ISSN: 0308-2237

(CV) NEWS LETTER 20

Comité Technique du Corpus Vitrearum

Physics, University of York 27 May 1976

CONTENTS

1 GENERAL

1.1 CONTROVERSIES OVER CHARTRES

When a polemical and emotional attack appears in a daily newspaper it is almost impossible to make an effective reply. If a reply is offered it will receive little attention because some other item of news then occupies the pages and, anyway, the readers will always remember the first impact, rather than the reply.

An unfortunate thing has happened to MM Grodecki, Taralon and Bettembourg, and also to Frau Dr Eva Frodl-Kraft (see item 2.1) because one of the French newspapers (L'Action Républicaine of Tuesday 21st October 1975) carried a two-page spread (pages D and E) prepared by an artist and an art-historian which made a stormy and unjustified attack on the restoration of the Jesse window at Chartres. Moreover, to add to the impossibility of preparing a reasoned and effective answer, the paper printed a special "Plea to the President" which it invited readers to cut out, sign, and send to the President of France (without a stamp on the envelope!) because only he can "put an end to what is happening"!

Although the event took place last October, it has only recently been published in Britain, eg "The Times" (London) of 20th April. It is, however, not too late for us all to offer our sympathy to MM Grodecki, Taralon and Bettembourg. Here I am reminded of Edmund Burke's advice:-

> "Those who would carry on great public schemes must be proof against the worst fatiguing delays, the most mortifying disappointments, the most shocking insults, and, worst of all, the presumptuous judgment of the ignorant upon their designs."

However, the Mayor and the other inhabitants of Chartres fully approve of what has been done and we hope that the restorations will continue without any irritating accompaniments.

1.2 OXIME-CURED SILICONES

Readers of N.L. No. 18 (item 3.8) will have noted that we are on the look-out for oxime-cured silicones because they do not release acetic acid on curing, which can attack the leads. Miss Anne Moncrieff, of the Victoria and Albert Museum, has written to say that Dow-Corning Building Sealant 780 is oxime-cured. She is also collecting information about other silicones.

1.3 AIR FLOWS IN ISOTHERMAL GLAZINGS

Dr E. Bacher, of Vienna, has kindly written to me about some measurements he has made in the interspace of the isothermal glazing on the church of St Walpurgis in Steiermark. In contrast to my statement in item 2 of N.L. No.15 he found the air-flow to be upwards; I said it would be downwards.

The isothermal glazing at St Walpurgis was installed in 1973(?) and follows the construction used at Graz (see ÖZKD 1973 27 66ff). Dr Bacher made the following measurements on south window II on 12th March 1976, at 12.30 when the sun was shining:-

outside temp. - 2°C, 59% relative humidity

temp. in building 0°C, 50% " "

The air flow in the interspace was followed by means of a Draeger smoke tube CH216 (see N.L. No.14, item 2.5) and it was found to be upwards with a velocity of about 50cm/s.

Dr Bacher points out that these results do not agree with mine, derived from the isothermal window at Sheffield, and that this emphasises the complexity of these situations. It shows once again that assumptions can all-too-readily be made about the effects of restoration procedures, and that in a different context the results may be the opposite from those expected. He appeals for many more measurements to be made, on as many windows as possible, under widely differing environmental conditions.

I am glad that he has obtained these results, and that they are different from mine because this makes people think more deeply about the problem. I rather suspect that his air-flow was upwards because the building was very cold inside, and the sunshine on the south-facing window caused the stained glass to become warmer (see N.L. No.16, item 2.2.4). Thus the air in the interspace would be warmer than 0°C, it would be less dense, and it would move upwards, rather like the situation which I found in the Beauchamp Chapel, Warwick (see N.L. No.18, item 1.3.2).

I do hope that more people will carry out experiments with these Draeger smoke generators because they are not particularly expensive, they are very easy to use, and they show exactly how the air is moving. We must learn as much as possible about air movements in the interspace when the ventilation is from the outside or from the inside.

1.4 REMOVING LEADS FROM OLD GLASS

The question of how best to remove leads from old glass was raised in item 1.1.6 of N.L. No.18, but so far only one reader has replied. Mr G.A.K. Robinson, of Joseph Bell & Son Stained Glass, Bristol has written to say that he does this by pinching the lead with pliers, stretching it away from the glass, and then cutting it. He says this is quite simple to do and the glass never breaks.

1.5 PROCEEDINGS OF THE 9th (PARIS) CVMA COLLOQUIUM

These have now been published in the Jan-Feb 1976 issue of Verres et Réfractaires Vol 30, No.1, pp 1-106.

1.6 GRANT FOR MELTING SYNTHETIC MEDIEVAL GLASS

The Nuffield Foundation has awarded the sum of £500 to Professor R.G. Newton for the purpose of obtaining ten new synthetic medieval glasses (model glasses) to be used in experimental work on conservation, further details will be given in a future News Letter.

2 "CONTRARY OPINIONS"

In this new feature of the News Letters, which started in No.19, I stated that differences of opinion can be expressed for which the Editor takes no responsibility. However, two of my correspondents have had such an extreme difference of opinion over the use of Viacryl resin on the windows at Chartres, that I have been reluctant to publish either letter in full; instead, in item 2.2, I have prepared my own summary of the situation.

In item 2.1 our distinguished correspondent, Frau Dr Eva Frodl-Kraft, expresses her legitimate feelings about the way she has been wronged by an article in a French newspaper.

2.1 A LETTER FROM FRAU DR EVA FRODL-KRAFT

"I am greatly distressed by the remarks made by M Popesco in the French newspapers (see item 1.1) concerning the conservation of the west windows at Chartres, (a) because his remarks are misguided, (b) because he has quoted without my permission from an unpublished document of mine written as long as thirteen years ago (!) and (c) because he has used my name as purporting to support his views, without any authority to do so.

