(CV) NEWS LETTER 18

Comité Technique du Corpus Vitrearum

Physics, University of York

23 February 1976

CONTENTS

1 GENERAL

1.1 RECENT NEWS

Now that these News Letters are written on behalf of the international Comité Technique, instead of the British Technical Sub-Committee, I shall welcome items of international news from other National Technical Committees.

1.1.1 European Science Foundation

In item 1.1 of NL No.17 news was given about the approach made to the European Science Foundation, and the possibility that a Study Group might be set up to consider problems in the conservation of medieval windows. A small group of experts will now be meeting in Munich on 25th February to make a start on the problem.

1.1.2 Constitution of the Comité Technique

The Comité Technique du Corpus Vitrearum is nearly complete, but nominations are still awaited from Poland and the USSR. The list, so far, is:-

Allemagne (BRD) - Dr Gottfried Frenzel, Nürnberg.
Allemagne (DDR) - Dr Karl Joachim Maercker, Halle.
Autriche - Dr Ernst Bacher, Wien.
Belgique - M. René Sneyers, Bruxelles.
Espagne - Sr. Carlos Muñoz de Pablos, Segovia.
Etats-Unis - Dr Robert Brill, Corning.
France - M. Jean Taralon, Paris.
Grande Bretagne - Prof. Roy Newton, Sheffield. (Président)
Italie - Prof. Guiseppe Marchine, Firenze.
Pologne - (vacant)
Pays Bas - Mr. A. Bogtman, Haarlem.
Portugal - Sr. Carlos Vitorino da Silva Barros, Lisboa.
Tchecoslovakie - Dr Ludvík Losas, Praha-Hradčany.
USSR - (vacant)
Suisse - Dr Jean-Claude Ferrazzini, Zürich.
- M. Jean-Marie Bettembourg, Champs-sur-Marne (Secrétaire du Comité).

An active programme of work has already been initiated and questionnaires have been sent out about (a) the preparation of a summary of conservation techniques and (b) the need for new synthetic "medieval" glasses and the compositions which should be used when new glasses are melted.

1.1.3 Dr R.H. Brill

I have had a letter from Bob Brill in which he says, "As of October 1, I resigned the directorship of the (Corning) Museum and returned to my duties as Research Scientist full-time. We found during the past three years that I simply did not have the time to devote to our research program. Tom Buechner will assume the directorship of the Museum, in addition to acting as President of the Museum, President of Steuben, etc.". He adds that this will be a most welcome change for him personally (the rest of us will also greatly welcome this increase in his research activities - RGN).

1.1.4 12th century blue glass in York Minster

In item 4.2 of this News Letter it is pointed out that, contrary to all expectation, some 12th century blue glass in one panel in York Minster has been found to be a soda-glass instead of a potash-glass. This discovery is so surprising, and so interesting, that we should like to know (a) whether there is any more 12th century soda-glass in any other panels of the Minster, (b) whether such soda-glass is always blue in colour, like the four pieces found already, or whether other colours also exist and (c) whether 12th century soda-glass exists in any other building!

In order to obtain answers to (a) and (b) a massive experiment has been planned to take place on 8th April, by kind permission of the Dean and Chapter. An attempt will be made to test most of the pieces of 12th century glass in the Minster to learn how much was made with soda and how much with potash. By arrangement with the National Radiological Protection Board, Northern Centre at Leeds, several scintillation counters (of the type mentioned in section 5.2 of this News Letter) will be used to test thousands of pieces of glass during the day. The cost of undertaking this survey (about £165) will be met from the Pilgrim Trust Special Grant for research at the York Glaziers Trust, and the project forms part of the YGT Research Programme. The answer to question (c) will be much more difficult to discover!

1.1.5 13th century ruby glasses

There is a problem in learning how the medieval glassmakers made their multi-striated red glass in the 12th and 13th centuries. One current view in the literature that "... the layers are formed by alternately plunging the cylinder of blown glass into the colourless and into the coloured molten glass ..." is surely wrong because the viscosity of glass would not permit such thin (10-20 µm) layers to be made by dipping alone. Moreover there may be 30 or more such thin red layers present and 60 or more alternate dips seem out of the question! Anyway, if they did know the secret of making layered glass, why were they not content to make a simple "flashed" glass, as was done in the 14th century and is still done today?

This question was asked briefly at the end of abstract No.209 on p.12 of NL No.17 and discussions subsequently took place with Mr Allenby Alder, of Hartley Wood & Co. in Sunderland and with Dr R.E. Bastick, lately of Chance Brothers in Birmingham, and various other possibilities have been suggested. A likely one is that small pieces of broken "red" glass were scattered on to a crucible of white glass, and the "gather" for the cylinder was made "through" this inhomogeneous surface layer.

Dr Martha Spitzer-Aronson has had great experience in analysing red glasses and has found that diffusion of copper occurs beyond the visible boundaries of the coloured layers. Pieces of modern red glass, made in various ways, have now been sent to her for study and it will be interesting if any show diffusion phenomena which she finds characteristic of the early ruby glasses.

1.1.6 Removing old leads from glass

There seems to be some interest in learning safe ways of removing old lead from glass. In item 202, on p.10, col.1, of NL No.17 Dr Eva Frodl-Kraft concluded that old lead-work can only be broken by inserting a sharp instrument between it and the glass, and this cannot be done without breaking some of the glass. On p.7 of NL No.17, Mr Frederick Cole states "The lead has to be cut in order to release the glass and, even so, the glass is at risk.".

Has anyone any comments to make?

1.1.7 Surveys of topics of current interest

From time to time readers of the News Letters have suggested that surveys of current topics should be included. For example, NL No.7 included a summary of the state of protective glazings as it was then, but subsequent developments have now rendered some of it out of date. Similarly, item 3 of the present News Letter has a summary of the position regarding the use of plastics and resins in conservation of medieval glass; I hope that it, also, will soon be rendered out of date.

Will readers please write to me, at 5 Hardwick Crescent, Sheffield S11 8WB, suggesting topics which they would like to be reviewed.

1.1.8 Seminar on conservation of stone and glass in buildings

This seminar, to be held at the Building Research Establishment on Wednesday, 16th June 1976, is intended for architects and consultants concerned with building conservation, and specialist contractors in restoration and supply of materials. The seminar will discuss ways of preserving the stonework of Buildings and Sculpture, including impregnation techniques and the control of plant growth. The preservation of Roman floors and medieval glass will be covered.

The fee is £13.50 and programmes and application forms are obtainable from Mrs J. Christensen, Application Planning Section, Building Research Establishment, Garston, Watford, WD2 7JR.

1.2 PROBLEMS WITH ACCELERATED WEATHERING TESTS

One of the problems in using accelerated weathering tests is the possibility that an increase in the concentration of an "active" ingredient of the environment may bring about an undesired change in another factor, and thus give misleading conclusions. For example, weathering tests on resin coatings can be accelerated by increasing the temperature but too great an increase in temperature could melt the resin and give a wrong result!

