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Comité Technique du corpus Vitrearum

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CONTENTS

1 GENERAL

1.1 SYMPOSIUM ON THE CONSERVATION OF STAINED GLASS, YORK, JANUARY 1977

Preliminary details of this symposium were given in Section 1.2 of N.L. No.22 and a summary of the provisional programme is given below:

Sunday 9th January 1977

16.15: Professor Roy Newton: "Current problems of conservation"
19.30: Ir J.M. Bettembourg: Work at the LRMH

Monday 10th January

09.30-15.45: Mr Peter Gibson and Mr David O'Connor: Visits to historic churches in York
16.15: Dr E. Bacher
19.30: Various speakers on contemporary stained glass

Tuesday 11th January

09.30-13.00: Discussion groups and visits to the York Glaziers Trust workshop
14.15: Mr Dennis King: Problems with the Ely glass
15.00: Mr Frederick Cole: "How the special problems of Canterbury are being solved"
16.15: Miss Corinne Wilson: Summary of the Symposium.

1.2 GLASS FROM ST MARTIN AT LIÈGE

Mlle Yvette Vanden Bemden tells me that eleven windows were removed from this church in 1968, in preparation for its restoration, ie, the five most important windows from the choir (c.1527, each of 63 panels) and six other windows (of 18 to 30 panels) which were much restored in the 19th century. These eleven windows are now in the Institut Royal du Patrimoine Artistique (1, Parc du Cinquanternaire, 1040 Brussels. Tel.735-41-60 à 69) in order to determine how they should be cleaned and restored; they can be inspected by interested persons who pass through Brussels.

1.3 FESTSCHRIFT TO HONOUR DR DONALD HARDEN

Dr Harden was the first person to make systematic studies of ancient glass (starting in 1927) and his 75th birthday has recently been celebrated by the preparation of a commemorative volume (Vol XVII, 1975) of the Journal of Glass Studies. It shows that Donald Harden published at least 180 papers between 1927 and 1974 and he is, of course, still very active in his studies on glass.

The volume contains 18 papers covering glass of all ages, and the four papers which are concerned with window glass, medieval glassworks, or surface studies are abstracted as Nos. 246-249 in Section 5.

1.4 TEST OF VIACRYL IN VIENNA

Frau Dr Eva Frodl-Kraft tells me that, for a few months to come, the Viacryl-coated test panel from St Maria-am-Gestade can be inspected at close quarters. This test panel was installed in December 1971 (see N.L. No.6, page 2) and an interim report on some lack of adhesion which was observable in 1974 was included in N.L. No.18, Section 3.9 and Fig.2. It has now been dismounted for an expert examination by Dr W.P. Bauer, of the Museum für Völkerkunde. This is an important experiment because the test panel has been exposed to the weather in an East Window of the church of St Maria-am-Gestade for five years, and it is the only medieval glass anywhere in the world which has been coated with Viacryl for this length of time.

Dr Frodl-Kraft tells me that, when the panel was removed from the window a few months ago, it was in "an astonishingly good state", and we look forward with great interest to reading Dr Bauer's technical report on the panel. Even if the report on the protective properties of the resin may have to be inconclusive (because the resin had not been applied to a cleaned window and hence we cannot learn whether clean glass is attacked by the weather underneath the Viacryl, as is claimed by Dr Ferrazzini in Section 3.6 below), it will nevertheless be possible to learn whether Cital 12-12 will remove the Viacryl coating without any difficulty after it has been in place for five years. (In Section 3.7 below Dr Ferrazzini claims that the Viacryl coating is not truly reversible and that it is difficult to remove it completely, especially from any pores in the glass.)

Anyone who is passing through Vienna, or who could make the journey there, and wishes to inspect the panel at close quarters, should contact Dr Frodl-Kraft at the Institut für Österreichische Kunstforschung des Bundesdenkmalamtes, Hofburg, Schweizerhof, 1010, Vienna. Tel. Vienna 52-55-21.

2 CONTRARY OPINIONS

There have been various public criticisms of the conservation procedure used recently at Chartres, and an important one has been put forward by the "Association for the defence of the stained glass windows of France". The association is known as the ADVF (Association pour la défense des vitraux de France) and an 8-page manifesto, under the signature of Jean Bazaine and Alfred Manessier, dated 3rd May 1976, put forward their point of view. This document is summarised below and I am grateful to Mrs Frederick Cole for kindly supplying an English translation of the manifesto.