When considering what might be done about preserving these windows at Chartres one must consider the west façade in its entirety. This fine example of medieval architecture (one of the most important from the Middle Ages) is extremely sensitive with regard to its surface relief. If external protective glazing had been used there would have been some architecturally disastrous changes in the external appearance of the three large and dominant windows which would seriously have affected the whole façade. Thus the use of external protective glazing, which has been widely employed in other situations was, right from the beginning, out of the question on aesthetic grounds and the conservators had no choice in doing what they did.

The protection of monuments creates difficult situations, not only due to the scientific and technical problems but also because the aesthetic aspects have laws of their own which we have to study and respect, or we will destroy the work of art at the same time that we are "saving" it in a physical sense.

Never in the history of conservation of windows in France has such thorough and painstaking preparatory work been carried out in the laboratory, nor have the safeguards been examined so carefully. Although we cannot be absolutely sure how the Viacryl coating will behave in the future, the regular inspections to be carried out by the Direction des Monuments Historiques will make it possible to detect any changes in the coating as soon as they occur. Thus any dangers to the windows can immediately be eliminated by taking the necessary measures.

I am writing this note because my name was drawn into the affair in a manner which was quite contrary to my own opinions, by using unpublished manuscript material prepared a long time ago, and I wish to make it widely known that, instead of supporting M Popesco in the way that he tries to claim, I entirely disassociate myself from his remarks."

2.2 THE VIACRYL COATING AT CHARTRES

Item 2.1, by Frau Dr Eva Frodl-Kraft, discussed the furore about the loss of the overall blue colour in the restored west windows at Chartres Cathedral but there is another extreme difference of opinion about the use of the "protective" resin coating, Viacryl VC 363.

Various people have written to me about the keen controversy which is raging at the moment, and I have been asked to open the columns of the News Letters to this correspondence. However, I am most reluctant to do anything which might spread the controversy and I shall therefore summarise the situation as I see it!

Dr J.C. Ferrazzini, who is the Swiss national representative on the Comité Technique, has written to Weltkunst (see abstract No.224 on page) expressing his conviction that, despite the careful work done at Champs (see abstract No.220) using small pieces of glass, the Viacryl coating at Chartres may (a) lose adhesion unless the outsides of the windows are cleaned more carefully than might be feasible (or even desirable from the point of view of general conservation) when restoring a large window and (b) the vibrations which are always present in large windows may cause the leads to scrub the Viacryl film away and thus permit water to reach the interface and damage the glass.

Dr Ferrazzini admits that his own experiments are not complete but believes that their obvious trends cannot be overlooked ("Meine Versuche sind heute noch nicht so weit vorangeschritten, dass entgültige Werte zur Verfügung stehen, doch sind eindeutige Tendenzen nicht zu übersehen"). He also states that his assertions are supported by experience in practice and from discussions with plastics experts ("Meine Aussagen in der Weltkunst, stützen sich auf Erfahrungen in der Praxis und auf Gesprächen mit Kunststoffspezialisten"). He also draws analogies with difficulties in the protection of metals against rust in cases where the Viacryl/Desmodur combination has actually been used, but I personally am not sure that such an analogy can be drawn. (RGN - he has not yet quoted his experimental results with Viacryl-protected glasses.)

The remarks in Weltkunst have naturally upset the French experts. Professor Louis Grodecki, the President of the Corpus, as well as of the French National Committee, has written to say that Dr Ferrazzini's arguments are tendentious, and some of them are wrong.

As I see it, neither side has yet produced experimental evidence about the real point at issue, that is whether the glass beneath the Viacryl can be attacked by weathering agents, and the correspondence is full of opinions. Even the work of Bettembourg (abstract No.220) involved many tests on the resin but there were no experiments on what happened to the surface of the glass beneath the resin (see also item 6), although this is now being done. I hope that the combatants will wait until more experimental results are available, for example along the lines of the Canterbury experiment, where glass which had been coated with Viacryl had been exposed to "accelerated weathering" in the form of wet sawdust, reported in Section 6.

3 SULPHUR DIOXIDE AND GLASS—PART 3

In section 5 of N.L. No.15 I raised the question about whether sulphur dioxide ever attacks glass, or whether it only produces the gypsum (which we find on the surface) by converting the hydroxides which are formed by attack by water. In section 2 of N.L. No.17 I again raised the question in connection with Fig. No.1.

Now Mr N.H. Ray, of the Corporate Laboratory of Imperial Chemical Industries Ltd. at Runcorn in England, has kindly written to me with a new, and extremely interesting, hypothesis.

He points out that four processes are known to occur in the corrosion of glass by aqueous solutions:-

3.1 ion-exchange between glass and solution,

3.2 dissolution of reactive gases from the atmosphere (sulphur dioxide and carbon dioxide) and their reaction with the products of 3.1,

3.3 diffusion of ions through the solution under the influence of an osmotic gradient, and

3.4 precipitation of insoluble salts.

There can be little doubt that 3.1 involves the exchange of cations from the glass (e.g. sodium, potassium, calcium, etc.) for hydrogen ions from the water. Two things happen: (a) a layer of hydrated silica is formed on the surface of the glass; (b) if no other agent (such as sulphur dioxide) is present the removal of hydrogen ions from the water causes the solution to become alkaline near the surface of the glass, and this would lead to further corrosion of the glass (because alkalis can dissolve hydrated silica).

But 3.2 occurs because sulphur dioxide and carbon dioxide (which are always present in the atmosphere) are absorbed by the alkaline solution and partially neutralise it. This has two effects: the dissolution of the hydrated silica is suppressed and the concentration of hydrogen ions is increased so that 3.1 can continue.

Glass exposed to the weather will be periodically wetted, followed by drying. The layer of hydrated silica is unstable on drying, so that it shrinks and cracks, forming fissures which lead down to the underlying, unaltered glass. When the glass is again wetted, water containing the reactive gases can penetrate the fissures.

There will also be an osmotic gradient in the water film because salts are deposited on the glass when it dries out, and the fresh rain which falls on it contains few salts. The osmotic gradient (3.3) causes the most soluble salts to diffuse from the glass towards the surface of the water.