A striking example has occurred recently with the use of accelerated tests for the attack by sulphur dioxide (SO_2). Even when the concentration of SO_2 is increased 100 times the test may take 3 days to carry out (see item 5 of NL No.15) and one experimenter therefore increased the concentration to 5% of SO_2 in moist air (an increase of more than one million times compared with a polluted atmosphere) in order to get a result quickly, which indeed he did! I am grateful to Dr A. Paul, of the University of Sheffield, for pointing out that this high concentration of SO_2 would produce quite a strong acid on the surface of the glass (pH value = 2.4). Most medieval window glass is "basic" in nature and hence easily attacked by such an acid, so that the observed attack on the glass could be attributed to the acid and not to the SO_2.

However, the results in Fig.1 of NL No.17 strongly suggest that SO_2 in normal amounts is not a primary agent in the deterioration of glass. The sulphates almost always found on the surface of medieval glass seem to be the result of a secondary reaction by SO_2 on carbonates already formed by attack on the glass by water. It is hoped to discuss this more fully in NL No.19.

1.3 ISOTHERMAL GLAZINGS

It has generally been believed that the earliest system of "isothermal" glazing (i.e. where the air from inside the building is allowed to pass between the stained glass and the external protective glazing) was that at Berne Minster, installed by Konrad Vetter in 1945 (see NL No.9, item 2.2) but information has been received about two much earlier examples.

1.3.1 Rome: St Paul's Within the Walls

Dr Bernard Feilden, CBE, has told me that this Italian Church, in the via Nazionale, was built about 1875 by the English architect, E.G. Street. Shortly after it was completed, mosaics were put around the east end by Burne-Jones, and the contemporary glass was moved up into the Clerestory and fixed behind the existing white glass in an isothermal manner.

Further information is being sought about these windows but it would seem that this glazing, installed before the end of the 19th century, is probably the oldest example anywhere. (N.B. the glass at the church at Lindena was not deliberately ventilated, either to the inside or the outside - see NL No.7 item 3.4 - but by now there is probably adequate leakage of air from the outside.)

1.3.2 Beauchamp Chapel, St Mary's Church, Warwick, England

Mr Dennis King, FSA, first drew my attention to the isothermally ventilated windows at the east end of the Chapel, and showed me photographs which demonstrated that condensation could occur on face 2 but not on face 3, even though there was no condensation on nearby unprotected glass. I have since visited the Chapel in the company of the architect, Mr Charles Brown, FRIBA, and made the measurements recorded below.

The Chapel was completed in 1463 and the contemporary glass was much damaged during the 17th century, mainly in the Civil War but also by hailstorms recorded in the 18th century. The remaining glass was collected mainly into the east window and, during a later restoration possibly in 1927, the panels were re-set in hinged bronze frames, formed from 15mm x 15mm angle, and re-hung 40mm behind plate glass fixed in the original glazing grooves. The total height of the window is 7m.

It seems likely that the intention of the then architect (Mr Philip Chatwin, FSA) in using bronze frames with rising-butt hinges (the top part of the hinge can be lifted off) was to make it easier to remove the medieval glass, e.g. in case of war. The frames are not sealed against the stonework and there is plenty of space for air to circulate. This system of mounting has a further advantage because the glass can be easily and cheaply removed for cleaning and restoration, as was recently done by Mr King. The external plate glass affords some protection for the medieval glass against thrown stones, though some panes were found to have holes in them and several were cracked. It might also be thought that the unrelieved plate glass would have objectionable reflections in it, but it is in fact not easy to see the outside of this window from ground level.

On 11th November 1975 the following measurements were made:-

Outside air temperature	8.3°C
Air temperature inside the Chapel	10.7°C
Air velocity near face 4	c.15 cm/sec upwards
Air velocity in interspace	c. 5 cm/sec upwards

The air flow rates were measured using "cold" smoke from a Draeger smoke generator (see NL No.14, item 2.5) and a stopwatch. It had been expected that the air flow in the interspace would be downwards, instead of upwards, but there was some weak sunshine on the east window and it is probable that the stained glass might have been warmed enough by the sunshine to raise the average temperature in the interspace above the 10.7°C of the Chapel, and cause the air to flow upwards.

1.3.3 Prato Cathedral, east window

The isothermal glazing at this Italian cathedral was described briefly in NL No.9, item 2.1.1 but no illustrations were included. A good account has just been published in "Fra Filippo Lippi nel Duomo di Prato" by Eve Borsook, Guiseppe Marchini and Leonetto Tintori, Mitteilungen des Kunsthistorischen Institutes in Florenz, 1975 19 (1) 1-196. Pages 194 and 195 describe the ventilated glazing system and Fig.110 (reproduced here as Fig.1) shows the sill with a ventilation hole (100mm x 40mm) (A) cut through it and the bent metal strip (B) which allows air to circulate but prevents light from shining into the cathedral.