The first page of the document has an introduction entitled "A painter's notes on the restoration of the 'Royal Portal' at Chartres" which expresses M Manessier's dislike of what has been done, together with a list of the 17 Founder Members; of these, 8 are artists, 4 are writers, and the other 5 are an architect, a conservator of books, a medieval historian, a professor of art and a scientist (Dr Paul Acloque, a physicist who was until recently Director of Research for the St Gobain glass manufacturing company).

The objectives of the Association are threefold:-

(a) in liaison with existing organisations to preserve and protect stained glass,

(b) to carry out researches and technical studies of all good conservation methods,

(c) to publish the reports of conferences, news bulletins and the notes of local committees.

The rest of the text is divided into six sections, set out in 2.1 to 2.6 below.

2.1 CRITICISM OF THE METHODS AT PRESENT IN USE BY THE DEPARTMENT FOR HISTORIC MONUMENTS

Objections are raised against the use of Viacryl VC 363 under five headings (here 2.1.1 to 2.1.5).

2.1.1 Before applying the resin the glass must be cleaned and hence it is not possible to discuss whether the glass would be more beautiful if left uncleaned. It is realised that the glass must be protected against humidity, micro-organisms, pollution, etc., that the interior surface must be cleaned to remove deposits of candle smoke, etc., and that the leads must be repaired. Manessier suggests that it was wrong to justify the complete removal of the weathering deposits so that the resin could be applied. Cleaning of some nave windows was carried out with water about 10 years ago but the windows are now beginning to darken again.

2.1.2 The resin has a refractive index close to that of the glass and Dr Acloque will shortly publish a report (by the ADVF) explaining why this is a disadvantage.

2.1.3 The permanence of the resin is guaranteed for only about 30 years.

2.1.4 In general, these 12th century windows do not have external decoration and there would not be a problem if the resin has to be removed. However, the 13th century windows in the same cathedral, which do have external paintwork, could not be given the same treatment.

2.1.5 The coefficient of thermal expansion of the resin is much greater than that of the glass and the large temperature changes which occur (examples are quoted of differences of 50 degC) would cause the resin to crack in 15 years or so. The humidity which invariably forms in the bottoms of cracks would be infinitely more dangerous than the rain, condensation, or the corrosion itself.

2.2 SOME REFLECTIONS ON THE BAD 19th-CENTURY TOUCHING-UP, AND ON THE "NOCTURNAL ASPECT" OF THE WEST WINDOWS

This has had the effect of impoverishing the colour and of upsetting the balance of colours in general. There is then a commentary on the relative colours in the three restored west windows, compared with the rose window above them.

2.3 A BRIEF DESCRIPTION OF THE METHOD PROPOSED BY THE GLASS SPECIALIST, PAUL ACLOQUE, AND ITS ADVANTAGES

The manifesto claims that the restoration techniques used on the three west windows are irreversible and alleges that they persuaded the Minister for Cultural Affairs to stop all such restoration work at Chartres as from 17th February 1976. (RGN - there seems to be some doubt about this.) An alternative, reversible, scheme has been proposed by Dr Paul Acloque, using layers of very thin glass to be made by the Gerrer Company (St Gobain) at Mulhouse. The suggestion is that each "element" of the window should be plated or double-plated with a very thin sheet glass (about 0.6mm thick). (RGN - it is not clear what is meant by an "element" of the window; the French is "une ou deux plaquettes à la forme et aux dimensions de chaque élément du vitrail", but a footnote on the sixth page seems to suggest that only badly-corroded pieces of glass would be treated in this way.) This procedure is claimed to have five advantages (2.3.1 to 2.3.5 below).

2.3.1 To retain what is advantageous in the patina, after moderate cleaning and treatment of the corrosion by a "scientific method based on ultra-violet or infra-red rays as the case may be". (RGN - unfortunately no information is given about these methods of cleaning.)

2.3.2 To retain the uneven visual characteristics of the surfaces of the ancient glass, which were undoubtedly put to best use by the master glaziers.

2.3.3 To transmit light totally, without any dulling or yellowing, for a life beyond that of the leads (e.g. 100 years).

2.3.4 The plating film would never, under any circumstances, touch the outer or inner painted decoration, nor put them at any risk.

2.3.5 To have the same coefficient of thermal expansion as the glass being conserved. (RGN - this would seem to be incorrect because medieval glass, with its high potash content, has a coefficient of expansion about twice that of modern glass.)

2.3.6 There are also comments (perhaps as future developments?) that these plating glasses might be toughened by chemical treatment (RGN - as in certain car windscreens) and that they would be sealed, in dry air conditions, with hermetically-effective edge seals. (RGN - presumably the air within the cavity would not remain dry for more than a few weeks.)

