der Aussenluft, eingeleitet und in Gang gehalten wird. Kondensfeuchtigkeit - der die Glasgemälde in situ über all die Jahrhunderte ja auch an der Innenseite ausgesetzt waren - dürfte hier offensichtlich die geringere Rolle gespielt haben. (Auch R.G. Newton kommt in seinem Beitrag zu ähnlichen Überlegungen.) Aus diesem Grund erscheint uns das "Zurückversetzen" der Verglasung ins Kircheninnere mit einer innenseitigen Belüftung als die grundsätzlich zweckmässigere Schutzmassnahme. Auf einer zweiten Ebene der Überlegungen sprechen für dieses System dann auch die Ergebnisse der Untersuchungen der MBVA für diese Variante, da sie die günstigeren klimatischen Bedingungen gewährleistet.

2.11 Zu einigen Punkten in dem Beitrag von R.G. Newton "A general discussion of the scientific aspects of external protective glazing" stellt Dipl.Ing. G. Schuecker noch fest:

2.11.1 Zum Problem der Schlitzgrösse der Schutzverglasung siehe die Stellungnahme vom 10.IV. 1978 Q 3 und C 1.

2.11.2 Auf Seite 4 im Kommentar R.G. Newtons zum Experiment 3 ist ein Lesefehler enthalten: Auch im Versuch 3 der Variante A war die Oberflächentemperatur am oberen Ende der Scheibe -4°C , also unterhalb des "massgebenden Taupunktes" ($T = +3,8^\circ\text{C}$). Siehe auch die Stellungnahme vom 10.IV.1978 zu C 2.

2.11.3 Zum Problem der Sonneneinstrahlung (Seite 4, vorletzter Absatz) siehe ebenso die Stellungnahme vom 10.IV.1978 zu C 2. Es ist klar, dass die Sonneneinstrahlung unter anderem die Gefahr der Kondensatbildung verringert, es wurden bei diesen Experimenten jedoch bewusst Extremsituationen untersucht, mit deren Auftreten auf Grund von Voruntersuchungen in Österreich gerechnet werden muss. Die Sonne ist in unseren Breiten relativ unverlässlich.

Die prinzipielle Möglichkeit, Experimente mit Sonneneinstrahlung durchzuführen, hätte bestanden. Die Speicherwirkung der im allgemeinen beträchtlichen Mauermassen und die damit verbundene Aufwärmung der dardüberstreichenden Luft ist sicher gegeben. Das Ausmass der Aufwärmung wird jedoch sehr unterschiedlich sein und abhängen von: Der Dauer der Kälteperiode, von der Orientierung der Fassade (Ost, West, Nord, Süd), von der Masse des Gebäudes, von der Windgeschwindigkeit, der Tageserwärmung durch Sonneneinstrahlung, der "Laufhöhe" der über das Mauerwerk streichenden Luft (Lage des Fensters über dem Boden), von der Innentemperatur des Kirchenraumes (beheizt oder unbeheizt), etc.

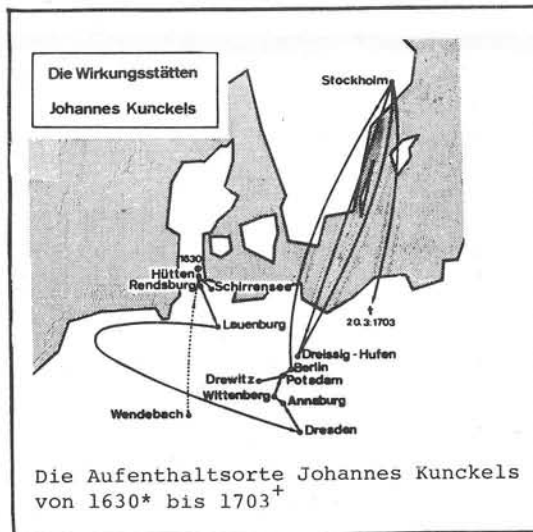
2.11.4 Zum letzten Absatz auf Seite 6 siehe die Stellungnahme vom 10.IV.1978 zu C 2.

3 kunckel gläser

3. VORSCHLAG ZUR THEORETISCHEN ERMITTLUNG DER ZUSAMMENSETZUNG DER GLÄSER VON JOHANNES KUNCKEL (1630-1703) - von J.C. Ferrazzini, Institut für Denkmalpflege der ETH, Zurich.

3.1 Vorwort: Die wichtigsten Lebensdaten und Aufenthaltsorte Johannes Kunckels

Die Familie Johannes Kunckels stammt aus Hessen, wo sie bereits im 15. Jahrhundert ansässig ist. Urkundlich ist festgehalten, dass der Urgrossvater Johannes in Wendebach bei Kassel eine Glashütte betrieb. 1574 wandert der Grossvater nach Hütten bei Rendsburg und eröffnet dort einen neuen Betrieb. Johannes wird 1630 in Hütten geboren, wo sein Vater im grossväterlichen Betrieb arbeitet. Um 1650 verlegt der Vater den Betrieb nach Schirrensee und Johannes geht nach Rendsburg als Lehrling in die dortige Hofapotheke. Rund zehn Jahre später wird dem dreissigjährigen Manne die Verwaltung der Hofapotheke in Lauenburg anvertraut. Es folgen Wanderjahre nach Holland, wo sich Kunckel intensiv mit Glastechnologie und der Kunst der Fajence-Herstellung befasst. Wir vermuten, dass in jener Zeit ein Zusammentreffen Kunckels mit dem italienischen Glasgelehrten Anton Neri stattfand, denn bei der Ankunft Johannes in Dresden, ist ihm die Wissenschaft Neri's bestens vertraut. In Dresden wird Kunckel zum Direktor des Laboratoriums des Kurfürsten Johann Georg II von Sachsen ernannt. Dieses Amt hat der Wissenschaftler von 1670 bis 1675 inne. Hier entdeckt und isoliert er den Phosphor, was ihm etwelchen Ruhm einbringt.