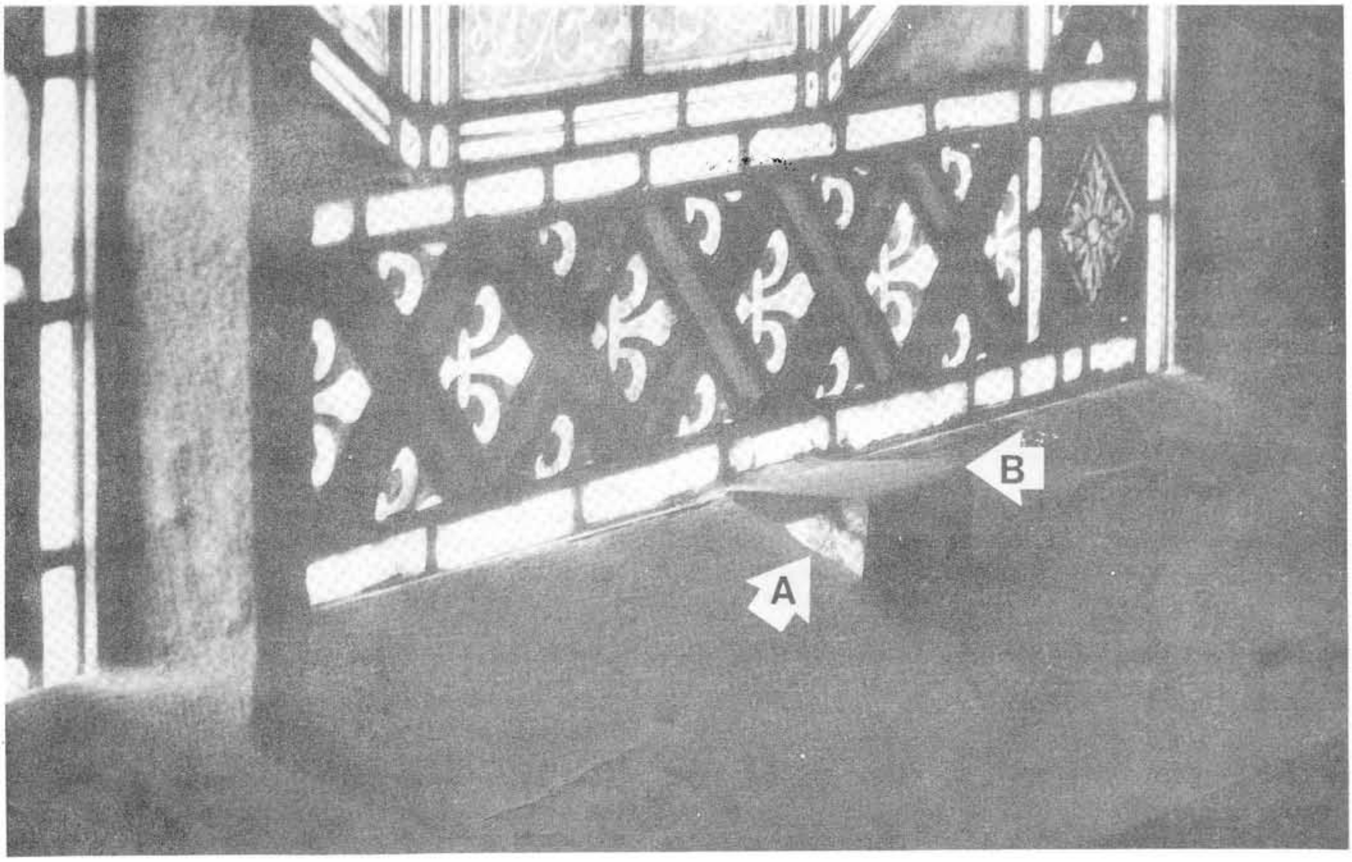

Fig. 1 This illustrates one of the lower ventilation apertures for the isothermal protective glazing of the East Window at Prato Cathedral – see item 1.3.3.

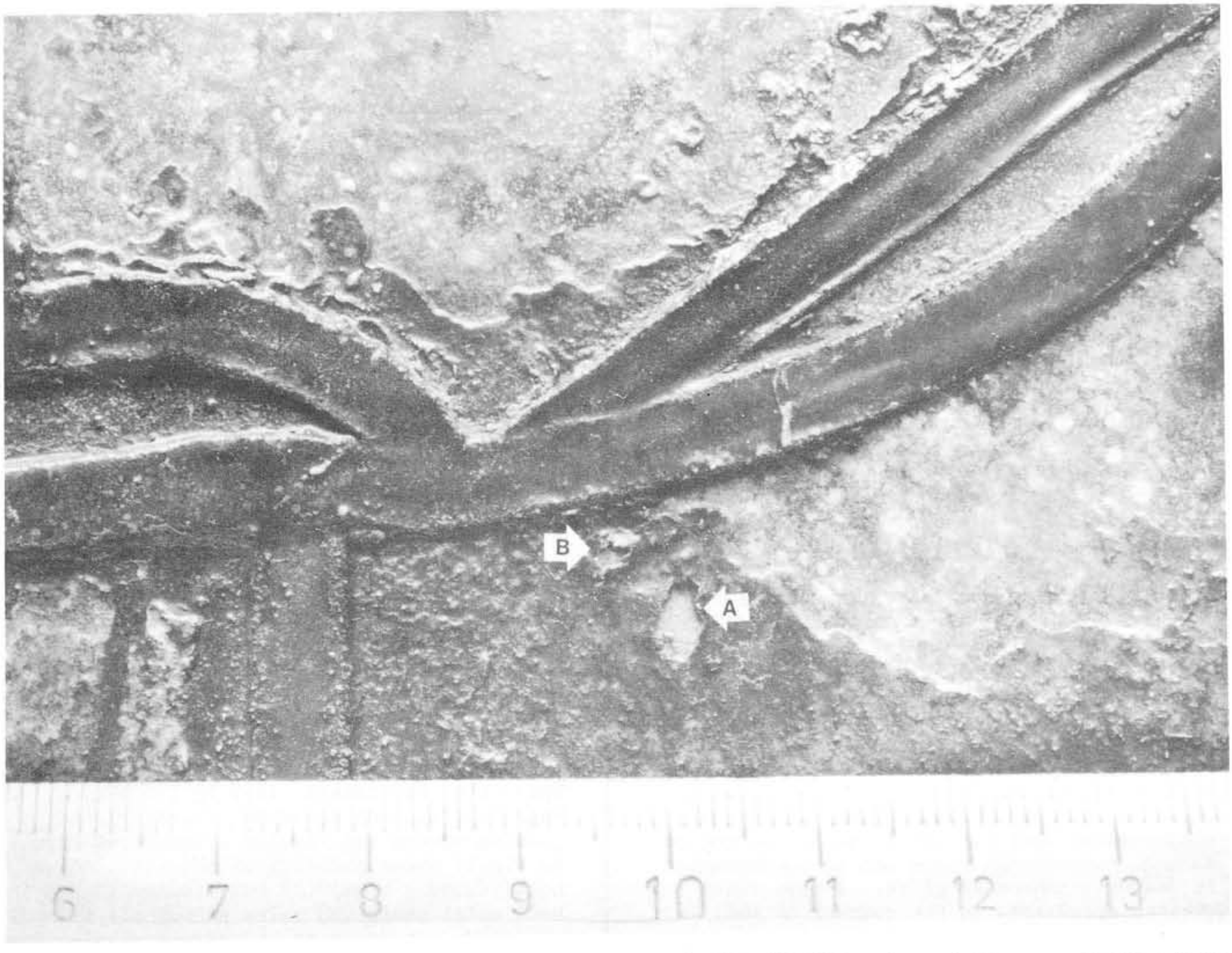

Fig. 2 This shows the two holes which appeared, after about four years, in the Viacryl VC363 coating applied, in one application only, to the lightly-cleaned 14th-century glass at St. Maria am Gestade in December 1971 – see item 3.9.

2 CLEANING OF GLASS

An important paper contributed to the Paris Colloquium in September was that by Dr W.P. Bauer of Vienna on the effect on glass surfaces of various methods of cleaning (Der Einfluss von Reinigungsmethoden auf die Glasoberfläche - Vorläufige Versuche und mikroskopische Untersuchungen). This paper is available only in German and it is considered to be of such interest than an English translation is included below. The lecture was accompanied by 12 slides and it is hoped that they will be published in the Proceedings of the Corpus Symposium.

* * * * *

Opinions differ about the various methods which have been recommended for the removal of weathering products and other deposits from old glass. These opinions concern both the efficiency of the methods and especially their effects on the "intact", old glass itself.

An optimum method of cleaning glass should satisfy the following conditions:

(a) It should remove the weathering crust and other deposits as gently as possible.