(RGN - It has not so far been possible to obtain samples of this 0.6mm glass but one of the fears of British craftsmen is that such thin glass would be difficult to cut.)

2.4 A BRIEF REPORT ON THE RECENT WORKING-SESSION WITH THE DEPARTMENT OF HISTORIC MONUMENTS, AT THE GAUDIN WORKSHOPS, AND THE REQUEST BY THE DEPARTMENT TO SUSPEND ALL CONTROVERSY

There is then a very brief report on the meeting which took place on 19th March 1976 between five representatives of the ADVF, nine representatives of the Department of Historic Monuments, and four independent persons. Dr Acloque explained his proposals which were then to be presented to a scientific meeting on 18th May.

2.5 A SUMMARY OF SOME ODD EXPERIMENTS MADE IN CHARTRES CATHEDRAL

Here Manessier describes his experiments on observing the windows and making careful notes; his observations as a stained glass artist are confirmed by Paul Acloque as a physicist.

In one experiment he compared various red colours, i.e. those in the semi-medallions of the Jesse Tree window which had been cleaned, and those of the Passion window which had not then been cleaned.

At a distance of 10m all the reds were approximately similar in colour and in brightness. In the nave the restored Jesse Tree reds were beginning to lose their colour and to darken but the reds in the Passion window had not altered. At the transept the restored Jesse Tree reds in the semi-medallions had entirely disappeared and the only reds remaining in this window were the robe of the sleeping Jesse and the selenium reds from the 19th century restoration in the top panel (above the figure of Christ). The unrestored reds in the Passion window had not altered in colour or brightness. (RGN - Apparently this phenomenon occurred only when sunlight fell on the window at 45° to the west facade.)

Dr Paul Acloque explains this (and other colour-phenomena which are difficult to translate with any confidence) in terms of the resin playing the rôle of a liquid, with a refractive index matching that of the glass, on the outside surface. Thus the external structure of the glass would disappear, as would the other refractive effects at that surface.

2.6 CONCLUSION

Whatever the final solution regarding the choice of protection for stained glass windows in France, we wish to put forward our dossier for the judgment of history. It is important that the points of view of all our Members, and the responsibilities which they have agreed to take, should be known and understood accurately.

The life and death of 50,000 m^2 of the most beautiful stained glass windows in France are at stake. (Copies of the Manifesto can be obtained from 22 rue d'Artois, 75008 PARIS.)

3 NEW TESTS ON VIACRYL

As was announced in Section 1.6 of N.L. No.22, Dr J.C. Ferrazzini has recently described his new researches on Viacryl in a paper "Untersuchungen über eine neue in Chartres angewandte Methode zur Reinigung und Konservierung von mittelalterlichen Glasgemälden". ("Investigations into a new method used at Chartres for cleaning and preserving medieval stained glass".) I have pleasure in being able to give readers an English translation below.

3.1 INTRODUCTION

The threat of decay, and particularly the dangerously advanced decay of some medieval painted glass, has alarmed art lovers, art historians, conservationists and especially technologists alike. Once again, the problem is how on the one hand to win the race against time without on the other hand having made adequate tests on the projected methods of conservation and protection. Time must be spent investigating the possible consequences of such methods.

Critical research into conservation is aimed at supporting all those to whom the fate of ancient painted glass is a matter of real concern. However, feelings of gratitude for all that has already been done towards saving this glass should not silence those colleagues who have serious misgivings about any of the methods developed and already in use. We would have considered it irresponsible not to express our objections to the method of restoration and conservation developed in France (1), and already put into practice, which was demonstrated to the assembled scientists on the occasion of the IXth Congress of the Corpus Vitrearum in Paris in September 1975: cleaning the glass with chemical agents and applying a protective two-component lacquer.

Without wishing to restrict the activities of the authorities involved, we consider it absolutely necessary to call a halt until thorough tests have been made on the investigations carried out by the Laboratoire de Recherche des Monuments Historiques in Paris (1) for possible harmful consequences. It will not detract from anyone's achievements if this is done before the method, used at Chartres (2) and elsewhere, is brought into wider use.

We therefore feel duty bound at this stage to make known to a wider circle the basic scientific research at present being carried out jointly by the Volkswagen Foundation in Hanover and the Institute of Conservation of the Zurich E.T.H., so that future conservation work everywhere can be approached with the necessary care and caution on the basis of unequivocal results. It is in this spirit, and only in this spirit, that the criticism which follows, and our own suggestions, should be regarded. There have been many public criticisms of this work, chiefly by the Association pour la Défense des Vitraux de France (3), and some constructive proposals to test the validity of the French work were discussed by a sub-committee of the European Science Foundation (4) but they were not adopted.