Hofintrigen, welche auf den Neid seiner Zeitgenossen zurückzuführen sind, zwingen Johannes Dresden zu verlassen und seine Wirkungsstätte auf die Annaburg, dem "Goldhaus der Fürstin Anna" zu verlegen. Bei seiner Ankunft 1675 auf der Annaburg beschliesst Kunckel das Buch Neri's "Ars Vitrea" (1612) ins Deutsche zu übersetzen und durch eigene Versuche, Kommentare und Anmerkungen zu ergänzen. Vier Jahre später (1679) erscheint Kunckels Übersetzung in seiner Erstauflage. 1677 hält Johannes an der Universität zu Wittenberg Vorlesungen über Experimentalchemie. Finanzielle Schwierigkeiten zwingen ihn im August 1678 nach Potsdam zu

übersiedeln, wo ihm die Oberleitung der Glashütte auf dem Hackendamm anvertraut wird. Auf wissenschaftlich Untersuchungen fundierend gelingt ihm dort die Herstellung des Goldrubinglases. 1679 wird ihm zudem die Leitung der 1674 gegründeten Glashütte zu Drowitz übergeben. Der Kurfürst und Protektor Kunckels, Johann Georg II, schenkt dem erfolgreichen Wissenschaftler 1685 bei Berlin auf der Pfaueninsel das Kaninchenwerder. Bis 1688 werden auf diesem Grundstück intensive Versuche zur Verbesserung der Herstellungsbedingungen von Goldrubinglas durchgeführt. Doch Friedrich III, der Nachfolger des 1688 verstorbenen Kurfürsten Johannes Georg II, ist Kunckel nicht wohlgesinnt. 1689 muss Johannes sein Haus in Berlin verkaufen. Im September 1692 bis zum 22. Oktober 1692 wird Kunckel im Gefängnis in Spandau eingekerkert. Im Frühjahr 1693 reist Johannes auf Einladung des Königs Karl XI nach Stockholm, wo ihm am 14. August 1693 der Titel "Schwedischer Bergrat" zuerkannt wird. Er wird geadelt und darf sich inskünftig "von Löwenstein" nennen. 1694 nach Deutschland zurückgekehrt, erwirbt Johannes das Rittergut Dreissighufen bei Prenden. Schikanöse Machenschaften aus dem Hof in Berlin zwingen Kunckel sein Domizil 1698 zu verkaufen und 1701 reist der Wissenschaftler zum zweiten Male nach Stockholm. Auf der Rückreise stirbt Johannes Kunckel am 20. März 1703. Sein Begrabungsort ist unbekannt.

Antonii Neri von der Glas Kunst.

57

I. Eine compendieuse Composition und beständiges Crystal-Glas zu machen.

Nimm schönen Sand oder Kiesel, aufs best und reinste pulverisirt 150. Pfund, wehlgeriebtete Petrasche, 100. Pfund, Kreide 20. Pfund, guten Braunstein 10. Peth. Dieses alles nach oben erwähnten Interdict wohl untereinander gemischt und abgeschmecken, gibt ein Glas, so schön als wohl mit zehnfacher Mühe der Autor gemacht haben.

Soar trägt sich auch hier mehrmalen zu, daß das Glas neblig oder dunkel aus dem Feuer kommt, die Ursach davon ist zuweilen die Kreide, zuweilen aber die Petrasche, nachdem nemlich solche gereinigt, oder nachdem sie von einer Art Holz gebrandt worden; wann aber solches geschicht, so wird es nur aus und ins Wasser geschöpft, wie oben bemeldt; so man es denn wieder schmelzt, wird es sehr schön; doch geschicht auch wohl, daß der Nebel zum ersten mal nicht davon will, alsdenn muß mans nur noch einmal ausschöpfen und wieder schmelzen; wann die Petrasche wohl und gebühlich gereinigt, wird dieses selten vornehmlich seyn: Wann man sie aber so rohe nimmt, wird man es fast allemal thun müssen.

Beispiel eines von Kunckel übersetzten Rezeptes von A. Neri.

3.2 Publikationen von Johannes Kunckel:

- Ars Vitrea (1679, 1689, 1743, 1756) (Vier Auflagen)
- Nützliche Observationes oder Bemerkungen von den fixen und flüchtigen Salzen Auro et Argento potable, Spiritus mundi und dergleichen (1676)
- Chymische Anmerkungen darin gehandelt wird von den Principiis chymicis ... (1677)
- Oeffentliche Zuschrift von dem Phosphoro mirabili und dessen leuchtenden Wunderpillen (1678) (Diese Veröffentlichung zeugt vom pharmazeutischen Interesse des Autors).
- Epistola contra Spiritum vini sine acido (1681)
- Proberstein de Acido et Urinoso, Sale salido et frigido (1685)
- Collegium physico-chymicum experimentale seu Laboratorium chymicum (1716) (post humen)

3.4. Folgende Annahmen wurden für die Berechnungen der Glaszusammensetzung aus den Herstellungsvorschriften getroffen:

3.4.1 Umrechnungsfaktoren als Folge chemischer Reaktionen:

Kunckels Beimengung	Zschimmers Reinheit	Annahmen Faktor	Ferrazzinis Reinheit	Annahmen Faktor
Sand, Kiesel Flintstein	100% SiO ₂	1,0 SiO ₂	100% SiO ₂	1,000 SiO ₂
Pottasche	85% K ₂ CO ₃	0,6 K ₂ O	75% K ₂ CO ₃ 15% K ₂ SO ₄	0,538 K ₂ O
Salpeter	-	0,4 Na ₂ O	95% KNO ₃	0,445 K ₂ O
Kreide	90% CaCO ₃	0,5 CaO	96% CaCO ₃	0,538 CaO
Knochenasche	100% "Knochenasche"		80% Ca ₂ PO ₄ ₃ 6,6% CaCO ₃ 0,5% CaF ₂ 1,4% Mg ₃ PO ₄ ₃	0,485 CaO 0,373 P ₂ O ₅ 0,007 MgO
Braunstein	100% Mn ₂ O ₃	1,0 Mn ₂ O ₃	100% MnO ₂	1,000 MnO ₂
Borax	100% Na ₂ B ₄ O ₇ · 10 H ₂ O	0,4 B ₂ O ₃ 0,2 Na ₂ O	52,7% Na ₂ B ₄ O ₇	0,347 B ₂ O ₃ 0,154 Na ₂ O
Arsenik	100% As ₂ O ₃	1,0 As ₂ O ₃	95% As ₂ O ₃	0,665 As ₂ O ₃ *
Weinsteinsalz	-	-	100% KOOC-(CHOH) ₂ -COOH	0,250 K ₂ O

*) 10% Sublimationsverlust während des Schmelzvorganges

3.4.2 Normierung der berechneten prozentualen Zusammensetzung:

Zschimmer normiert die Summe der berechneten Komponenten auf 100%. Wir haben die Summe des SiO₂-, K₂O- und CaO-Gehalts auf 89,13% normiert. Die verbleibenden 10,87% sind ein berechneter Durchschnittswert für sämtliche restlichen Oxide des Glases. Für diese Berechnung basierten wir auf die Summe der SiO₂-, K₂O- und CaO-Konzentrationen von 117 analysierten, mittelalterlichen Waldgläsern. Diese Beträge erfüllen die Bedingungen für die Normalverteilung. Der arithmetische Mittelwert beträgt 89,13 die Standardabweichung 3,75.