(b) The agents used should not have so radical an effect as to remove some of the glass, or of the black paint or to destroy the undamaged glass surface. (RGN - if the glass has been corroded it is difficult to see how any "undamaged glass surface" can still remain.)

(c) Attempts to recover transparency should be kept within limits compatible with conservation.

The different methods used at the present time for removing weathering crusts - the airbrasive, acid polishing, Bettembourg's solvents - were tested on small pieces of glass from the painted glass panels from St Michael in Wachau (1st half 14th century). In basic composition, these St Michael glasses are typical gothic glasses of Austrian origin. On average, their principal components are as follows: 46.6% SiO_2; 19.7% K_2O; 0.24% Na_2O; 23.3% CaO; 4.4% MgO.

The investigations of Collongues and Perez y Jorba classify glasses of this composition in Group II (NL No.11). During weathering they form thick, surface weathering crusts of gypsum and/or syngenite rather than pits in the surface.

In the preliminary practical experiments particular attention was paid not only to the cleaning effect as such but also the effects of the different cleaning methods on the surface layer of the old glass. Recently particular significance has been attributed to the topmost layer of glass (the skin) in so far as conservation is concerned (see NL No.12, item 2; also in NL No.15, the abstracts of papers by Brill (No.186) and Ferrazzini (No.187)). Apart from the aesthetic aspect, which must be directed at maintaining as far as possible the original appearance and avoiding the loss of material of documentary importance, such as the black enamel linework, the fact that the surface skin of glass is now considered to have some protective effect is also significant. (RGN - this view is <u>not</u> accepted by everyone, see item 2 of NL No.13.) A decisive factor in this protective effect is the alkali impoverishment (or freedom from alkalies) of this skin. It is assumed that if such a surface zone does exist then the glass would deteriorate less rapidly than if this zone had been lost and consequently higher alkali concentration were present in the surface zone. In this case reactions rapidly occur with the protons present in the environment (Ferrazzini).

The various illustrations show the ways in which the different cleaning methods act on the glass surface:

(1) <u>Airbrasive cleaning</u>. Removal of the whole weathering crust by means of an airbrasive device (Type: Sorensen AG, Zurich - Model K). A roughening of the surface can be observed, both macroscopically and from the photomicrograph.

(2) <u>Acid-polishing</u>. The outside of a piece of glass was first cleaned by airbrasion and then subjected to Cole's so-called acid-polishing (NL No.13, item 2.1), the outside surface of the glass being immersed for 10 minutes in 40% HF. In this method of treatment, <u>the hydrofluoric acid crept on to the inside of the glass bearing the black enamel</u>. The black enamel linework, which had previously had good adhesion, began to lift, starting at the edges. After 10 minutes' immersion in hydrofluoric acid the outside of the glass was greyish-white and cloudy. When the glass was subsequently washed in running water this grey layer came away like a transfer. It was not possible to polish the surface by acid-polishing with hydrofluoric acid (NL No.15, item 1.3). In fact the glass surface became even more rough than it was after the airbrasive treatment and assumed a greyish-white colour. The photomicrographs show a very 'open' and etched glass surface. To obtain a polished effect, Cole will have to combine the hydrofluoric acid treatment with some special treatment.

(3) <u>Bettembourg's cleaning agents</u>. J.M. Bettembourg has suggested two solutions for removing adhering crusts of sulphates and carbonates from medieval glasses (NL No.7, item 2.4 and No.13, item 181.A):

Solution (A): 10% sodium thiosulphate ($Na_2S_2O_3 \cdot 5H_2O$)
5% sodium pyrophosphate ($Na_4P_2O_7 \cdot 10H_2O$)

Solution (B): 3% EDTA / 3% ammonium bicarbonate (NH_4HCO_3).

Half of a piece of glass was first completely immersed in the milder solution (A) and left there for 12 hours. Only part of the weathering crust came away. However, the black enamel painting on the inside (which still had good adhesion) was not damaged at all. To continue the experiment, the immersion time was extended to 48 hours. After this time a considerable amount of the weathering crust had already dissolved. A half-tone wash, underneath the weathering crust, which had not previously been visible, appeared on the outside of the glass. Despite the relatively long immersion in the cleaning solution, the underlying glass surface does not show any sign of damage.

The second half of the piece of glass was then treated with the stronger solution (B) for comparison with the cleaning results achieved with solution (A). First, the outside of the glass was immersed in the cleaning solution. To achieve a significant effect as regards possible damage of the original glass surface underneath the weathering crust, the outside of the glass was immersed in this solution for 48 hours. (In comparison, the average cleaning times of 2-3 hours quoted by Bettembourg are relatively short and mild; see NL No.7, item 2.4.)

During the cleaning process, a rise in the pH value from 7.2 to 8.8 was recorded. After the glass had been removed from the cleaning bath it was washed in running water. Some of the weathering crust came away in the cleaning bath and some under the running water, so that it was almost completely removed. Small residues could easily be removed by rubbing with the finger-tip. In this case too the outside of the glass showed no damage of the original glass surface (roughening, etc.), which might have indicated attack by the cleaning agent, when the weathering crust was removed. In fact, here too, despite the visibly stronger action of this cleaning solution, a previously unseen half-tone glaze appeared undamaged on the outside of the glass.

The inner face, with the black enamel, was then immersed in Solution B overnight (approx. 12 hours). The solvent turned a pale bluish green colour, showing that in this case the solution had had an aggressive effect. The experiment was interrupted and the inside rinsed under running water. Parts of the black enamel linework came away during this rinsing. Before the treatment the black enamel linework had appeared to have good adhesion.

3 RESINS FOR PROTECTION OF GLASS

There has recently been much discussion, and also much misunderstanding, about the properties of plastic materials when used for the conservation of stained glass windows. In an effort to clarify the situation I have had some discussions with the well-known British Consultant on plastics and adhesives, Dr William C. Wake, FRIC, FPRI, who for some years has been a Visiting Professor in Adhesion Science at The City University and is an examiner in polymer science at other Universities.

The results of our discussions are set out below and it will be seen that the situation is complicated, that some points are still obscure, and that more experimental work is needed. Nevertheless, it is hoped that these notes will be helpful in bringing many known facts together, and in pointing out where more work is needed, but it must always be remembered that few resins have had effective lifetimes longer than 10 years when exposed to the weather and none has been in use for more than about 30 years.

3.1 PERMEABILITY OF PLASTICS TO WATER VAPOUR

Water alone is responsible for the weathering of glass surfaces and hence coatings of plastics or resins are intended to stop water from getting to the glass. Can they do this? No polymer can be completely impervious to water vapour although non-polar materials such as polyethylene have a good resistance to it, but they are not so suitable for coating glass as are the polar materials which are much more permeable to water vapour. The values for the permeability to water vapour of thin films for a selection of plastics (in 10^{-10}g/cm^2.s.cmHg) are given in Table I.