3.2 THE PROBLEMS OF REMOVING WEATHERING CRUSTS FROM MEDIEVAL PAINTED GLASS BY CHEMICAL SOLVENTS

Weathering crusts on medieval glasses consist principally of calcium salts: the double sulphate syngenite and gypsum (5,6,7). Attempts have been made to loosen such products by chemical treatment with ion-selective agents and thus remove them from the surface of the glass. This method involves some risks. A product which sequesters metal ions cannot distinguish between ions which originate from the corrosion products and those which are dissolved out of the base material, the glass. Any metal ion which is accessible, and capable of reacting, is dissolved at random out of its original bond and borne away. So it is not surprising that there have already been criticisms (8) of the method published by Bettembourg and Burck (9).

Agents which sequester metal ions, such as complexons, polyphosphates etc., are components which in particular bond bi- and tri-valent metal ions such as Ca^{2+}, Pb^{2+}, Zn^{2+}, Mg^{2+}, Ba^{2+}, Al^{3+}, Fe^{3+}, B^{3+} etc.

If the weathering crust on a glass is treated with a product of this kind, the undesirable weathering layers are removed in succession. In theory, this process can easily be controlled. By varying the temperature, the treatment time and the concentration of the solution, the reaction can be stopped before it affects the glass. However, this assumes a weathering crust which is perfectly homogeneous and of uniform thickness; a requirement which does not occur in practice. In addition, the bare glass often found under the leads or at fracture- and crack-faces is destroyed at the very beginning of such chemical treatment.

In practice, the careful local treatment of specific weathering crusts involves too much work. The repeated application and washing off of the cleaning solution takes much time because the object has to be dried in between times to avoid any creeping of the solvent through the porous layers of the weathering crust. To carry out this work with precision might make a restoration project much too long.

Glass surfaces which have been treated with compounds which sequester metal ions have a scaly, fissured structure. The glass has a reduced content of metal ions on the outside and is more susceptible to corrosion than the untreated sample.

We treated medieval glasses with Complexon III (the EDTA solution described by Bettembourg (9)) and with water containing Calgon. Some of the weathering crust could only be removed satisfactorily after prolonged treatment with these chemicals. The fractured faces have suffered much from the treatment (Figs 1 and 2). All the samples show a characteristic severely fissured surface. The substrate underneath the layers of weathering crust which have been removed presents a normal, corroded surface to the naked eye. However, such glasses are approximately twice as susceptible to renewed corrosion as those from which the weathering crust has been removed mechanically. In Fig. 3 each row of samples was treated in two ways. In all cases the lower parts of the samples were cleaned mechanically. In the top row the upper parts of the samples were cleaned in a bath of Calgon. In the bottom row the upper parts of the samples were cleaned in a bath of EDTA solution (Complexon III). All the samples were then weathered under the same conditions.

3.3 WHAT IS VIACRYL?

The short description "Viacryl" is applied to a two-component lacquer comprising a product of the Vianova company (an Austrian subsidiary of the Hoechst group) called Viacryl, and the product Desmodur prepared by Bayer, Leverkusen in Germany. By "Viacryl" the manufacturer means all the acrylic resins produced by this company. The French scientists recommended Viacryl VC 363, which is now marketed under the name SM 564. It is characterised by a high, lasting gloss, good colour stability and excellent weather resistance. It is used primarily for industrial lacquers. The acrylic resin, which is capable of forming polyisocyanate cross-links, is marketed in the form of a 65% solution diluted with ethylglycolacetate. "Desmodur" is also a collective name for a group of products. Like our French colleagues we confined ourselves to tests with Desmodur N, a polyfunctional, aliphatic isocyanate. The main field of application of this material is in high-quality coating lacquers applied on top of an anti-corrosion base lacquer on vehicles, traffic signs, plastics parts etc. Desmodur N is marketed in the form of a yellowish, low-viscosity liquid. A mixture of ethylglycolacetate and xylene 1:1, added at the rate of 25%, is used as a stabiliser. To achieve optimum film properties the acrylic resin should be cross-linked between 100 and 150 per cent. According to our calculations, this desirable condition is fulfilled when the equivalent amounts added are 80.8 Viacryl: 19.2 Desmodur parts by weight (Bettembourg's recommendation is 80:20 (1)).