Für die "Borosilikat"-Gläser von Kunckel dienten andere analysierte Gläser zur Berechnung der Referenzwerte. Hier betragen die Parameter der Gausschen Verteilung $\bar{x} = 93,33$ Gew.%, $s = 3,82$ für die Summe der SiO₂, K₂O, Na₂O-, B₂O₃- und As₂O₃-Konzentrationen.

3.4.3 Mathematische Ermittlung der Zusammensetzung der "Kunckel-Gläser":

Rezeptur aus der 3. Auflage der ARS VITRARIA von Kunckel		Berechnung durch	
		Zschimmer	Ferrazzini
1. Rezept auf Seite 55			
60 Pf. Sand oder Kiesel	SiO ₂	69,4	61,91
40 Pf. Pottasche	K ₂ O	27,7	24,44
5 Pf. Kreide	CaO	2,9	2,78
2. Rezept auf Seite 55			
60 Pf. Sand oder Kiesel	SiO ₂	64,9	59,19
45 bis 50 Pf. Pottasche*	K ₂ O	32,4	27,29
5 Pf. Kreide	CaO	2,7	2,65
*) Zschimmers Berechnungen basieren auf die Zugabe von 50 Pf. Pottasche, Ferrazzini rechnet mit 47,5 Pf. Pottasche. .			

*) Zschimmers Berechnungen basieren auf die Zugabe von 50 Pf. Pottasche, Ferrazzini rechnet mit 47,5 Pf. Pottasche.

Rezeptur aus der 3. Auflage der ARS VITRARIA von Kunckel		Berechnung durch	
		Zschimmer	Ferrazzini
1. Rezept auf Seite 57			
50 Pf. Sand oder Kiesel	SiO ₂	60,16	60,78
100 Pf. Pottasche	K ₂ O	27,20	23,99
20 Pf. Kreide	CaO	4,50	4,36
10 Lot Braunstein*	Mn ₂ O ₃	0,14	MnO ₂ 0,13
*) Ferrazzini rechnet hier mit einem Pfund gleich 32 Lot.			
2. Rezept auf Seite 57			
60 Pf. Sand oder Kisling	SiO ₂	63,9	60,38
40 Pf. Pottasche	K ₂ O	25,5	23,84
10 Pf. Knochenasche	Knochen- asche	10,6	CaO 4,91 MgO 0,07 P ₂ O ₅ 3,76

Rezept für a) milchweisses und b) opales Glas auf Seite 58 der 3. Auflage der ARS VITRARIA von Johannes Kunckel			Berechnung durch			
a)	b)			Zschimmer a) b)	Ferrazzini a) b)	
130 Pf.	130 Pf.	Kisling oder Flintstein	SiO ₂	67,7 68,6	69,56	68,18
			K ₂ O	3,7 3,8	18,26	17,90
70 Pf.	70 Pf.	Salpeter	CaO	- -	1,31	3,05
12 Pf.	12 Pf.	Borax	Na ₂ O	15,7 16,1	0,99	0,97
12 Pf.	12 Pf.	Weinsteinsalz	B ₂ O ₃	2,5 2,5	2,22	2,18
5 Pf.	5 Pf.	Arsenik	As ₂ O ₃	2,6 2,6	1,77	1,74
5 Pf.	12 Pf.	Knochenasche	Knochen- asche	7,8 6,4	- -	- -
			MgO	- -	0,18	0,42
			P ₂ O ₅	- -	1,00	2,35

4 Rezepte für "Borosilikat- Gläser" auf Seite 186 der 3. Auflage der ARS VITRARIA von Johannes Kunckel		Glas-Nr.				
		I	II	III	IV	
Flintstein		3	3	2	6 1/2	Teile
Salpeter		2	2	-	2 1/4	Teile
a) Pottasche oder b) Weinstein		-	-	1	1	Teil
Borax		1	1/4	1/2	1/8	Teil
Arsenik		1/2	-	-	1/8	Teil

	Berechnung Zschimmer				durch Ferrazzini				
	I	II	III	IV	I	II	III a	III b	IV
SiO ₂	61,2	76,0	69,0	79,3	58,95	69,76	65,67	74,50	76,57
K ₂ O	-	-	20,7	7,3	17,66	20,68	19,44	9,41	14,71
Na ₂ O	20,4	21,5	3,4	11,2	3,38	0,88	2,53	2,90	1,41
B ₂ O ₃	8,2	2,5	6,9	0,6	6,81	2,01	5,69	6,52	0,50
As ₂ O ₃ *	10,2	-	-	1,6	6,53	-	-	-	0,14

*) Zschimmers Berechnungen basieren auf As₂O₅

4 polychromatic glass

The Corning glass company has recently publicised an important new glass, one which can "photographically" be made to assume any colour from the spectrum (or even any pattern of colours) in a permanent manner.

This development may provide a future means of replacing pieces of stained glass with a desired non-uniform colour of glass, or (if the colour-range can be improved) perhaps even of "copying" medieval panels so that the originals may be placed in a safe place in a museum.

The glass is given its colour by first exposing it to ultraviolet (UV) light, then giving it a heat treatment, following that with another UV exposure and then another heat treatment. Thus the technique is far from simple, and it is even possible that it may never come within the reach of the craftsman, but the new development is so interesting that everyone should know what has been achieved even though there may be difficulties in using it.

In addition, the coloured design can be developed within the thickness of a lump of glass, so that the glass-artist may find that he has an exciting new procedure available to him.

At the moment little scientific information has been published, but a detailed paper, by S.D. Stookey, G.H. Beall and J.E. Pierson, has been submitted for publication in the *Journal of Applied Physics* and its appearance will be awaited with interest, especially if it gives more details about the composition of the glass, its treatment and, above all, its durability - will it survive exposure to the elements for more than 800 years?