TABLE I Permeability of polymers to water vapour

High density polyethylene	0.01
PTFE	0.03
Polyester packaging film	0.18
PVC (unplasticised)	0.2
Polystyrene	0.8
Epoxy resins	1.0
Perspex	3.0

These numbers will mean more to conservators if we consider how long it takes for a noticeable amount of water to pass through a typical polymer film and reach the glass. If the experiment is carried out at 22°C and 50% relative humidity (a combination which gives a water vapour pressure of 1cm Hg) then a just-noticeable amount of water (1mg/cm^2) would form on the glass from diffusion alone in about 5 weeks if a film of Perspex (the worst in Table I) were used or in about 30 years if high density polyethylene were used (the best in the Table). Thus water must eventually reach the glass and then start passing out again until equilibrium is reached, but the discussion in 3.2 below shows that osmotic pressure may also need to be taken into account. With an epoxy resin the glass would be expected to start deteriorating in less than six months unless, perhaps, some additional treatment is given, as in 3.3.

3.2 OSMOTIC EFFECTS

As soon as <u>some</u> water, e.g. the first few molecular layers, reaches a poorly-durable medieval glass, ion exchange will take place; the water will become alkaline and quite a different effect (osmotic pressure) will come into play. In calculating the diffusion rates quoted above it was assumed that the driving force would be a partial pressure of water vapour of 10mm, but the potential osmotic pressures are vastly greater. The solution expected to be formed on a poorly durable glass (such as British glass No.2) behind the Perspex film, after the five weeks quoted above, would have an osmotic pressure of 950mm! This will upset the equilibrium and cause more water to stay on the surface of the glass than would be expected from diffusion alone, but it is difficult to calculate how much. Some direct experiments should be carried out! The accumulation of this water explains why polymer films readily become detached from poorly-durable glasses in accelerated weathering tests (see NL No.6, p.5 and NL No.14, p.8) and it should be possible to determine how much water lies between the film and the glass, and how much alkali is contained in that water. Such work is urgently needed.

3.3 DISPLACEMENT OF NON-REACTIVE POLYMER FILMS BY WATER

The fact, mentioned immediately above, that resin films generally become detached from poorly durable glasses during accelerated weathering tests, deserves some theoretical consideration. There are theoretical reasons for believing that non-reactive polymer films (all those discussed in 3.1) adhere well to any glass by a process of adsorption (by means of van der Waal's attractive forces) but water can displace the polymer from the glass if an increase in "free-energy" occurs in the process. Whether or not the water will displace the polymer can be calculated from a formula which is mainly concerned with the contact angle of the water with the polymer. The separation occurs less readily if the water has a low contact angle and such polymers are mainly hydrocarbons or fluorinated materials. Those with a high contact angle are polar materials such as polymethyl methacrylate (Perspex), and they would be expected to be displaced (peel away from the glass) more readily in the presence of water (see item 3.9 and Fig.2).

In the discussion in Section 3.1 it was assumed that the glass was completely covered by resin, and even then water can get to the surface of the glass and cause the polymer to lift away. If, as is probably more frequently the case, the resin is applied to one side of the glass only, then the separation will start taking place as soon as the water reaches the interface, at the edge of the coating. The same thing would apply at a pinhole in the coating.

3.4 CHEMISORPTION OF POLYMER FILMS TO SUBSTRATES

The surface of freshly-made glass is covered with water molecules which, in a chemical sense, "hide" the otherwise reactive silanol groups (the "unused ends" of those silica molecules which are at the surface). However there is a special group of compounds called <u>coupling agents</u> which can form a chemical linkage (a coupling) between the silanol groups in the glass and other suitable groups in an organic polymer coating. The combined layer is not necessarily any more impervious to water vapour than were the simple polymer films discussed in 3.1 above, but Dr Wake tells me that the presence of the coupling agent will reduce the tendency of water to displace the film (as in 3.3); in fact any displacement by water may occur only when the resin film, or the coupling agent, has been broken down chemically. It must also reduce the accumulation of water near the glass, although it is not clear what the effect will be on the development of osmotic pressures. Thus there is much here which still has to be considered in more detail but it is hoped that this can be done, both theoretically and experimentally as an extension of the practical work which was suggested at the end of Section 3.2

3.5 EFFECT OF SHRINKAGE-STRESSES ON ADHESION

Thin resin coatings on glass must be in a state of strain when first applied due to the shrinkage which occurs, and there is no known method of applying a polymer film to glass without introducing strain. If the temperature does not change, the stress associated with the strain may gradually relax but we never have unchanging temperatures on medieval windows, even on the north side of the building, see NL No.16, item 2.2.2. The chief reason for the renewal of stress is the large difference in coefficient of expansion between resin and glass (see Section 3.6) but changes in humidity can also set up stresses.

In a polymer film the stress is highest at the edge and this leads to peeling from the edges. If the stresses are severe, crazing of the polymer can occur and this is yet another source of entry for water to reach the glass.

3.6 COEFFICIENTS OF LINEAR THERMAL EXPANSION

All resins have higher thermal expansions than does glass, representative figures being given in Table II (in 10^{-6}cm/degC).

TABLE II <u>Coefficients of linear thermal expansion (x 10^{-6})</u>

Perspex	50-90	Epoxy resins	45-90
Polystyrene	60-80	Modern window glass	8
Silicones	200-400	Medieval window glass	8-15

The differences in thermal expansion are so large that mechanical stresses will be set up whenever the temperature changes. In south facing windows at York Minster, changes of more than 40 deg.C have been found in the summer and some workers claim that 100 deg.C can be encountered in Central Europe (from -20°C to +80°C).

3.7 ACRYLIC RESIN COATINGS

Much use has been made of acrylic resins and especially acrylic co-polymers (Acrylek, Bedacryl 122X, Viacryl VC363, etc.) because they show good adhesion to "high energy substrates" such as metals and dry glass, and they are resistant to the ultra violet light which occurs in sunlight, to atmospheric oxygen and to ozone. Viacryl VC363, which has attracted much attention as being the best of the acrylic resins so far found (see NLs 11 (170); 13 (181,C,D); 14 (5)) appears to be an acrylic copolymer which has a hydroxyl content of 2.4% available for reaction with the isocyanate hardener (Desmodur N.75) to produce some urethane bondings. These urethane linkages will be susceptible to weathering and break down hydrolytically in the course of time; such resins absorb traces of water which will migrate to the interface.

The attraction of these acrylic resins is real. They are resistant to weathering and are very good adhesives which are simple to apply and relatively cheap. Alternatives which have superior weathering properties (such as polyvinyl fluoride) are difficult to apply and would require an intermediate polymer to (a) fasten them to the surface and (b) provide a barrier against the possible release over many years of minute amounts of hydrofluoric acid. All the alternative candidates for use possess other objections. The ideal coating would be "coupled" to the glass" (Section 3.4); would not contain aromatic cross-linking agents nor hydrolytically sensitive groups; and would have a very low water absorption and permeability to moisture.