Viacryl was first used for an experiment on the conservation of medieval glasses about five years ago in Vienna. The case in question was an experiment in situ in which different methods were used for cleaning the glass and for applying the plastic material. After five years a protective film ought not to show any real damage but some damage has occurred (10). As we have to guarantee the preservation of works of art for hundreds of years we have to resort to accelerated weathering in suitably severe conditions. In pharmacy, a product is introduced only when it is certain that the active ingredient will fulfil its task, even if the problem requires lengthy and expensive research.

3.4 THE WATER PERMEABILITY AND WATER ABSORPTION CAPACITY OF VIACRYL FILMS

The corrosion of glass by atmospheric agents, of the kind which we see every day, is only possible if sufficient water is present to promote the reaction (11). A basic safeguard against further destruction of works of art is to keep the object in an atmosphere with a relative humidity between 30% (12) and 60% (6). If a plastics film is used as the protective material these conditions can only be maintained in outdoor conditions if the product used is impermeable to water vapour. We tested the behaviour of Viacryl films towards water by two methods. For the first test, we investigated the water absorption and water release of the plastics material as a function of time. It soon became apparent that the diffusion rate of moisture in Viacryl is so high that it can only be measured with any certainty by incorporating a retarding factor. This meant that we had to carry out our experiments on thick samples (with a diameter of 30mm and a thickness of 3.5mm). If thin films are used, the transfer of water is so rapid that it is not possible to measure the time accurately. The films which we used are produced by painting Viacryl on to a non-adhesive base. We can get different layer thicknesses depending on the fullness of the brush and the number of coats; thus one coat can have a thickness between 0.02 and 0.08mm, and three successive coatings will give a film thickness between 0.10 and 0.18mm.

The test pieces were first dried for at least a week at 60°C. The whole test cycle then took place at this temperature. The samples were placed in water and the increase in their weight was recorded continuously. Once a constant weight had been reached, the samples were dried in air. This cycle of immersion in water and drying was repeated as many as five times on each sample. From the total of the measured values, which showed a maximum individual deviation of 2% from the ideal curve, mean values were calculated. These results are shown in the Table.

Fig.4 shows the curves of the water retention of Viacryl films plotted as a function of time.

When converting these results to the case which would apply to thin films it must be borne in mind that water equilibrium would then be achieved within a few minutes.

These results show how rapidly the water content of Viacryl protective films can reach equilibrium with the prevailing climate. A coating with a thickness of 0.05mm reacts approximately 35 times more rapidly to changes in atmospheric moisture than do our thick test

TABLE: THE WATER ABSORPTION AND RELEASE OF VIACRYL SLABS AS A FUNCTION OF TIME

Water Absorption			Water Release	
% of the total water content	wt. % water	Time in hours	% of the total water content	Residual content (wt. % water)
25	0.55	0.83	25	1.64
50	1.10	4.0	50	1.10
60	1.31	7.25	60	0.88
70	1.54	11.25	70	0.65
80	1.75	18.0	80	0.44
90	1.97	30.0	90	0.22
95	2.08	42.5	95	0.11

pieces. A change in climate thus affects the glass within a very short time.

Our second experiment concerned the effect of the climatic conditions of the atmosphere in our Zurich laboratories on the water permeability of a Viacryl film. For this experiment we used the set-up shown in Fig.5. A Viacryl film 0.144mm thick (equivalent to a twice repeated thick coating) was dried for a month at 60°C. This membrane was stuck firmly with Viacryl to a glass vessel with a 7.30cm^2 aperture. The relative humidity in the container was 32%. The increase in weight, i.e. the amount of water which diffused through the membrane into the container, as a function of the relative atmospheric humidity of the laboratory atmosphere, was measured sporadically. The results are summarised in Fig.6. It can be seen that the measured values correspond closely to the data from the meteorological office (13).

During the test period of 27 days 0.18g water was absorbed under the conditions described. This corresponds to a film of water 0.25mm thick underneath the surface of the membrane, i.e. almost a hundredth of a millimetre (10 µm) a day. These two experiments clearly show that enough water for the corrosion reaction might very rapidly collect under a Viacryl film.

In addition, wet Viacryl becomes milky white, or quite translucent, in thicker layers, if super-saturation occurs as the result of a change in temperature. We noticed that wet Viacryl had an opal appearance and that pieces of Viacryl saturated with water, which had been dried for an hour, still showed in the middle a milky appearance, whereas the edges had become clear and transparent again. By the next day the same piece had become glass-clear again. Water can be visibly present in the Viacryl structure.