In the meantime this note, prepared by Roy Newton, summarises some of the information which has been made available, i.e. in the following "documents":

- (1) "Polychromatic Glass", an illustrated folder of information, produced in full colours, available from Mr Archer N. Martin, of the Corporate Communications Division, Corning Glass Works, Corning, New York 14830, U.S.A.
- (2) "Full-colour Photosensitive Glass", being Report L-1986, available from Dr Pascal A. Joly, Manager, Product Engineering and Development, Sovirel, 77167 Bagneux-sur-Loing, France.
- (3) "Microstructure of glass ceramics and photosensitive glasses" by G.H. Beall, *Glass Technology*, 1978 19 109-113 (Polyphotochromic glasses are discussed on pp.111-3).
- (4) A sample of polychromatic glass, bearing the words "Polychromatic Glass" produced in a range of colours and the word "CORNING" produced in a two-colour line-pattern, the red lines being 0.05mm wide and the green ones 0.1mm wide; thus the "photographic colour resolution" of the glass is excellent. There is a good range of strong colours but (in my sample, at least) there is not a "good" red; the "y" is a purplish red and the "1" is an orange-red. The

sample can be obtained free of charge from Mr Benjamin J. Garbowski, Marketing Development Specialist, at Corning (address given in (1) above).

The new glass is said to be a sodium, zinc alumino-silicate, containing 1-5% of fluorine, together with another halide (chlorine, bromine or iodine) and traces of silver (100 p.p.m.), cerium, tin and antimony, as sensitizers. Being a true glass, it can be formed into various shapes using any of the conventional glass-forming techniques.

The first exposure to UV light is given at a wavelength of 300 nm. The length of this exposure is said to determine the colour which will eventually be produced; examples are given where a 10-second exposure leads to a green colour; 30 seconds to a blue colour; and 105 seconds gives a red-orange. Thus the production of a full colour-pattern would seem to require a complicated procedure for giving different lengths of UV exposure to different parts of the glass, but graduations in one colour would presumably be easier to obtain. The exposed glass is then heated for 1 hour at 450°C which produces a photographic image containing photo-nucleated silver particles, and a further heating is given at 500-550°C to grow sodium fluoride crystals upon these nuclei.

A second exposure to UV light is then given, and this one determines the intensity of the colours, and a second heat-treatment (this time at 300-410°C) develops the desired colour pattern.

The "optical" mechanism for producing the colour is interesting because the particles of silver are described as being "sub-colloidal" and too small to scatter light. The colours are therefore due to selective absorption of light by randomly orientated particles, containing some silver, and having controlled anisotropic shapes. The speck of silver is only 50 nm long and the particle of sodium fluoride (having the silver at its tip) is in the shape of a long narrow pyramid, less than 0.25µm (less than 250 nm) long.

The colours are stable up to 400°C and hence it would not be possible to "fire" a painted design on to glass which had already been "coloured"; there is no information as to whether the coloured design could be developed in polychromatic glass which had already had a trace-line fired on to it.

5 recent british work

5.1 Studies of the simulated medieval glasses

Ten simulated medieval glasses were made by Pilkington Brothers, with a Grant from the Nuffield Foundation as part of the European Science Foundation programme of research into the conservation of medieval stained glass (see News Letter No.25, pages 3-5). These were made up into sets of 10 glasses and about 20 such sets have already been distributed in the UK and the USA. Workers in France and Northern Europe can obtain sets of these glasses from Ir. J.M. Bettembourg, Laboratoire de Recherche des Monuments Historiques, Château de Champs-sur-Marne, 77420 Champs-sur-Marne, France. Workers in Germany, Austria, Switzerland, and Southern Europe, can obtain sets from Dr J.C. Ferrazzini, Institut für Denkmalpflege, CH-8092, Zürich, Switzerland.

5.1.1 Chemical analyses

Although sets of samples have been sent to many laboratories, only two have yet supplied information about the results of their chemical analyses. The weight-percentage figures are given in the tables below and, in order to maintain anonymity, the laboratories have been labelled A and B. Neither laboratory analysed all the oxides present in the glass. For example, Laboratory B did not determine the silica or the alumina, and hence their

totals are always much less than 100%, ranging from 34.5% to 53.7% (see Table 2). Laboratory A carried out computer-processing of their analytical results and, in order to do this, they assumed as correct the values obtained by Pilkington Brothers for MgO, TiO₂, MnO, CuO, ZnO and PbO, but values for P₂O₅ seem to have been ignored entirely. Thus the totals for this laboratory range from 90.8% to 98.5% (see Table 1).

When these results are compared with those from Pilkington Brothers (see Table IV on page 5 of N.L. No.25) it will be seen that the CaO figures from Laboratory A are always smaller than those from Pilkingtons, the average difference being 0.81 (3.3% of the mean value) and this is believed to indicate that there is something unsatisfactory about the values for lime from Laboratory A (because Laboratory B agreed with Pilkingtons whereas A was always smaller)

5.1.2 Other scientific work on the simulated medieval glasses

Two laboratories have reported the results of scientific studies made on these simulated medieval glasses. The Physics Department of the University of York have carried out Auger Electron Spectroscopy (AES) on glass No.144, see Abstract No.340 in Section 7. The Materials Engineering Department of the University of Florida has carried out Infra-red Reflection Spectroscopy (IRRS) on glasses Nos. 145 and 147, see Abstract No.342, in Section 7.

Table 1. LABORATORY "A"

Code numbers of the simulated glasses

Oxide	144	145	147	148	149	150	151*	159	77/33
SiO ₂	43.7	41.5	48.1	53.4	57.0	55.8	56.0	43.8	49.0
Na ₂ O	0.08	0.10	0.04	0.04	0.05	9.4	4.8	0.05	20.8
K ₂ O	29.0	24.6	14.6	14.7	14.5	1.5	7.4	14.2	0.06
CaO	19.8	28.1	29.0	25.2	20.6	21.5	18.5	33.9	22.0
Al ₂ O ₃	3.7	3.8	3.9	4.0	3.9	4.3	3.8	4.0	4.2
Fe ₂ O ₃	2.2	0.04	0.03	0.38	0.03	0.28	0.29	0.14	2.4
Totals	98.5	98.1	95.7	97.7	96.1	92.8	90.8	96.1	98.5

*Sample No.158 was not tested because its durability was too low to allow its surface to be sputtered satisfactorily

Table 2. LABORATORY "B"

Code numbers of the simulated glasses

Oxide	144	145	147	148	149	150	151	158	159	77/33
Na ₂ O	0.1	-	0.1	0.1	0.1	8.1	3.7	-	-	22.2
K ₂ O	30.0	24.2	15.2	14.6	14.6	1.6	6.9	23.2	13.9	-
MgO	0.04	0.06	0.06	0.07	-	6.5	3.0	0.10	0.08	0.06
CaO	20.6	29.2	30.2	26.0	21.2	22.4	19.9	28.8	34.0	22.8
Fe ₂ O ₃	2.4	-	-	0.4	-	0.7	0.4	-	0.1	2.8
MnO	0.03	0.1	-	0.2	1.4	-	0.3	0.1	0.6	0.04
CoO	-	-	-	-	0.25	0.09	-	-	-	-
NiO	-	0.1	-	0.08	-	-	-	0.1	-	-
CuO	-	-	1.8	0.08	0.82	-	0.1	-	0.5	-
Totals	53.2	53.7	47.4	41.5	38.4	39.4	34.3	52.3	49.2	47.9

- = too small to determine

Many durability tests on all ten glasses have been carried out in the Department of Ceramics, Glasses and Polymers of the University of Sheffield, but the results have not yet been published.