Three useful reference books are:- "Fibres, Films, Plastics & Rubbers" by W.J. Roff and J.R. Scott, Butterworth, London 1971, price £15; "Adhesion and the Formulation of Adhesives" by W.C. Wake, Applied Science, London, due for publication in March 1976, price about £14; and "Glass Reinforced Plastics", Edit. B. Parkyn, Iliffe, London, 1970.

3.8 ATTACK ON LEADS BY SILICONES

Silicone mastics are being widely used in the conservation of medieval windows, especially since they were recommended as the best available by J.M. Bettembourg (NL No.11 (169); 15 (169)), but a case has recently occurred where they were used in a "plating" and a white deposit appeared not only on the lead but also on face 3 of the externally-plated panes. Discussions with Dr Wake showed that the self-curing types (mono-packs, or RTV = room temperature vulcanising types) will release acetic acid which is usually dispersed harmlessly into the atmosphere, but when used in an enclosed space the acetic acid vapour can attack lead which is not even in contact with the sealant and produce an unsightly white deposit. (The acetic acid is released during the curing process because this type of siloxane sealant contains acyloxy groups which absorb moisture from the atmosphere and become hydrolysed, forming active hydroxyl groups which cause the curing to take place and releasing acetic acid and water which will then cause further hydrolysis, etc.)

It would seem that, in these cases where the acetic acid cannot readily escape, it might be helpful to protect the leading with a clear varnish, and not position the plating glasses until the last moment. It is understood that oxime-cured silicones are on the market but their composition and properties are not yet known; however, they may release alkaline vapours into a closed space.

Dr Wake comments that adhesion to lead is never an easy matter because the lead oxide surface has a low cohesive strength and can change during the lifetime of an adhesive due to the ingress of moisture and oxygen. Thus it is perhaps not as surprising as it seemed at the time that smoke can be introduced at so many of the lead joints at York Minster (NL No.15, item 2.2)!

3.9 THE EAST WINDOW AT ST MARIA AM GESTADE

A most important experiment on the natural weathering of a resin coating applied to a medieval window is in progress at the church of St Maria am Gestade, in Vienna. Here one window was divided into panels and treated in December 1971 in five different ways: (1) left untouched, (2) only cleaned, (3) given one coating of Viacryl VC363, hardened with Desmodur N.75, (4) with two coatings of Viacryl and (5) with three coatings of Viacryl. In May 1974 I examined this window and saw one hole in the coating (A in Fig.2). In 1975 an additional hole had appeared (B in Fig.2) and Dr Ernst Bacher has kindly sent me the following note about the experiment (in translation):-

"Since 1971 the (Austrian) Bundesdenkmalamt has been observing a test panel in the church of St Maria am Gestade in Vienna coated with a protective film of Viacryl VC363 (also reported in OZKD 1973 <u>27</u> 62-63). For a long time the protective film showed no adverse change in adhesion surface appearance or transparency. However in 1974 at the lower part of the test panel a small hole appeared in the Viacryl film, apparently because a loose piece of upstanding weathering crust was pressed down during the mounting of the panel, and it subsequently broke away (the site of the damage is in panel No.3, where one coat of Viacryl had been painted on to the uncleaned surface). The size of the flake of weathering crust which broke away, and of the resulting hole in the protective film, is about 3mm x 4mm (see A in Fig.2). In 1975 a second, somewhat smaller, hole appeared in the immediate vicinity of the damaged area, probably due to a similar cause (see B in Fig.2).

"Even if these holes are due to mechanical damage associated with the uncleaned crusted surface of the glass, and not to failures of the protective film itself, it will be of great interest to photograph it periodically and follow any further loosening of the protective film."

4 WINDOW GLASS OF DIFFERENT DATES

The research programme of the York Glaziers Trust produced an interesting report in the middle of 1975, entitled "Some dangers in using the chemical composition of stained glass as evidence of date" (YG/75/1), 15 July 1975; briefly, it drew attention to some dangers in assuming that all medieval glass has a high content of potash, and a relatively small amount of soda.

4.1 INTRODUCTION

Roman and Saxon glass certainly were soda-rich materials and, as explained in Section 5.1, stained glass from the 12th century onwards is generally high in potash because it was made from wood ash from forests instead of ash from maritime plants. These "forest-type" glasses are also characterised by being relatively high in lime and in phosphorus, again because the ash from the furnaces was used as the source of alkali.

Professor W.E.S. Turner stated that "During the medieval period, the potash, particularly in window glass, plain or coloured, dominates the soda in the glasses of England, France and Germany ..... (but) A reversion to the older type of glass, such as rochetta or barilla, must have taken place in some areas in the fifteenth and sixteenth centuries.". When a study is made of 136 glasses analysed in the last 10 years by R.H. Brill, J.M. Bettembourg, the British Glass Industry R.A., Pilkington Brothers and Dr Wilhelm Bauer in Vienna, it is found that they agree with the statement made by Turner. None of the glasses from the 12th to the 14th centuries had more than 3.8% soda nor less than 4.8% potash, although most had less than 10% soda and more than 10% potash. Thus at first sight there seems to be a complete confirmation of Turner's statement.

4.2 SOME BLUE 12th CENTURY GLASS FROM YORK MINSTER

This was the view held when the radiation-monitoring experiments were started in York Minster. One piece of genuine 12th century dark blue glass, from the Norman roundel at the bottom of the central lancet of the "Five Sisters" window, gave a surprisingly low result (see Table V in Section 5.3), indicative of a soda-glass instead of the potash-glass which had been expected.

At first this result could not be explained and, by kind permission of the Dean and Chapter, this piece of glass (Sample No. 268) together with two other dark blue pieces from the same panel (Sample Nos. 269 and 270) were removed for closer study. At that time sodium could not be analysed on the Isoprobe at the University of York and hence the samples, together with a similar piece (Sample No.228) from the "bank" at the York Glaziers Trust, were taken to Buxton, where they were kindly analysed non-destructively by Mr M. Joceylin of Link Systems Ltd. using their MECA 10-6 instrument (see also NL No.15, item 4) which can detect sodium at 1 part in 10,000.

All four glasses were found to be rich in soda, and relatively low in potash! Thus the mystery of the relative absence of radiation from the 12th century glass has been explained, but a new mystery has taken its place; where were these unusual pieces of glass made, and why do they differ so much in composition from all other pieces of European medieval glass so far analysed?

As sample No.228 had a similar composition to the three pieces from the Norman medallion, and as it was from the "bank" and did not have to be returned to the Five Sisters window, part of it could be analysed destructively, and this was kindly done by Pilkington Brothers Ltd., by courtesy of Dr D.S. Oliver, their Director of Group Research and Development; the results are given in Table III below.