The most soluble salts are the acid sulphites such as $Ca(HSO_3)_2$ and $Mg(HSO_3)_2$; the former has a solubility of 11g per 100g of solution at 20°C and the latter is very soluble. Near to the glass surface the anions will be hydroxide, acid sulphites, minor amounts of acid carbonates and perhaps some sulphates. The acid sulphites which migrate to the surface will be affected by the wind and some sulphur dioxide will be lost, thus converting acid sulphites to normal sulphites. Magnesium sulphite is very soluble but calcium sulphite is practically insoluble (0.004g per 100g at 20°C) and will be deposited, as stage 3.4.

Hence one would expect little or no calcium to be found near the glass surface, a high concentration of deposited calcium sulphite in the fissures, and a slightly lower concentration at the surface of the pit where it has been oxidised to the more-soluble gypsum (solubility is 0.2g per 100g at 20°C); this is precisely what is shown in Fig.1 of N.L. No.17.

4 RESEARCH FACILITIES IN EUROPE–PART 2

In item 4 of N.L. No.19 I started listing the organisations which possess suitable experimental facilities, and other expertise, which could be helpful in the study of stained glass; four (nos. 4.1 to 4.4) were listed in N.L. No.19.

The list is extended, below, by an additional six organisations; they are numbered 4.5 to 4.10 to avoid confusion with the first list, and to make reference easier.

4.5 CORNING Corning Museum of Glass, Corning, New York 14830, USA.

Since 1960, the Scientific Research Program at The Corning Museum of Glass has been devoted to the use of chemical analyses and other types of scientific investigations to learn as much as possible about ancient glass and ancient glass technology. For the most part, the program has dealt with glass of earlier historic periods, but in 1962 projects were initiated dealing with medieval stained glasses. Until 1967, these dealt mainly with chemical analyses, isotope studies, and other methods of examination aimed at the classification of stained glasses according to the places, dates, and methods of manufacture. In 1967 part of this effort was turned towards conservation work, and both lines of research are currently being pursued.

While The Corning Museum of Glass does not have a laboratory of its own, the Museum is able to draw upon the extensive research facilities of the Corning Glass Works. In the past, the Museum has prepared several series of synthetic stained glasses for use in evaluating the durabilities and weathering resistance of stained glasses, the physical properties, and the effects of various components on the properties. Experiments have been carried out on methods of cleaning (in particular, the air abrasive cleaner) and certain preservation techniques. For the most part, these have consisted of experiments with inorganic coatings. At present Dr Brill, the Research Scientist at the Museum, is co-operating with Dr Peter Sparks of the University of Delaware in testing the effectiveness of thin water-repellent films in the preservation of stained glasses. The assumption, which requires further verification, is that water repellency may confer protection to glasses exposed to the weathering elements. This system has the advantage of being inexpensive and easily applied - perhaps when the glasses are cleaned. Great longevity is not the goal, because, if a process is inexpensive and the protection easily renewed, that might suffice. A group of synthetic glasses duplicating known compositions is being produced so as to standardise the testing procedures. It is hoped that sufficient glass will be available to provide other laboratories with samples.

The greatest need at present of American scientists doing research in stained glass is that of travel funds which will allow them to keep in close personal touch with their counterparts in the United Kingdom and Europe.

4.6 MURANO Stazione Sperimentale del Vetro, 30121 VENEZIA-MURANO, via Briati 10, Italy. Tel. 739002-3.

This institute, which serves the Italian glass industry, is well-equipped to assist also in studies of medieval windows and its publications include some papers on the history of early glassmaking. It can carry out chemical analysis of glasses, determinations of physical properties, accelerated weathering tests, and the preparation of experimental melts of glasses.

The equipment in the chemistry section includes flame photometry, atomic absorption spectrometry, various spectographs, X-ray diffraction and fluorescence analysis. The laboratory is well known for its studies of the durability of glassware and its contributions in this field to the work of the International Commission on Glass. Further information can be obtained from Professor Bonnetti.

4.7 PARIS The Laboratoire de Recherche des Monuments Historiques (LRMH), 77420 CHAMPS SUR MARNE, France. Tel. 957-25-56.

The researches carried out by the LRMH, under the authority of the Direction de l'Architecture du Secrétariat d'Etat à la Culture, have a double function:-

(a) to use systematic studies to provide fundamental knowledge about ancient materials and techniques;

(b) to improve the techniques of restoration through scientific recording and by researches on new procedures, or products, and their application.

Beyond this double rôle (of applied research and operational activities) the laboratory has the task of co-ordinating long-term researches in certain other institutes in France through a series of contracts whereby their expertise and equipment is put to the best use. For example:-

(i) atomic absorption spectroscopy at the Laboratoire de Recherche des Monuments Historiques is used for the analysis of glasses and of corrosion products;

(ii) X-ray fluorescence analysis, and X-ray diffraction are used at the Laboratoire des Musées de France for general analyses;

(iii) electron microscopy, microprobe analysis and X-ray diffraction are used at the Ecole Nationale Supérieure de Chimie de Paris, or at the College de France, to study the corrosion processes in glass.

These techniques are thus combined in the best way to gain a better knowledge of the compositions of ancient glasses and their corrosion processes. In parallel with this, restoration processes (cleaning) and conservation techniques (protective films) are studied.

4.8 SHEFFIELD (2) The British Glass Industry Research Association, Northumberland Road, Sheffield S10 2UA, South Yorkshire, England. Tel. (0742) 686201.

BGIRA has several facilities that may be useful to conservationists in the field of stained glass. Chemical analyses are undertaken using "wet chemistry" or instrumental techniques, including X-ray fluorescence, atomic absorption spectroscopy and gas chromatography, while chemical durability testing in various forms has been a feature of the Association's research activities for many years. Measurements of most of the major physical properties of glass can also be carried out on a consultative basis. Although none of the current research programme is directly concerned with stained glass, the RA has recent experience in this field having completed a contract for the Department of the Environment in the spring of 1975. Further information can be obtained from Mr C. Thorpe, the Director.