5.2 Climatic monitoring in cathedrals

The recording equipment has now been moved to a north-facing window in York Minster (the north window of the Chapter House; window No.56 in the Minster series; window NIII, Chapter House, in the Corpus numbering) and air taken from close to the stonework is still warmer than the air 250mm from the Minster wall by an average of 1.7 degC, even during the night, and warmer than the air in an open field 3km to the east, where the meteorological station is sited, by about 3.5 degC. Thus the unexpectedly high temperature of the "external ventilation air", found for south-facing windows and reported in Section 2.4 above, is found also on north-facing windows! It will be interesting to see what happens on a cold winter's night.

5.3 The Ballidon burial experiment

As part of a long-term "durability" experiment in an alkaline environment, samples of nine different glasses (including simulated Roman, and medieval glasses) were buried in a limestone mound at Ballidon, in Derbyshire, in 1970 (see J.Glass Studies, 1972, 14, 149-151). Samples were removed after 1 and 2 years, and those which had been buried for 8 years were recovered on 1st November 1978.

Of the nine types of glass which had been buried in an alkaline soil (pH=9.1) for eight years, two modern, highly-durable, glasses seemed on visual inspection to be quite unaltered ("E-glass" and "Pyrex"). Occasional iridescent spots, 1mm diameter, had appeared on the simulated Roman glass. Some slight iridescence had appeared on plate glass which had been ground and polished, and on some soda-lime optical glass (70.1% SiO₂, 9.5% CaO, 10.6% Na₂O, 5.1% K₂O, etc.) but there was more iridescence on the plate glass samples which had been buried in the "as produced" condition. This is interesting because it suggests that the improved durability of a flame-finished surface does not last for more than eight years in an alkaline environment.

There was easily-noticeable iridescence on two samples, a lead-optical glass (54.2% SiO₂, 33.6% PbO, 8.0% Na₂O, 4.1% K₂O, etc.) and a simulated medieval glass (50.1% SiO₂, 18.6% CaO, 16.7% K₂O, 4.3% Al₂O₃, etc.).

The sample which was in much the worst condition was the simulated poorly-durable medieval glass (46.5% SiO₂, 21.6% CaO, 16.4% K₂O, 4.6% P₂O₅, etc.), where the flame-finished surfaces showed marked crazing. Samples have been sent to Professor Hench, so that he can carry out tests similar to those described in Abstract No. 342, in Section 7.

The next opening of the burial mound is expected to take place in 1986, if we can arrange for someone to remember to do it! The one after that is due in the year 2002, but no plans have yet been made for that excavation.

6 book reviews

6.1 Glas: Natur, Struktur und Eigenschaften by H. Scholze, 2nd Edition, 342 pp., Springer-Verlag (1977). DM98, US\$45.10.

This second edition of Professor Scholze's book, on the nature, structure and properties of glass, has been completely revised from the 1964 edition. Many recent developments are discussed such as the important one of phase separation which is now realised to occur more widely than had previously been thought. In fact the whole section on structure (the first 122 pages) provides a good insight into why the properties of glass can seem so variable, and almost elusive, to those who encounter them for the first time.

The properties of glasses are discussed in nine sections (the remaining 220 pages): viscosity, thermal expansion, density, chemical durability, surface tension, and optical-, mechanical-, electrical- and thermal-properties. In each of these sections there are sub-sections on methods of measuring the property, its dependence on temperature and on the composition of the glass (and there are usually useful sub-sections on methods of calculating that property of the glass from the chemical composition).

There are about 200 clearly-drawn diagrams (161 numbered diagrams, many of which consist

of two parts) and nearly 900 references. It is, in fact, an important encyclopaedic book on glass to have on your shelves. (Review by Roy Newton).

6.2 Readings in Glass History, No.8, by Anita Engle, 87pp, Phoenix Publications Jerusalem (1977); Price \$7.00 for individuals.

This book is devoted to a summary of the attempts to unravel the inter-relationships between the English glassmaking families in the Elizabethan period. The basis for English glassmaking in the sixteenth century lay in the large numbers of skilled workers who came to England as refugees in the second and third decades of the reign of Elizabeth I. The manufacture of window glass was established by immigrant glassmakers from Normandy and Lorraine, and that of crystal glass (*facon de Venise*) by Italian craftsmen, but it is paradoxical that little is known of Jean Carre of Arras and Jacob Verzelini. This book has chapters about each of these gentlemen (No.1 about Carre and Nos. 3-5 about Verzelini) and there are Appendices with copies of their wills, and other relevant documents such as the "Contract by Aliens to Introduce Glassmaking" (1568), etc. The other chapters in the book are about related families. (Review by Roy Newton).

- 6.3 Readings in Glass History, No.9, by Anita Engle, 73pp., Phoenix Publications, Jerusalem (1977), price \$7.00 for individuals.

This book is described as an "Index to Nos.1-8" but it is much more than that, being a useful reference book in its own right. First, there is a seven-page summary of the first 8 issues, followed by a 17-page general index to those volumes. Next (Chapter 3) is a seven-page special index of all the references to "glass" itself under 29 headings, such as "glass artefacts", "glassmaking centres", "glassmaking tools", etc. Chapter 4 is a 13-page "Register of Glassmakers and Glassmaking Families" (with dates), for example from Ennion (1st century BC) to Richard Ensell in 1833 (to choose almost consecutive entries in one column); this chapter contains 550 names. Chapter 5 is a bibliography in its own right as well as being an author-index to the other volumes; it consists of 29 pages and contains about 1200 entries. In all, the book is an invaluable one for the glass historian. (Review by Roy Newton).