3.5 PERMEABILITY TO SULPHUR DIOXIDE GAS

In his paper (1), Bettembourg maintains that filter papers impregnated with Viacryl are impermeable to SO_2 gas. Unfortunately, the test set-up shown in Fig.4 of the French publication has a fundamental fault. Sulphur dioxide gas is approximately two-and-a-half times heavier than air and consequently cannot diffuse so readily from the liquid phase through the long, narrow hose connections to the permanganate solution. Pockets of SO_2 gas form in the lower parts of the apparatus and it is difficult to empty these by gaseous diffusion alone. (This effect can in principle be observed in the open freezer chests of modern grocery stores, where heavy cold air remains in the refrigerator.) Even when the Viacryl-impregnated filter paper is removed the gas is unlikely to surmount the barriers which have built up, so that if the arrangement of the apparatus is not altered the permanganate solution will not really lose its colour.

For our series of tests we adapted a piece of apparatus developed earlier (11). As Fig.7 shows, the measuring head consists of two half-chambers with a Viacryl film of a given thickness inserted between them. The test area is 15.2 cm^2. There is a constant flow of air enriched with sulphur dioxide in the upper chamber (2.3mg of SO_2 per minute). In the lower half of the measuring unit an acidified potassium permanganate solution is kept in motion by means of a magnetic stirrer. The diffusion time required for a given amount of gas is based on the known proportion of permanganate which has reacted. The time required is a linear function of the thickness of the Viacryl film tested. The diffusion time for a given quantity of gas at constant partial pressure is proportional to the thickness of the protective film of Viacryl. The change in partial pressure is also subject to a linear law, and the values obtained are shown as dots in Fig.8. A filter paper saturated with Viacryl produced by Schleicher and Schuell AG, and weighing 81.2 g/m^2, falls right outside the curve obtained (triangle in Fig.8); here the gas moves much more rapidly along the paper fibres and through the many pores of the cellulose than through pure Viacryl. The plastics material itself is not attacked by the aggressive gas and retains its properties, but cannot be recommended as a protection against SO_2 for a substrate. In industry it is possible to give corrosion protection to the base coating by means of a base lacquer. In this case, a Viacryl covering lacquer has an aesthetic function and determines the external appearance of the object, so that it must obviously be weather-resistant itself.

3.6 THE BEHAVIOUR OF MEDIEVAL GLASSES UNDER A VIACRYL COATING DURING WEATHERING WITH MOIST SULPHUR DIOXIDE GAS

We treated samples of medieval glass by Bettembourg's method. They were cleaned with a solution of Complexon III and given a coating of Viacryl. In the first phase of the weathering with moist SO_2 gas some protection can be observed and under optimum conditions this might last for a few years in situ. Subsequently the corrosion process underneath the protective coating was greatly accelerated compared with unprotected glass. This behaviour is a result of the successive unfavourable microclimates which form and which have devastating effects on the glass. As weathering continues the condition of the 'protected' glasses becomes worse than that of untreated samples. The condition of the samples after weathering is shown in Fig.9, where the upper parts of the test pieces show an undamaged Viacryl film. Below this are some of the thickest corrosion layers, which are lifting the film from the substrate. The lower parts of the samples were cleaned by conventional mechanical methods before being subjected to weathering under the same conditions.

3.7 THE COEFFICIENT OF PERMEABILITY OF A VIACRYL FILM FOR SULPHUR DIOXIDE GAS AND WATER VAPOUR

By permeability we mean the penetration of plastics films by materials which dissolve in them and diffuse through them. The rate at which such materials pass through, the permeation, rises with the solubility and the diffusion coefficient of the permeating material in the plastics. Permeation processes are of particular significance for the penetration of gases and vapours. The permeability is usually described by the permeability coefficient P, which is defined as the amount of gas permeating per unit of time under the influence of a pressure gradient through unit of area and thickness of the plastics. P is dependent on temperature, so that the permeability increases significantly as the temperature rises.

On the basis of the experiments described above, we calculated the permeability coefficient of a Viacryl film. The P value for sulphur dioxide gas is 443×10^{-10} and that for water vapour 0.21×10^{-10} (cm^2/sec.cm. Hg). The P value for SO_2 gas is exceptionally high and can be compared with that of plastics with good gas permeability, like silicone rubber, for example. The water vapour permeability is of the order of magnitude of the permeability of PVC films. The exceptional behaviour of filter papers saturated with Viacryl, from the P-value established for SO_2 gas, can be attributed to the Knudsen flow which occurs. However, this measurement may be distorted by reason of the fact that there is simultaneous flow through fine holes. A measuring set-up of this kind cannot be used as a basis for determining a reliable permeability coefficient because too many unknowns are involved.