4.9 VIENNA Museum für Völkerkunde, Neue Burg, Corps de Logis, A 1010 WIEN.

Dr Ing. Wilhelm P. Bauer is a member of the Austrian Technical Sub-Committee and he carries out investigations on the chemical composition of ancient glass, corrosion products and weathering processes on ancient glass, with special emphasis on methods of conservation and restoration.

4.10 WÜRZBURG Institut für Silicatforschung der Fraunhofer-Gesellschaft, Neunerplatz 2, 8700 WÜRZBURG, Germany. Tel (0931) 4.20.14.

This institute replaced the former Max-Planck-Institut für Silicatforschung in 1970. Professor Dr H. Scholze has been the Director since 1971.

The institue is concerned with applied research on non-metallic inorganic materials, and an essential part of the research work is done in the field of glass, with particular emphasis on surface properties.

Two special fields of research are of interest in connection with medieval glasses. The durability of commercial glasses, and also of the so-called "sick" glasses, is being studied. Dipl-Ing. M. Koutecky has a project for detecting "sickness" and for preventing it as far as possible. Dr I. Bakardjiev is concerned with the chemical durability of glasses, the main result of his work being the discovery that the speed of the corrosion processes is determined by the hydrogen ions and not by the network modifiers.

In addition, the new techniques of SIMS and ESCA are being used to analyse glass surfaces to a depth of a few Ångstroms. Dipl-Phys. H. Schillalies has a project in this field to study the changes in surface composition which result from forming processes or from storage of the glass.

The institute also has a scanning electron microscope, X-ray fluorescence, X-ray diffraction, and many types of spectrometer.

5 12th CENTURY SODA GLASS AT YORK MINSTER

In N.L. No.18, item 1.1.4, it was pointed out that soda-glass is extremely scarce in the 12th century but four pieces, all of them blue in colour, had accidentally been discovered in the lower central Normal medallion of the "Five Sisters" window at York Minster. On 8th April, by kind permission of the Dean and Chapter, a massive experiment was carried out with the object of testing every panel from the Minster which contained 12th century glass.

With the available equipment an experiment of this kind can only be carried out in a place where the environmental radioactivity (the "background radiation") is extremely low. The normal background radiation (2-3 counts per second) is too high but it was found that the K.O.Y.L.I. Chapel had a low background count of only 0.5 to 1.5 per second and the ever-helpful Dean and Chapter gave permission for the experiment to be carried out there. Accordingly, all the 12th century glass which was transportable (100 panels) was brought to the chapel for testing. Two panels were in situ and hence a ladder was placed against the sill of the "Five Sisters", and scaffolding was erected in front of window No.37 so that the "Jesse Tree" panel and the Norman medallion could be tested, making 102 panels in all.

5.1 THE TESTS

Mr A.P. Hudson, of the National Radiological Protection Board (Northern Centre) kindly brought the scintillation counters from Leeds (see item 5.2 of N.L. No.18). Tests were carried out throughout the entire day with the assistance of voluntary helpers from Sheffield, and from the University of York. In all, 1838 tests were carried out on an estimated total of 20,000 pieces of glass in 105 panels (three panels were accidentally tested twice). The probe of the scintillation counter was placed over single pieces of glass (if they were large enough) or over groups of small pieces. If the radiation was above 5 counts per second, all the glass under the probe was considered to be potash glass. If, for a single piece of glass, the radiation was less than 1.5 counts per second then an adhesive label was placed on the glass. If, for a group of pieces the radiation was less than 5 counts per second, then pieces of lead sheet were placed on the pieces of glass until the one which gave the low count was isolated, and a label was attached.

As each panel was completed, Mr Peter Gibson examined all the pieces which had labels to decide whether they were genuine 12th century or whether they were recent replacements; the labels were then removed from the replacements.

5.2 THE RESULTS

A total of 72 pieces of 12th century soda glass was discovered (about 0.3%). Of these, 67 were blue and five were of other colours (1 white, 2 green, 1 red and 1 brown) but all of these non-blue pieces were rather small and each ought to be checked carefully on the Isoprobe before they are confirmed as being 12th-century non-blue soda glass. (It must be emphasised here that there were very many pieces of 12th-century blue glass which were radio-active, and hence contained potash, but seemed to be "exactly the same" in colour as the soda glass. Hence it seems that the 12th-century craftsmen used blue glass of a suitable colour for their work and they were apparently indifferent to its origin.)

The blue soda glass was not found in every panel; 76 panels had none. Of the 72 pieces of soda glass, 32 were found in two panels; 17 in the Norman medallion (and perhaps even more, because many pieces were too small to test) and 15 in the Jesse Tree panel. There were 8 pieces each in windows C.23, C.24 and C.25, 5 in C.26 and 4 in C.27; none of the other windows contained more than 2 pieces of soda glass.

5.3 THE SPECULATIONS

Speculations have already started as to how this quite exceptional soda glass came to be in the Minster at all, and three quite different hypotheses have been put forward.

5.3.1 Professor Roy Newton has been told that Dr W. Bauer has analysed two pieces of glass, dated to 1150 from Phrygia (Turkey) and that they are both soda glasses of a similar composition to the York soda blue (see Table III on p.9 of N.L. No.18). He therefore asked whether the Crusaders might have brought some Turkish blue glass back with them, but Dr Peter Newton, FSA, of York University, thinks that this is most unlikely because there is no mention of glass in Paul E.D. Riant's "Exuviae Sacrae Constantinopolitanae" 3 vols Genevae 1877-1904.

5.3.2 Frau Dr Eva Frodl-Kraft, of Vienna, has remarked that Theophilus (Chapter XII De diversis vitri coloribus non translucidis) describes a special blue glass which he calls "saphiri graeci" which was made by melting antique blue stones (i.e. glass). The York Minster 12th century blue soda glass is extraordinarily durable, as is also the "bleu de ciel" at Chartres and she asks whether there might be a link between the two. Here I am delighted to have the opportunity of giving a preliminary note about a result which has arisen from the co-operation between Dr G.A. Cox of the University of York and M J.M. Bettembourg of the LRMH at Champs-sur-Marne. On 4th May M Bettembourg took three pieces of blue glass from Chartres to York to have them analysed by Mr Mark Pollard. The two 12th-century pieces were soda-glass and the 13th-century piece was a potash-glass (fuller results will be reported in a later News Letter).