- 6.4 Gotische Glasmalerei in der Steiermark by E. Bacher, in Ausstellungskatalog Gotik in der Steiermark, Stift St. Lambrecht, 1978, pp.151-171.

The exhibition "Gothic art in Styria" (the south-east province of Austria) contained 28 stained glass panels from the late 13th century to the middle of the 15th century. Panels were taken from museums (Landesmuseum Joanneum Graz; Osterr.Museum für angewandte Kunst, Wien, and others were taken from those churches where the Bundesdenkmalamt had installed external protective glazing during the last few years, thus making it much easier to remove panels. The illustrated catalogue of the exhibition contains art-historical information about the different panels, together with a comprehensive survey of Gothic stained glass in Styria. (Review by E. Bacher).

- 6.5 The Museum Environment by Garry Thomson, Butterworths (London) 1978. ISBN 0 408 70792 5 £16.00. US\$32.00.

This book of 270 pages is the first of a series to be published by Butterworths on Conservation in the Arts, Archaeology and Architecture. It is divided into two parts: Part I (pp.2-154) being written for conservators and museum curators to explain how light, humidity and air pollution can damage the exhibits in a museum, and how to reduce any damage to the minimum. Part II (pp.156-246) deals with the same three harmful agents but in a much more technical manner; it is written for the benefit of research workers and gives the scientific background to the statements made in Part I.

Only a very small part of the book deals directly with stained glass windows; nevertheless there is much in the book which is of great importance to those who want to conserve stained glass and who wish to control the possibly harmful agencies (condensation and air pollution) and to reduce their effect on the windows.

Much attention is given to the effects of light on museum exhibits (104 pages, 61 in Part I and 43 in Part II) because it can be so harmful to paintings, textiles, leather, feathers etc.

Although light is not directly harmful to stained glass (except for producing some solarisation) this chapter is nevertheless of great interest to those who want to measure the colour values in stained glass windows (pp.53-8 and 187-198). A few years ago there was some feeling in the Corpus Vitrearum that ultraviolet light should be excluded from windows, but anxiety here seems now to have diminished; however, if anyone wishes to measure the amount of UV radiation falling on his windows, and to remove it, pp.16-21 tell him how to do it.

Humidity (85 pages, 58 in Part I and 27 in Part II) and condensed moisture can certainly be damaging to medieval windows and this book gives a good account of how the relative humidity alters with temperature, whereas the water content of the air does not (pp.64-79). For anyone who wants to make measurements of the humidity, there is much helpful advice including a hygrometric table (pp.72-73) and several hygrometric charts (pp.76-80 and 213-222). The permeation of water vapour through resin films is discussed (pp.223-6) and there are maps which show how the annual humidity values are affected by climate (pp.87-90).

Air pollution (53 pages, 31 in Part I and 22 in Part II) is discussed and figures are given for the pollution levels in various towns in Europe (pp.126-132) but most of these sections (Parts I and II) are devoted to the damage which occurs to stonework (pp.133-154); in addition to the photographs showing how buildings deteriorate there is one (Fig.56, p.137) which shows how a book can be damaged by air pollution.

I was very glad to see that mention is made (p.148) of the damage which can be caused to the leading of windows by organic acids (especially acetic acid) released into the atmosphere by unseasoned oak.

There is a good general index and 260 references to the literature, but it is a pity that these are not in alphabetical order, nor is there an author index; thus it is not easy to locate in the text the results of a particular author's work. (Review prepared by Roy Newton).

6.6 Corpus Volumes at reduced prices

This is an important notice to all Members of the Corpus Vitrearum. The publishing house in Vienna, Verlag Hermann Böhlaus Nachfg., Ges.m.b.H., A-1061, Wien, Postfach 167, has kindly offered a special discount to all Members of the Corpus Vitrearum, on the retail price of CVMA Volumes published by them.

(1) A reduction in price of 20% is offered for the following volumes:

E. Frodl-Kraft "Die mittelalterlichen Glasgemälde in Wien", Wien (1962). The retail price is 1 278 Austrian Schillings, or DM188. (It should be noted that the Volume on Vienna, of which only a very few copies remain, can be offered only at the full retail price.)

E. Frodl-Kraft "Die mittelalterlichen Glasgemälde Niederösterreichs. 1. Teil, Albrechtsberg bis Klosterneuburg", Wien (1973). The retail price is S.1678, or DM248.

E. Bacher "Die mittelalterlichen Glasgemälde der Steiermark, 1. Teil, Graz und Strassengel" Wien (1978). The retail price will be about S.1650, or DM. about 240.

(2) In a similar manner, a price reduction of 30% is offered on the following two CVMA Volumes if they are obtained through Verlag Böhlaus:

Frantisek Matous "Mittelalterliche Glasmalerei in der Tschechoslowakei", Prag (1975)

Erhard Drachenberg, K.J. Maerker, and Christa Schmidt "Die mittelalterlichen Glasgemälde in der Ordenskirchen und im Angermuseum zu Erfurt", Berlin (1976).

The retail price of these two volumes is, for the time being, S1420, or about DM205.

In all cases, where appropriate, the costs of packing and postage must be added.

The entire Membership of the Corpus Vitrearum, throughout the world, is entitled to benefit from these reductions, and orders must therefore be placed through the Austrian Institute for Care of Monuments, their address being:

Institut für Österreichische Kunstforschung
des Bundesdenkmalamtes, A-1010 Wien, Hofburg,
Austria.

7 abstracts

The first six abstracts (Nos. 334-339) are of papers presented to the Second Meeting of Projektgruppe "Glas", held in Bonn on 13th March 1978, see Section 1.2 of this News Letter, and also Section 1.3 of News Letter No.27.

334. FERRAZZINI, J.C. (1978) "Vorschlag zur theoretischen Ermittlung der Zusammensetzung der Gläser von Johannes Kunckel (1630-1703)" (Suggestion for the theoretical investigation of the compositions of Johannes Kunckel's glasses (1630-1703)).

Johannes Kunckel set out numerous recipes for making glass, in his book Ars Vitrea but so far only E. Zschimmer has dealt with the problem of the actual compositions of the Kunckel glasses in his article Der Goldrubin (Sprechsaal 63 (1930) 642-644).

Ferrazzini found that assumptions had been made which could usefully be reconsidered. Thus the addition of bone ash mentioned by Kunckel ought to be distinct from the addition of lime, phosphorus and magnesia. As far as arsenic is concerned, consideration must be given to the purity of the added material and its volatility from the melt. There are also doubts as to whether Kunckel really used sodium nitrate and not potassium nitrate.