TABLE III Chemical analysis (weight percent) of 12th century dark blue glass, Sample No.228

Silica (SiO_2)	61.7
Soda (Na_2O)	12.4
Potash (K_2O)	6.4
Magnesia (MgO)	2.2
Lime (CaO)	8.5
Manganese oxide (MnO)	0.9
Copper oxide (CuO)	0.2
Lead oxide (PbO)	0.3
Alumina (Al_2O_3)	2.8
Iron oxide (Fe_2O_3)	1.0
Phosphorus oxide (P_2O_5)	2.5
Total	98.9

The results from the MECA 10-6 instrument showed that, compared with No.228, there were slight but distinct differences between the other samples. Nos. 269 and 270 contained rather more lead and manganese than 228 and 268, and rather less lime. Thus this does not seem to be a case of one crucible of glass having an unusual composition, but at least two melts (and probably very many more) were made at some place where soda-rich low-lime blue glasses were being melted in the 12th century, and not the usual medieval composition which has so far been found in the 12th century glasses at York Minster and elsewhere.

4.3 FUTURE WORK ON OTHER 12th CENTURY GLASSES

In order to help in solving the mystery, two lots of work are being planned. First, it is hoped to study a large number of 12th century pieces very rapidly, for the presence or absence of potash, by using the scintillation counter mentioned in Section 5.2 (see item 1.1.4); this will show whether it is only the blue glass which is rich in soda or whether any other colours show the same effect. Second, with the help of M J.M. Bettembourg in Paris, it is hoped to borrow some pieces of blue glass from the West Window at Chartres for a similar non-destructive study which would show whether there are any similarities between the blue glass at York and at Chartres.

4.4 ANALYSIS OF EUROPEAN GLASSES FROM THE 18th TO THE 20th CENTURIES

The discussion above shows that four pieces of 12th century blue glass have anomalous compositions, but what about the other end of the time scale? The data in Table V of Section 5.3 show that glasses in the 16th and 17th centuries contained less potash than did the medieval glasses, and that the three 19th century glasses studied might have contained very little potash.

Some recent analyses, three of which were carried out by the British Glass Industry Research Association, are given in Table IV from which it can be seen that, after about 1770 when Dennis Hall was built in Stourbridge, the potash content may well not exceed 1%, with the notable exception of the Nailsea sheet glass in the period 1850-1873.

The lime content was generally more than 15% until the middle of the 19th century. However, the great period of Victorian restoration probably used glass which can readily be detected by any of the means discussed in the paper from the York Glaziers Trust.

TABLE IV The major components of window glasses in the 18th to 20th centuries

<table>
<tr><th>Component</th><th>Buxted Park ≠</th><th>Dennis Hall ϕ</th><th>St Helens (a)</th><th>Nailsea sheet glass(b)</th><th>Hartley Wood (c)</th><th>Kersten*</th><th>Dumas*</th><th>Noel Heaton (d)</th><th>1900-1920(e)</th></tr>
<tr><td>Silica (SiO_2)</td><td>55.5</td><td>73.3</td><td>64.3</td><td>61.6</td><td>68.5</td><td>60.4</td><td>64.7</td><td>66.9</td><td>71.8</td></tr>
<tr><td>Soda (Na_2O)</td><td>2.1</td><td>6.0</td><td>16.7</td><td>3.9</td><td>11.8</td><td rowspan="2">14.4</td><td rowspan="2">19.8</td><td rowspan="2">14.1</td><td rowspan="2">12.2</td></tr>
<tr><td>Potash (K_2O)</td><td>8.2</td><td>4.4</td><td>0.7</td><td>3.0</td><td>0.7</td></tr>
<tr><td>Magnesia (MgO)</td><td>5.6</td><td>5.0</td><td>?</td><td>3.5</td><td>?</td><td>0.4</td><td>?</td><td>0.4</td><td>?</td></tr>
<tr><td>Lime (CaO)</td><td>23.2</td><td>12.5</td><td>17.0</td><td>20.2</td><td>18.1</td><td>13.4</td><td>12.0</td><td>11.8</td><td>13.5</td></tr>
<tr><td>Alumina (Al_2O_3)</td><td>2.7</td><td>1.8</td><td>1.2</td><td>5.5</td><td>1.0</td><td>6.1</td><td>3.5</td><td>2.4</td><td>2.0</td></tr>
<tr><td>Iron oxide (Fe_2O_3)</td><td>1.1</td><td>0.8</td><td>?</td><td>1.5</td><td>0.8</td><td>3.1</td><td>?</td><td>2.9</td><td>?</td></tr>
<tr><td></td><td>98.4</td><td>103.8</td><td>99.9</td><td>99.2</td><td>100.9</td><td>97.8</td><td>100.0</td><td>98.5</td><td>99.5</td></tr>
</table>

≠ demolished in 1722
ϕ built in 1770
* quoted by Fowler in 1880 as examples of "recent glass"
(a) composition of glass made at the St Helens Sheet Glass Works, based on a recipe book of 1855
(b) samples of the period 1850-1873 collected by Sir Hugh Chance
(c) sample of "smoked glass" dated 10th November 1877
(d) based on a sample taken from 0.5 ton of comminuted glass collected by Noel Heaton and reported in 1909
(e) Pilkington's cylinder glass of the period 1900-1920, based on the batch formula, by kind permission of Pilkington Brothers Ltd.

5 RADIOACTIVITY OF MEDIEVAL GLASS

A report (YG/75/4A) has just been issued as part of the York Glaziers Trust Research Programme and it describes the work which has been done on the in-situ identification of medieval glass by the detection of its natural radioactivity. This seven-page document can be obtained from Mr Peter Gibson at a cost of 50p for photocopying and postage; it is summarised below for the benefit of readers of the News Letters.

5.1 INTRODUCTION

There is sometimes a need for distinguishing between genuine medieval glass and subsequent replacements, especially the clever Victorian "reproductions" of weathered medieval glass. This can be done without removing the glass from the window because most medieval glass was made with potash whereas both earlier and later glass was made with soda, and the potash can easily be detected by its radioactivity.

Unfortunately there are no sharp dates for these changes in alkali content and some 12th century blue glass from York Minster has been found to contain soda instead of potash but it is not known where it was made (see Section 4.2). The change from soda to potash in the 12th century was a result of the increasing demand for window glass and the migration of glass workers from the original coastal sites to woodland sites where wood fuel was more readily available. As a result, the soda-rich ash from maritime plants was replaced by potash-rich ash from beech wood or bracken and the glass had a significantly different composition (see Section 4). In the 17th century soda ash (as barilla) started to be imported from Spain and both soda and potash were used in making glass but it was not until the 19th century that the potash content dropped to negligible proportions when chemical soda ash was used.

Potash contains very small quantities (0.01%) of a naturally-occurring slightly radioactive component (the isotope ^{40}K) and this proposal for identifying medieval glass by means of its potash content is based on the assumption that all medieval glass was made in woodland sites and all replacement glass was made with modern chemicals; this has been found to be generally true (but see Section 4.4).