5.3.3 Mr Kenneth Harrison, FSA, has suggested that some of the glass from the Saxon Cathedral at York (which would surely have been a soda glass) might have been re-melted in Norman times to make the large pieces which now exist. It is not known that any Saxon glass has ever been found, but Mr Peter Addyman and Mr Derek Phillips have some glass from the North Transept of the Cathedral which was burnt down in 1137 and it is hoped that Dr G.A. Cox will carry out some analyses on these pieces to throw light on their place in the scheme of things.

Finally, it is necessary to thank the Pilgrim Trust for supporting the cost of these studies with their special grant for scientific research.

6 VIACRYL VC 363 AND SAWDUST

It is not easy to devise accelerated weathering tests for medieval glass to produce in a few months a visible effect on the surface which resembles the effect of exposure to the weather for several centuries! By accident it was discovered that exposure of the poorly-durable "No.2 glass" to wet English Oak sawdust for six months could produce clearly visible pits in the surface up to 60 µm deep - see N.L. No.16, item 3.3.

Thus a possible accelerated test procedure had been discovered, despite its rather unorthodox ad hoc nature.

This test has been criticised by J.C. Ferrazzini at the Paris Colloquium in September 1975 during the discussion of my paper on triangular diagrams (see page 33 of Verres et Réfractaires, 1976, 30) on the grounds that atmospheric weathering of medieval glass does not involve organic acids such as are present in sawdust. However, he has verbally agreed with me that the acids present are relatively weak ones and that if a Viacryl VC363 resin coating fails to protect poorly durable glass against attack by wet sawdust, there would be a strong indication that the resin coating would also fail to protect the glass against attack by the weather. Just such a result is reported in item 6.2 below.

In N.L. No.16, item 3.3 it was stated that the second piece of No.2 glass would remain in the wet sawdust for another six months (i.e. for one year in all) and that a piece of polished plate glass would be put in the sawdust for six months. The results of this experiment are reported in 6.1 below.

6.1 EXPOSURE OF GLASS No.2 TO WET SAWDUST FOR 12 MONTHS

It will be remembered that the description of the 6-months' experiment (N.L. No.16, item 3.3) contained an error. It had wrongly been assumed that the smooth surface of the glass, in which the pits had formed, was the same as the original fire-finished surface of the glass. However, it was subsequently realised (N.L. No.17, item 2.2) that the original surface could be seen only where the edge of the glass had been protected by the leads, thoughtfully applied by Mr Gibson before the experiment started.

It was then realised that the wet sawdust had had two effects on the fire-finished surface: it had produced the pits shown diagrammatically in Fig.8 of N.L. No.16, and in the photograph in Fig.2 of N.L. No.17 (at C); but it had also removed the rest of the glass between the pits and produced a fairly smooth surface which was about 10 µm lower than the original surface (a kind of acid-polishing seems to have occurred). Also, where the glass had been airbraded (FGJK in Fig.8 of N.L. No.16) the surface seemed to have been lowered by about 9 µm with the result that it appeared smoother than before.

The continued attack by the sawdust on the second sample (for the period from 6 months to 12 months) produced a rather surprising result because the pits in the surface are now much less evident. The "Talysurf" trace produced a CLA value (see item 6.2 below) which was only 19 micro-inches (0.48 µm) compared with the 120 micro-inches (3.05 µm) of roughness which had existed a year before. The remnants of the pits (at least those encountered by the trace) were only 3 to 5 µm deep and the vertical magnification on the Talysurf had to be increased to 2000x in order to obtain a reasonable display. Further sophisticated study of both samples (6-months' and 12-months' treatments) will be required before we can be sure whether the 12-months' pits are shallower because the surface of the glass between them has been "polished" away or whether some other explanation should be sought. There is also the possibility that the original (6-months') pits were produced by localised attack from point contacts with damp sawdust before all the sawdust became so wet that the surface was covered with an acid liquid which could attack the whole surface.

Two other samples were exposed to the wet sawdust for this period of six months; a piece of polished plate glass and a piece of "acid-polished" Glass No.2. The very durable plate glass seemed to be quite unaffected by the treatment, e.g. reflections of objects in the surface showed no detectable distortion. The "acid-polished" sample had been so badly attacked by the hydrofluoric acid that the surface became iridescent and this part of the experiment was a failure.

6.2 EXPOSURE OF VIACRYL-COATED GLASS TO WET SAWDUST

As part of the research programme of the Canterbury Glass Restoration Studio, a sample of Glass No.2 was airbraded for 30 seconds using No.3 powder and then sent to Sheffield so that the roughness could be measured on the Talysurf; see the upper trace in Fig.1. It was then returned to Canterbury to receive a coating of Viacryl VC363, hardened with 20% of Desmodur N75, cured at room temperature for 24 hours, and then sent to York to be placed in the wet English Oak sawdust in the Deanery "Dug-out".

I am indebted to Mr Frederick Cole at Canterbury and Mr Peter Gibson at York for their helpful co-operation in carrying out this important experiment, and for allowing me to report the results here.

After remaining in the wet sawdust for $4\frac{1}{2}$ months the sample was sent to Sheffield where the Viacryl coating was removed by immersion for 5 minutes in Cital 12-12 and the roughness again measured on the Talysurf (see the lower trace in Fig.1).

The Talysurf makes a trace of the roughness on an enlarged scale (in Fig.1 the horizontal scale has been magnified 20 times, and the vertical scale 1000 times, so there is a 50-fold distortion of the roughness) and it will also measure the average surface roughness in relation to any curvature in the surface. The CLA (Centre-Line-Average, or the average deviation from a centre line which itself represents the average surface) figure thus gives the true roughness of the surface, as if the surface was quite flat.

Three test-lines on the surface were defined by marks made with a scriber and the CLA values before coating with Viacryl are given in Table I.