A first step in the mathematical study of Kunckel's recipes for glass batches is to standardise the sum of the main ingredients at some average value. A study of 117 analyses of medieval "forest-type" glasses shows that 89.13% by weight is made up from silica, lime, and potash. All the remaining oxides are represented in the balance of 10.87% by weight.

These values from the 117 analyses are normally distributed with a standard deviation of 3.75%. Medieval glasses would form an appropriate basis for the calculation of Kunckel's "calcium-free borosilicate".

The results of this work were presented to the meeting in pictorial form and it was remarkable that the silica content was so high, from 60 to 75% by weight, the potash content was 15 to 30% by weight but the lime content was remarkably low, being always less than 5%.

In the discussion, in which Drs Heimann, Hierl, Scholze and Schulze participated, it was pointed out that these glass compositions would sometimes have produced glasses having very poor durability. By limiting the basis for the calculations strictly to "Kunckel glasses" it is probable that a more significant result might be expected. As regards the statistical distribution of the compositions of the forest-type glasses, it was "normal" according to all the statistical criteria, and the double-maxima, which could be seen in some of the histograms, could have arisen accidentally as a result of the grouping chosen. (See also Section 3 above.)

335. NAUER, G. and KNY, E. (1978) "Zur numerischen Klassifikation römischer Gläser aufgrund ihrer Elementgehalte" (A numerical system for classifying Roman glasses on the basis of their chemical composition.)

The successful application of methods of numerical classification depends on the availability of a significant selection of samples. For this purpose, 177 samples of glass from the 1st and 2nd centuries A.D. were available from Regensburg, together with 74 blue glasses of the 1st century A.D., but from various places.

As the basis for the numerical classification, the contents of 17 (or 14) chemical elements were determined spectrographically and the values were used in heirarchical and non-heirarchical cluster programs in the FORTRAN system MINT (M/ni-NTsys) and the program K-Means in a version specially adapted for the actual problem. The data-matrix for the initial entries was standardised before being used for the classification procedures.

An essential conclusion of the results from the Regensburg glasses was that they could be divided into two groups which differed significantly in their contents of additive materials (manganese and antimony), one group being attributable to the military precinct whereas the other group, and its three sub-groups, were characteristically from civil areas.

Among the blue glasses, the existence of a "standard glass" could be discerned whereby two regional production centres could be distinguished, one around Krain and the other around Turin. On the other hand it was found that glasses which were chemically closely related could be distributed over wide distances geographically, perhaps because they had been articles of trade, either as cullet or as finished articles. Small groups showed high contents of trace elements in which they deviated distinctly from the formula of the standard glass.

Cobalt was predominant as the colouring element and the variable concentrations of the accompanying elements suggest that different ore deposits had been used. Further investigations which are in progress are concerned with the Regensburg glasses and with closely-dated Egyptian glasses.

In the discussion, in which Drs Camara and Schulze participated, it was pointed out that the "clear glasses" had a light blue colour typical of Roman production. The existence of four separate glass furnaces in the Regensburg area can be deduced, not only by this numerical classification but also from the archaeological discoveries of glass slags.

336. SCHOLZE, H. (1978) "Charakterisierung 'kranker' Gläser" (The characterisation of "sick" glasses.)

Some glasses from the 17th and 18th centuries weather very rapidly owing to their high contents of potash and low lime contents, leading to the formation of an alkali-deficient hydrated gel layer on the surface. The actual composition and condition of this surface layer depends upon the humidity of the environment. The determination of the water content can be carried out non-destructively by using an isotope-exchange technique, and the condition of the surface can be examined by using the scanning electron microscope on replicas taken from the surface.

In the discussion in which Frau Dr. Marschner, Frau Strunk and Drs Camara and Ferrazzini participated, it was pointed out that the stoichiometry of the water within the gel layer is determined by the composition of the glass. The gel layers have a very low micro-hardness. Glass samples which have weathered in the atmosphere do not have the lamellar surface crust which can be found on glasses which have been excavated from the ground. From the point of view of the $H_2O \rightleftharpoons D_2O$ exchange, between the gel layer and the atmosphere, a distinction must be made between the exchange of hydrogen ions and the exchange of water molecules.

337. SCHULZE, G. (1978) "Untersuchungen an Rubinglas aus Rastatt" (Researches on ruby glass from Rastatt.)

The great chandelier at Favorite Castle is attributed to Bohemian glassmakers. Many of the pieces are of a red colour and the use of VIS-Spectroscopy, AAS and Neutron-Activation analysis showed that gold ruby glass was present. At that time - based on J. Kunckel's discovery - the highly-developed procedure of making gold ruby glass was a carefully guarded secret of the Potsdam glassworks.

The Rastatt gold ruby glass can be distinguished from the original Kunckel's glasses in its contents of silica, potash, lime and magnesia. This may be an indication that the Potsdam monopoly had been broken. This assumption may well be confirmed by a remark found in Kunckel's records, where he mentioned that a glassmaker from Potsdam had been recruited by the Duke of Lauenburg.

In the discussion, in which Frau Dr. Spitzer-Aronson and Professor Scholze parti-

cipated, it was pointed out that a striking feature of the Rastatt gold ruby glass was the homogeneity of the red colour. Variations in the colour could be due to variations in the lead content. The relatively high lead content might enable the source of the lead to be investigated by the use of the lead-isotope ratio.

338. SELLNER, C. and CAMARA, B. (1978) "Untersuchungen von Waldgläsern (17. Jahrhundert) mit der UV - VIS - NIR Spektroskopie und der Elektronenspinresonanz (ESR)" (The use of UV - VIS - NIR Spectroscopy and Electron Spin Resonance (ESR) for studying 17th century forest-type glasses)

Forest-type glasses excavated from sites at Glashorn (Biberquelle/Spessart), Hilsborn (Hils/b. Grünsplan) and Ederkreis (Oberhessen) have widely different colours. The main colouring agents are iron and manganese but a few glasses also contain some cobalt. By using ESR they were able to show that the widely different colours were derived as a result of changes in the redox equilibrium $Fe^{2+} - Fe^{3+} - Mn^{2+} - Mn^{3+}$. This equilibrium itself depends on the partial pressure of oxygen in the furnace atmosphere, and these conclusions will involve reconsideration of the technology by which these glasses were melted.