5.2 THE INITIAL EXPERIMENTS

The first calculations suggested that the radioactivity from medieval glass would be too small to detect but experiments with radiation monitoring films in York Minster showed that enough darkening would occur in two months, especially as the background radiation inside York Minster was lower than outside.

The success obtained in that building led to attempts to measure the radioactivity instantaneously, using a scintillation counter, and it was found that glass from the 12th to the 16th centuries gave 3 or 4 counts per second whereas 19th and 20th century glass gave only 0.5 count per second, indistinguishable from the natural background of radiation in the Minster. Thus it would be perfectly possible to identify more than 100 disputed pieces per day, if they could be reached easily and if the natural background were as low as that in York Minster. The cost of hiring the equipment with an operator to carry out such a survey would be of the order of £100 per day.

5.3 THE LATEST EXPERIMENTS WITH WATERPROOFED FILMS

The rather convenient situation in York Minster (with the low background radiation) could not be expected in most other locations. Moreover, it is often easier to reach the outside of a window than the inside, and the film would then be affected by rainwater unless it was waterproofed. Experiments were therefore carried out with waterproofed packs which also contained a control film. Briefly, the two monitoring films each "faced outwards" and they were separated by a layer of Perspex 6mm thick. The Perspex absorbed all the (β) radiation from the glass so that the inner film measured the glass radiation and the outer film measured the background radiation, and hence acted as a control.

A comprehensive trial was then carried out at York Minster using 17 sites on glass surfaces inside the Minster and 7 sites on the outside of the glass, covering the full range from 12th to 19th century glasses. The effective darkening of the films from the 24 sites in 3 months is shown in Table V.

TABLE V Darkening of the films by glass of different periods

Date of glass (century)	Effective darkening of the monitoring film		Statistical error of a representative point (± sigma)
	Inside Surfaces	Outside Surfaces	
12th	3*,58,59	56	± 4.5
13th	43,51,55	-	± 2.5
14th	41,43	49	± 3.5
15th	38,42	50	± 2.5
16th	15,21	38	± 2.5
17th	32	18	± 2.5
18th	14,16	19	± 1.8
19th	6,7	2	± 1.8

* This is one of the apparently rare 12th century soda-containing blue glasses which occur in York Minster (see Section 4.2).

5.4 CONCLUSIONS

It can be seen from the table that, with the exception of the rare soda-containing blue glass, all the glasses from the 12th to the 15th centuries have values between 38 and 59, whether the films are attached to the inside or the outside of the glass. From the 16th to the 18th centuries the values lie between 14 and 38 and these seem to correspond with the glasses made with imported barilla mixed with the wood ash; they can thus be distinguished from the earlier, medieval, glasses. The 19th century glasses have values lying between 2 and 7 and are again easily distinguished.

The self-contained pack, which costs £1.20 plus VAT at 1975 prices including development and interpretation of the films, has proved reliable and convenient to use. These packs can be obtained from Mr A.P. Hudson, at the National Radiological Protection Board, Northern Centre, 20 Clarendon Road, Leeds LS2 9PD, England.

All the films for the experiment were provided free by the National Radiological Protection Board and the work in the Minster was made possible by the ever-helpful Dean and Chapter.

6 NEW ABSTRACTS

214. DONNET, J.B., BATTISTELLA, R. and CHATENET, B. (1975) "A study of the surface of glass fibres", Glass Technology, 1975 16 139-148.

This is a highly technical paper which is abstracted here because of its bearing on the commencement of weathering of glass. Using extremely sophisticated techniques the authors showed that the surfaces of their glass samples are micro-porous, with pores about 1nm diameter, and that in about one month the surface becomes covered with about eight layers of adsorbed water. Electron microscopy showed that the originally smooth surface became irregular (lumps developed on it) after only a few days at 20°C and 65% RH. Thus detectable weathering of their durable glass starts at isolated points almost as soon as the glass is made.

215. ENGLE, Anita (1974) "The De Gands of Ghent", Readings in Glass History No.4, July 1974, pp 42-54.

This article uses family names in Hebrew, Flemish, French and English to trace the relationships between glassmaking families as they migrated from Asia Minor to Sicily, Lombardy, Lorraine, Normandy and eventually to England. References are made to many documents, e.g. from Tournai (1227), Cambrai (1309), Liège (1339), Troyes (1590), etc.

216. FRENZEL, Gottfried (1975) "Restaurierung und Konservierung Mittelalterlicher Glasmalerein" (Restoration and conservation of medieval stained glass), pages 5-10 of "Glasfenster aus dem Freiburger Münster, being the booklet for the Freiburg Exhibition, 15 June to 31 August 1975, 39 pages.

Freiburg Minster has a 10-year restoration programme which started in 1971, and pages 5-10 of this booklet describe what has been done to the windows. As a prophylactic measure, isothermal external protective glazing has been installed. It is realised that the mirror-effect of the external window may be criticised but preservation is urgent and must come first.

Little restoration work is required because the work of Fritz Geiges in 1908-1927 was so thorough. Fractures are edge-joined using colour-matched Araldite. Great care is needed when using acetone to remove the extensive cold over-painting carried out by Geiges. Loose black paint is fixed by repeated over-painting with a colourless synthetic resin solution, and about half of the weathering crust is removed with glass-fibre brushes and a scalpel. There are twelve excellent photographs illustrating these latter points, and also (in the catalogue of the exhibition) photographs showing the deterioration which has occurred in the panels.

217. LADAIQUE, Gabriel (1975) "The Glassmakers of the Vôge", Readings from Glass History No.5, April 1975, pp 1-17.

This article has been summarised by Dr Ladaique from his 1000-page thesis "Les Verriers de la Vôge, 1369-1789". It includes a sketch map showing the positions of the glassworks and provides much information about the four closely-interwoven families (Hennezel, Thietry, Thisac and Bisseval) whose members had to swear before a notary "before mid-day" to keep the secrets of the pots, raw materials, founding techniques and glass-making processes.

218. SCHOLZE, Horst, HELMREICH, Dieter and BAKARDJIEV, Ivan (1975) "Untersuchungen über das Verhalten von Kalk-Natrongläsern in verdünnten Säuren" (Studies of the behaviour of soda-lime-silica glasses in dilute acids), Glastechn. Bev. 1975 48, 237-246.

This rather technical paper is of particular interest for conservation because the authors found two interesting new features in the attack of glass by acid solutions. The first was that, in glasses with molar compositions $R_2O = 20$; $CaO = 6$; $SiO_2 = 74$, the extraction phenomena were quite different when R_2O = soda, or potash. Second, other glass compositions gave different extraction phenomena, even in this comparatively simple 3-component system. This helps to explain why there has so far been no uniform formula to describe the extraction phenomena, and hence the course of weathering.

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NOTE: Will readers of these News Letters please draw my attention to any papers which should be abstracted here. It would be particularly helpful if photocopies of the papers could be supplied. My address is 5, Hardwick Crescent, Sheffield, S11 8WB, England.

Roy Newton

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