TABLE I CLA values before coating with Viacryl VC363

	Average surface roughness	
	Micro-inches	µm
Line 1	120	3.05
Line 2	97	2.46
Line 3	111	2.81

TABLE II CLA values after $4\frac{1}{2}$ months in wet sawdust

	Average surface roughness	
	Micro-inches	µm
Line 1	80	2.02
Line 2	82	2.08
Line 3	100	2.54

After removing the Viacryl the airbraded surface seemed to the unaided eye to be unaltered, but microscopic examination showed that the surface was now "crazed" with a random network of fine cracks, suggesting that the acid liquid from the sawdust had reached the glass and affected it.

The Talysurf measurements, also, indicate that the glass had been attacked. First the average CLA value from Table I is 2.81 µm and the average from Table II is 2.21 µm, showing a loss of roughness of 21% in $4\frac{1}{2}$ months. Also, in Fig.1, the trace made before treatment had an effective width (between the lines AB and CD) of about 19 µm but after treatment (between the lines EF and GF) the effective width was only about 14 µm, showing a loss of 5 µm, or 26% The assumption, therefore, is that the acid liquid from the sawdust succeeded in penetrating the Viacryl VC363 coating and in attacking the glass, removing about 5 µm of its thickness.

This smoothing of the airbraded surface was less than had occurred when no protection was used on the glass, as in Figs 7 and 8 of N.L. No.16, where a loss of 9 µm occurred in six months. If we assumed that a loss of 5 µm in $4\frac{1}{2}$ months would correspond to a loss of $6\frac{1}{2}$ µm in 6 months, then the sample with no protection would have lost 9 µm of thickness in that time whereas the sample coated with Viacryl would have lost $6\frac{1}{2}$ µm, or 70%. On this basis one might conclude that the Viacryl coating gave a "protection" of 30%.

In this experiment the Viacryl had been applied in one coat only and it is possible that "pin-holes" in the coating had allowed the acid-liquid to reach the glass. The same piece of glass was therefore given two successive coats of Viacryl, being allowed 3 days to harden between the two coatings. It has now been replaced in the wet sawdust and will remain there for 12 months. It is hoped that the results of this test will be reported in News Letter No.25 or thereabouts!

Only Viacryl VC 363 was used in this test, and not any other resin, because there is no doubt that Viacryl VC 363 is the "best" resin available (see N.L. No.14, item 5, and Abstract No.220).

The out-of-pocket costs of this work, such as the Talysurf tests, etc., were met from the Pilgrim Trust Special Grant, to the extent of about £20.

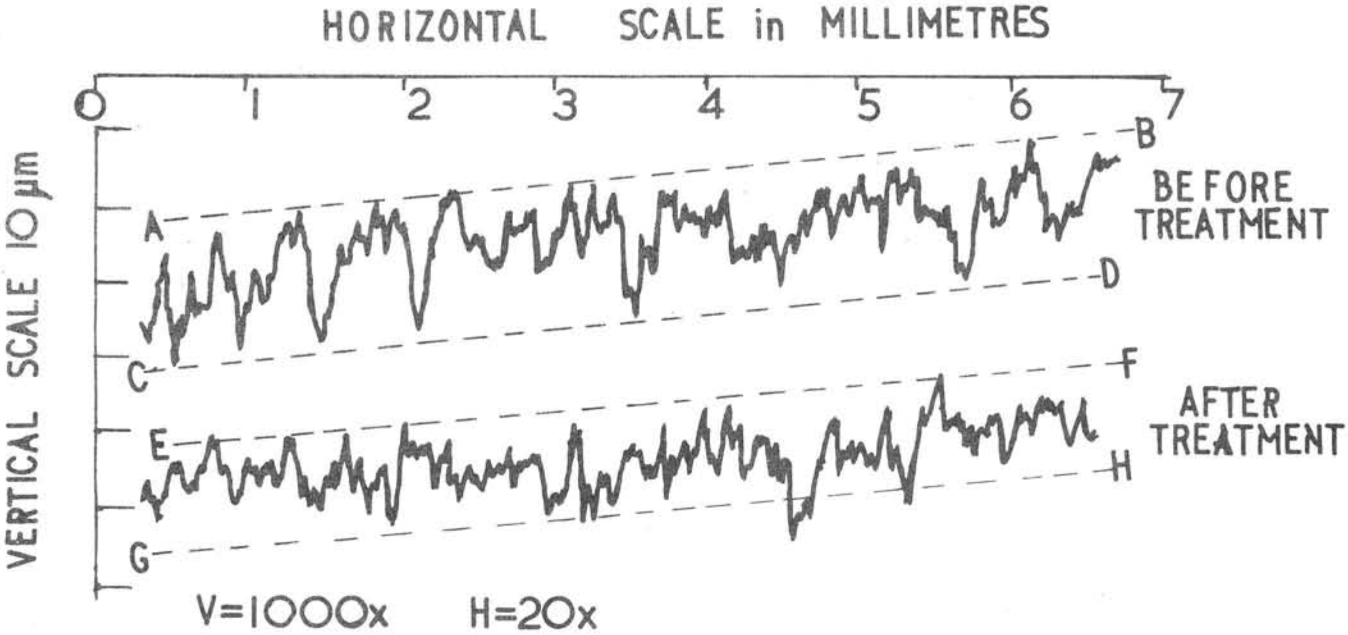

Fig. 1 These two charts show greatly enlarged traces of the roughness of the airbraded surface of the poorly-durable glass before the experiment and after being coated with Viacryl VC 363 and exposed for 4½ months to wet English Oak sawdust. The surface after the treatment is less rough than the surface before treatment and this indicates that the slightly-acid liquid from the sawdust has penetrated the 'protective' coating of Viacryl VC 363 and attacked the surface of the glass below it. Thus the Viacryl coating was not completely protective. In the diagram the horizontal scale has been magnified 20 times and the vertical scale 1000 times; thus there is a 50-fold distortion of the roughness of the surface. The charts slope upwards to the right because the glass was not quite flat, by about 1 in 600 ! These charts can be compared with *Figs. 7* and *8* in N.L. No. 16.– See item 6.2.