In the discussion, in which Frau Dr. Marschner, and Drs Ferrazzini, Heimann, Knoll and Scholze participated, it was pointed out that the very low partial pressures of oxygen in the furnace atmosphere, produced by reducing conditions in the flame, are controlled by the Boudouard-Equilibrium which determines the process of the incomplete combustion of the carbon present as charcoal. Variations in the partial pressure of oxygen, produced by varying the supply of combustion air, which can be used for altering the colour of fired pottery, could be supposed to have a comparable effect on a glass melt. (But it would take much longer in the case of a glass melt - comment by Roy Newton.) A comparison of the analyses of approximately 200 medieval glasses from York Minster showed that a wide range of colours were found in glasses which differed little in their iron and manganese contents. This also raises the question as to whether there was deliberate addition of these colouring elements or whether their presence was more or less accidental (see also Abstract No. 343.) The relatively large separation between the ESR signals for Mn^{2+} and Fe^{3+} enables some distinction to be made of signal-splitting due to the presence of anisotropic material.

339. SPITZER-ARONSON, Martha (1978) "Titan als möglicher Indikator mittelalterlicher gemalter Gläser" (Titanium as a possible indicator of medieval stained glass)

The titanium content of medieval stained glass tends to be variable due to the presence of inhomogeneities. Nevertheless the author concludes that the determination of the titanium content of the glass provides the means of locating the glassworks, of deciding whether the coloured and colourless parts of the window have the same or different origins, discriminating between glasses in one cathedral and detecting changes in the compositions of the sands used throughout the centuries.

These results, although not always very distinct, correspond with the results of earlier investigations, using different physical methods, which have been used to establish correlation diagrams. These show, along certain defined lines on the sample, and with a resolution of 1 μ m, the distribution of the elements, of the colour, and of some other physical properties. The use of this technique was demonstrated for many glasses, particularly red glasses of different origins.

Professor Scholze then remarked that the reduction in titanium concentration in the vicinity of the coloured layers (in the early ruby glasses) supports the probability that those layers were produced by mixing separately-melted coloured glass with a colourless base glass.

(Editorial Note: Nos.334-339 were originally prepared in German by Dr G. Hierl, together with the reports on the discussions, as part of his official report (Protokoll) of the meeting, and they have been translated into English by Bruno Mhlthaler and Roy Newton.)

340. DAWSON, P.T., HEAVENS, O.S., and POLLARD, A.M. (1978) "Glass surface analysis by Auger electron spectroscopy", J.Phys.C: Solid State Phys., 1978, 11, pp.2183-2193.

Specimens of glass with compositions corresponding to (a) modern bottle glass and (b) medieval window glass have been examined by Auger Emission Spectroscopy. The chemically cleaned surfaces initially show the presence of carbon, which decreases with irradiation time. Calcium signals increase to a steady value as the attenuating effect of the carbon decreases. Alkali metal signals generally increase and then subsequently decrease steadily, indicating a loss mechanism for these ions from the surface regions. The results indicate the limitations of AES as a method for glass studies. (Authors' abstract).

Additional commentary by Roy Newton: in their introduction the authors state: "The motivation for these studies stems from the need to devise methods of protecting the ancient glass in our mediaeval buildings. Some of the samples studied, therefore, have compositions close to those of typical mediaeval glasses." The medieval glass used for the tests was No.144, from the European Science Foundation melts prepared by Pilkington Brothers Ltd., see News Letter No.25, pages 3-5 (see also Section 5.1.2, above). The work has not yet reached the stage where the results are useful to conservators, but the group at the University of York is intending to make progress in that field.

341. HENCH, L.L., and CLARK, D.E. (1978) "Physical Chemistry of glass surfaces" J. Non-Cryst Solids, 1978, 28, pp.83-105.

Commentary by Roy Newton: This paper has the same title as in Abstract No.268 (see page 10 of N.L. No.25, and page 11 of N.L. No.27) but there is now an additional author (D.E. Clark). Much of the text, and the illustrations, are the same but there is now a discussion of the durability of those glasses which are used for the storage ("encapsulation") of waste nuclear material, and of the permanence of the

organic coatings used to cover the glass fibres used for optical communications systems.

Fig.10 shows how the corrosion pattern of a glass can differ depending on whether a freshly-fractured surface is used, or one which has been lightly ground and polished. The "mixed-alkali effect" is now discussed much more comprehensively than in the previous paper, and Fig.11 shows how the position can be very complicated. There is also a useful discussion (Fig.13) of the improvement in durability which takes place when alumina is added to a glass.

342. HENCH, L.L., NEWTON, R.G., and BERNSTEIN, S. (1978) "Use of infrared reflection spectroscopy in analysis of durability of medieval glasses, with some comments on conservation procedures. Glass Technology in the press)

Infrared reflection spectroscopy (IRRS) is used to obtain a non-destructive surface analysis of the structural changes associated with the aqueous corrosion of two simulated medieval glasses. Variations in aqueous corrosion time and temperature, and differences in glass composition, appear as changes in the IRRS "fingerprint" of the glass surface. Sequential polishing removal of two different types of glass surface damage, e.g. silica-rich skin formation and pitting corrosion, were able to be followed using the IRRS Method. Applications in conservation procedures are suggested. (Authors' abstract).

Additional commentary by Roy Newton: the two simulated medieval glasses were Nos.145 and 147, from the European Science Foundation melts, prepared by Pilkington Brothers Ltd., see News Letter No.25, pages 3-5, (see also Section 5.1.2 above). The authors show that the IRRS spectra of the surface weathering can be correlated with mechanical properties of the damaged surface, and a surface abrasion index could provide a technique for conservators to use in diagnosing the correct restoration procedure to be employed.

343. NEWTON, R.G. (1978) "Colouring agents used by medieval glassmakers" Glass Technology 1978 19 59-60.

This study of analyses available in the literature is intended to provoke discussion by suggesting that the great variety of colours in medieval stained glass were not produced by deliberate colouring agents to the glass (except in the case of red, and perhaps also of blue, glass) but were produced more or less accidentally. Any control over the colour which glassmakers might have exercised would have been through alterations in the furnace atmosphere and by prolonging the melting time. A careful reading of Theophilus supports this viewpoint. (Author's abstract).

344. PAUL, A., and YOUSSEFI, A. (1978) "Alkaline durability of some silicate glasses containing CaO, FeO and MnO" J.Materials Science, 1978, 13, 97-107.

This paper, originally abstracted in N.L. No.25 as No.272, has now been published.