The question arises of the extent to which poor cleaning of the substrate - in our case residues of weathering crust on the glass - affects the permeability. Under some circumstances the possibility of the occurrence of Knudsen flow, or even direct diffusion through the pores, represents a latent threat to the security of the glass, as can be observed in cases where cellulose films are used.

3.8 THE TEMPERATURE RESISTANCE OF VIACRYL FILMS AND VIACRYL COATINGS

Viacryl which is not applied to a substrate burns very readily, giving a very sooty flame. Films applied to a non-combustible base behave quite differently. The substrate conducts away the heat required to maintain combustion and the plastics material cannot maintain the flame itself. It is worth noting that Viacryl coatings cannot be ignited with a bunsen burner in either a reducing or an oxidising flame. A flame from the bunsen burner directed steadily at a point on a glass sample, painted with Viacryl, first cracks the glass (as a result of the stresses set up) and then the coating boils gently and turns brown and finally evaporates.

No further experiments in this field (e.g. by thermo-gravimetric methods) were carried out.

Viacryl coatings show good fire-resistant properties for our requirements.

3.9 THE REVERSIBILITY OF THE METHOD

Viacryl coatings are extremely resistant. Their inert behaviour towards chemicals means that special preparations have to be used for removing the material once it has hardened. "Cital 12-12" (1), produced by the firm of Cital GmbH, D-775 Constance, was recommended as a "solvent" agent. The manufacturer gave us the precise composition of the product in confidence. Besides methylene chloride, an unsaturated hydrocarbon, a monomeric aromatic compound, a tertiary amine and a secondary alcohol are present in the solution. An acid wetting agent is also added to the product. In theory, these components are not really capable of attacking glass.

Cital 12-12 is not a true solvent for a hardened Viacryl film but more a product for softening highly cross-linked synthetic resins. The Viacryl swells up and only extremely few bonds can be broken under certain conditions, mainly by the monomeric aromatic compound.

Various Viacryl films varying in thickness from 0.05 to 0.2 mm were immersed in Cital 12-12 for 24 hours. The plastics films were then taken from the bath and dried in the air. After about six hours' drying at room temperature the films had regained their original properties. This experiment can be repeated several times with the same plastics. If the Viacryl films softened in Cital 12-12 are stretched so that the swollen product tears, we get a sticky, dough-like, viscous pulp with nodules in it.

On a smooth surface, products of the consistency described above can easily be rubbed off. However, corroded glasses have a highly fissured, fine-pored surface. Under such circumstances the removal of a lacquer by the method recommended is unacceptable from the modern point of view for conservation of ancient monuments. It is not possible to remove swollen Viacryl mechanically from the pores of the glass - it may perhaps be compared with cleaning pumice stone saturated with gelatine!

In addition, after treatment with Cital 12-12, Viacryl shows 40% linear expansion. Although the swollen products have a certain degree of elasticity, the splitting effect should not be underestimated. It is true that at Chartres no painted areas were treated with Viacryl. However, unfortunately no reference has previously been made to this disadvantage of the method recommended, which involves considerable risks, especially in the case of loose paint and fragments of glass with poor adhesion.

Cital 12-12 alone has no harmful effects on glass. Even after immersion for more than a week in a warm bath at 40°C medieval glass reacts to corrosive agents in the atmosphere in just the same way as untreated material. Fig.10 shows a test of this kind. The upper parts of the samples of medieval glass were left for nine days at 40°C in Cital 12-12 and the samples were then weathered in air containing moist sulphur dioxide. The corrosion behaviour is uniform over the whole sample.

3.10 THE SEARCH FOR AN ALTERNATIVE

As our research has shown a Viacryl coating is not a reliable protection against decay for medieval painted glass. The performance demanded of a protection against corrosion must be based on a true concern for conservation. Any solution of the problem must be based on the concept of a list of priorities which will satisfy the most stringent demands. These include first of all reliable corrosion protection for intervals between restorations of at least a hundred years, reversibility of the process with the survival of the work of art fully guaranteed, an aesthetically satisfactory solution, both for the object itself and for its surroundings, and a minimum of technical difficulties in application to the original and for the restorer. In addition, the process should satisfy a few other requirements, such as favourable fire-resistant properties, economy of cost, etc.