7 NEW ABSTRACTS

Nos 219 to 226, and also 171, and 202-206

219. BETTEMBOURG, J.M. (1976a) "Composition et alteration des verres de vitraux anciens" (Composition and weathering of glasses in ancient windows.) Verres et Réfract. 1976 30 36-42.

The author discusses the mechanism of weathering of glass, and includes biological agents such as mosses and lichens which encourage the formation of humid conditions on the surface of the glass; his Figs 1 and 2a show excellent colour-photographs of attack by lichens and algae. The many chemical analyses of medieval window glasses now becoming available (he quotes 44 in three tables) are opening the way to establishing correlations between glass composition and weathering behaviour.

In discussing the effect of composition of the glasses, the author defines three parameters:-

"Si" = Si + Al + P + Fe + Ti ....

"R_2" = Na + K ....

"R" = Ca + Mg + Cu + Co + Mn + Pb ....

He then shows that a plot of "Si"/"R_2" against "R_2" gives a smooth curve with points for 36 glasses lying close to the line, so that he has clearly established an important relationship. Durable glasses have SiO_2 above 54%; glasses which weather by pitting have SiO_2 = 48-57% and K_2O = 15.5-17.5%; those which weather "uniformly" (i.e., by crusting have SiO_2 = 46-52% and K_2O = 15-27%.

Because water plays such an important part in the corrosion of glass he studied the solubility of medieval glasses in water, using a standard grain test. He also concluded that SO_2 attacks the corrosion products, rather than the glass.

220. BETTEMBOURG, J.M. (1976b) "Protection des verres de vitraux contre les agents atmosphériques. Étude de films de résines synthétiques. (Protection of window glass from atmospheric agents. Study of coatings of synthetic resins.) Verres et Réfract. 1976 30 87-91.

The first part of this paper is exactly the same as that abstracted as No.170 in N.L. No.11 but three new sections have been added: IV permeability to SO_2; V adhesion of resin films; and VI re-fixing of loose paintwork. In studying the permeability to SO_2 the resin film was applied to a filter paper which was exposed to a concentration of SO_2 either 1,000 times, or 10,000 times greater than that of a very polluted atmosphere (500 $\mu g/m^3$) at elevated temperatures. The Viacryl VC363 film showed no permeability to SO_2, nor any discolouration after long periods of exposure. The adhesion of the resins to medieval glass was assessed by a scratch-test after accelerated ageing. Some resins lost adhesion but the Viacryl showed the best adhesion. After all ageing treatments the Viacryl remained soluble in "Cital 12-12".

Before cleaning the glass, the paint (both the lines and the half-tones) must be carefully inspected. If the paint is loose it can be fixed and consolidated by using a diluted solution of Viacryl in ethyl acetate which is applied carefully to the paint, using a capillary tube. Cleaning and re-fixing can be carried out simultaneously. Any excess resin can be removed with ethyl acetate on cotton wool.

221. BETTEMBOURG, J.M. and PERROT, Françoise (1976) "The restoration of the windows on the west face of Chartres Cathedral" (La restauration des vitraux de la façade occidentale de la cathédrale de Chartres.) Verres et Réfract. 1976 30 92-95.

This article falls into two parts; accounts of the visits by the delegates from the 9th CVMA Colloquium to the Gaudin Workshop and to Chartres Cathedral; and a history of the many restorations which had taken place in the cathedral. The study of the Jesse Tree window enabled the effects of earlier restorations to be seen, especially that at the beginning of the 13th century and that in the first quarter of the 15th century. After the fire in 1836 a big restoration was planned but it never took place, although the account exists. The present restoration was undertaken because the panels were so seriously bulged as to put the glass at risk.

The blue glass was almost unaltered but all the other colours were heavily corroded with an opague crust so that only the blue colour was evident (see their Figs 3 and 4). The Jesse Tree window was generally pitted whereas the Infancy of Christ was generally crusted. The restoration techniques are described: briefly, total re-leading was inevitable; the outside of the glass was cleaned with the LRMH solution of EDTA (see N.L. No.13, 181A); broken glass was edge-joined with silicone adhesive (see N.L. No.13, 181B); after cleaning, those pieces of glass which had corroded were treated with Viacryl VC363, i.e. the blue glass was not so treated. During the visit to the cathedral everyone could see in the Jesse Tree window how there was a re-creation of the interplay of colours originally intended, and not dominated by the blues as in the Passion window.

222. COLLONGUES, R, PEREZ Y JORBA, M, TILLOCA, G and DALLAS, J-P. (1976) "New aspects of the corrosion phenomena of the ancient windows of French churches" (Nouveau aspects du phénomène de corrosion des vitraux anciens des églises françaises.) Verres et Réfract. 1970 30 43-55.

This paper is a valuable sequel to the equally valuable paper abstracted as No.171 in N.L. No.11 (and then wrongly attributed to Professor Collongues - see item 171 at the end of the abstracts below). The authors discuss severe types of corrosion, but especially those of pitting, pitting with radial fractures, and uniform crusting; they claim that the type of corrosion can be explained unambiguously in terms of the content of ions which modify the silica network. They studied five medieval glasses, and the chemical analyses are given in a table. Glasses with less than 16% alkali decay by isolated pits, and the authors differ from El Shamy as regards the supposed equivalence of magnesium and calcium on the durability of glass. They find that magnesium is extracted from the pit but the calcium is extracted only in a layer quite close to the glass. Sulphur is found only in the fissures of the filling of the pit. Phosphorus is leached from the area near the glass in the same way as for calcium, and it seems possible that brushite ($CaHPO_4.2H_2O$) is formed.

When more than 16% of potash is present it seems that syngenite accompanies the gypsum. One sample from l'Aube formed scales of quartz and cristobalite but another had a thick layer of calcite.

They develop a general theory on corrosion phenomena based on Stevels' factor Y (the mean number of bridging oxygen atoms per polyhedron). Y decreases as the proportion of network-modifiers increases, and corrosion takes place more readily. When Y is larger than 3, sulphates do not form and the glasses are durable. When Y is between 2.8 and 3, corrosion is weak and very fine isolated pits are found (ca 100 μm). When Y is less than 2.8 a crust of gypsum forms as a fine powder, and when it is less than 2.7 syngenite forms as well. They refer to some dealkalisation experiments in the literature to argue that pit-formation may be the consequence of the existence of a protective layer on the glass. Thus the condition of the surface (the thermal history) can be important, and the state of the surface (the presence of scratches) can encourage pit-formation.

(Note by RGN:- Professor Stevels' "Y" factor, as described in 1948, is rather out-of-date and there are various problems connected with its use. For example, his calculations for non-bridging oxygen atoms assume that alkalis (R_2O) are the network-modifiers, but divalent cations (RO) also produce non-bridging oxygen atoms and thus RO and R_2O are indistinguishable in his formulae, although they have profoundly different effects on the durability of the glass. Another problem is in calculating Stevels' "Z" (also used in the paper but not referred to in my abstract). In a glass which is based on silica the calculation of "Z" is straightforward, but when phosphorus (P_2O_5) and alumina (Al_2O_3) are also present some ambiguity is introduced.)

223. FERRAZZINI, J.C. (1976a) "The influence of corrosion on the rate of decomposition on medieval glasses" (L'influence de la corrosion sur la vitesse de décomposition des verres du Moyen Age.) Verres et Réfract. 1976 30 26-29.

Corrosion of glass takes place in several stages and it is not easy to differentiate them. The first stage is ion-exchange by the "tunnel effect". The author tried to reproduce this effect with medieval glass using 1N hydrochloric acid and obtained an ion-exchanged layer 1 mm thick in 1 hour, or 4 mm thick in 5 days! There is a loss of volume of the glass, surface cracks form, and calcium ions are released. When sulphur dioxide is present the upper part of the glass is covered with pure gypsum and the lower part with pure potassium sulphate. The higher the concentration of potassium in the glass, the greater is the danger of corrosion by sulphur dioxide.

The author studied the rate of corrosion by means of special apparatus he designed which enriched a current of air with sulphur dioxide and water vapour by passing it through a solution of sulphurous acid. By changing the temperature of the acid, so could the concentration of sulphur dioxide be increased. During the corrosion of the glass an alkali-deficient skin was formed which reduced the corrosion rate. During the restoration of glasses it is important that the protection factor provided by such a skin should not be reduced. But the products of corrosion stimulate more corrosion and they should be removed during restoration work. Hence restoration must be carried out with great care.

224. FERRAZZINI, J.C. (1976) "A new method of conservation of stained glass" (Eine neue Methode zur Konservierung von Glasgemälden.) Weltkunst, 1976 No.6, 15th March p.508.

The author discusses methods of protecting newly-restored medieval windows against further deterioration and comments that the use of external protective glazing may not be satisfactory owing to harsh reflections in it, but it has the great advantage of being completely reversible. About four years ago an experiment on the use of Viacryl protective resin was started in Vienna but it is not yet complete. In the meantime Viacryl has also been tested by the French research workers at Champs-sur-Marne and found to be a useful material. It has therefore been used extensively at Chartres on the newly-restored west windows.

The author then goes on to claim that the protective capacity of the resin film may be impaired if the glass is not cleaned satisfactorily or if the vibration of the windows causes the lead to scrub the film away, but he does not quote any such failures and his opinions may be speculative. He claims that, to detect the failures which he postulates, the windows must be closely inspected on a regular basis and that this may be an expensive process. (RGN - I understand that the windows are in any case examined regularly by inspectors and architects in the State service.)

225. HUSBAND, T. (1976) "A stained glass Tree of Jesse in the Metropolitan Museum of Art". Verres et Réfract. 1976 30 69-72.

The author discusses the provenance of the six Jesse Tree panels from the Costessey Collection, points out how they differ from the St Denis Jesse Tree, and gives reasons why they were attributed to the 13th century. He then describes the ways in which the originally very weak panels were strengthened and restored for exhibition. It was concluded that the leads were not later than the 14th century but they were weak and the panels were therefore framed in stainless steel. Only 6.5% of the glass was not original. Pieces of 19th century glass were replaced with coloured casts which were made from Araldite because the panels would be kept in museum conditions, but they can be removed at any time.

226. MARCHINI, G. (1976) "Restoration of paintwork" (La restauration de la grisaille.) Verres et Réfract. 1976 30 65-68.

The author considers that the restoration of stained glass should be approached in the same manner as for other forms of painting, thus lost paintwork should be replaced, but no mistakes may be made and the process must be reversible. Decorative parts can be restored more easily than pictorial parts and full lines can be easy (see his Fig.1) but half tones were difficult until he accidentally discovered that graphite could be rubbed onto the surface of the glass with the fingers. The graphite would adhere to the parts which had been painted and it was then "fixed" with a suitable varnish. A drapery appeared in all its modelling and even a layer of wash was reproduced on a face to reconstruct all the features (see his Fig.4).

Some papers which were abstracted in earlier News Letters have now been published:-

No.11 (171) Perez y Jorba, M., Tilloca, G., Michel, D., Dallas, J-P, now in Verres et Réfract. 1975 29 53-63.
No.17 (202) Frodl-Kraft, E., Verres et Réfract. 1976 30 73-76.
" (203) Hayward, J., Verres et Réfract. 1976 30 77-79.
" (204) Newton, R.G., Verres et Réfract. 1976 30 35.
" (205) Newton, R.G., " " " 1976 30 30-34.
" (206) Newton, R.G., " " " 1976 30 80-86.
No.18 item 2 Bauer, W.P. " " " 1976 30 62-64.

* * * * * *

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.

8 INDEX TO NEWS LETTERS NUMBERS 11-20

The references are generally to the News Letter and the Section, e.g. 14(2.4.1) means News Letter No.14, Section 2.4.1 but three-figure numbers are to bibliography references, e.g. 20(226) means abstract No.226 in News LetterNo.20. Occasionally a page number may be given if it aids the location of the item.

Roy Newton