We know that the aesthetics of the external appearance are the great problem of the external architectural complex of external protective glazing. The effect of reflections has unpleasant consequences for the unity of a facade. In addition, our eyes are used to glass with a patina. Consequently, the gloss of Viacryl which is even greater than that of new modern glass, also looks unnatural.

We have tried to analyse the problems described here and to reconcile them with each other in order to build up a satisfactory picture. The search for a solution has been set in motion. We are striving to develop a method, and a suitable plastics material, which will also not significantly disrupt the outside. This protective material is fixed to the leads, so that a hermetically sealed cavity is formed. Figure 11 shows the film which is being developed. Various optical impressions are recorded here, but the problem of sealing the cavity has not yet been taken into account. The freedom of design of the external appearance presents the restorer with an opportunity of achieving the optimum aesthetic effect. There is no need to interfere with the glass.

3.11 SUMMARY

The new method developed in France of a Viacryl protective coating for the conservation of medieval painted glass has some significant defects.

Cleaning the glass with ion-selective agents affects the healthy glass and makes it susceptible to corrosion.

Viacryl coatings are permeable to water and sulphur dioxide and are not a suitable protection against corrosion. The protective factor must be regarded as unsatisfactory. Viacryl itself is extremely resistant to weathering - a fact which has also been investigated and demonstrated by Bettembourg.

The swelling of the protective film during treatment with the "solvent" agent Cital 12-12 causes a linear expansion of 40% on the part of the Viacryl. This effect can cause loose particles to break away. Since Cital 12-12 is not a true solvent, but a softening agent, the plastics material has to be scraped off mechanically. There is then always the latent danger that it will be impossible to remove all the Viacryl without damaging the surface of the glass. Glass does not react with Cital 12-12; it is quite indifferent to it.

Thin coats of Viacryl have astonishing resistance to burning. The flame-resistant properties of the material can be regarded as good.

A new prophylactic method is presented as an alternative means of conserving medieval painted glass. This possibility is being investigated.

3.12 REFERENCES

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8. Bauer, W.P. (1976) "Der Einfluss von Reinigungsmethoden auf die Glasoberfläche - Vorläufige Versuche und mikroskopische Untersuchungen." Verres et Réfractaires 1976 30 62-64. (A fuller account is given in N.L.18, Section 2.)

9. Bettembourg, J.M. and Burck, J.J. (1974) "Restauration des vitraux anciens. Methodes testées par le laboratoire de Recherche des Monuments Historiques." 10 pages of typescript. (See N.L.13, abstract No.181 and N.L.7, Section 2.4.)

10. Bacher, E. (1976) "The East Window at St Maria am Gestade." N.L.18, Section 3.9 and Fig.2.

11. Ferrazzini, J.C. (1976) "L'influence de la corrosion sur la vitesse de decomposition des verres du Moyen Age" Verres et Réfractaires, 1976 30 26-29. (See N.L.20, abstract No.223.)

12. Brill, R.H. (1975) "Crizzling - a problem of glass conservation." Congress on Conservation in Archaeology and the Applied Arts, Stockholm 2-6 June, 1975, pp 121-131. (See N.L.15, abstract No.186.)

13. Meteorologische Zentralanstalt, Zürich. Tägliche Durchschnittswerte der registrierten Messungen.

FULL CAPTIONS FOR THE ILLUSTRATIONS

Fig.1 Fractured faces of glass samples which have been damaged by Complexon III (EDTA).

Fig.2 Fractured faces of glass samples which have been damaged by Calgon.

Fig.3 Each row of samples has been treated in two ways. In all cases the lower parts of the samples were cleaned mechanically. In the top row the upper parts of the samples were cleaned in a bath of Calgon. In the bottom row the upper parts of the samples were cleaned in a bath of EDTA solution (Complexon III). All the samples were then weathered under the same conditions.

Fig.4 The water retention of Viacryl slabs (3.5 mm thick) as a function of time. One hundred units on the ordinate correspond to the maximum water absorption capacity of the Viacryl (2.19% by weight).

Fig.5 The simple arrangement used for measuring the water permeability of Viacryl membranes.

Fig.6 This diagram shows how the amount of water which diffuses through a Viacryl membrane depends on the external partial pressure of water vapour.

Fig.7 The apparatus used for measuring the permeability of Viacryl to sulphur dioxide. On the right is an enlarged view of the measuring head.

Fig.8 The permeability of sulphur dioxide through Viacryl films of various thickness as a function of time.

Fig.9 Samples of cleaned medieval glass after exposure to moist sulphur dioxide. The upper parts of each sample had been coated with Viacryl but corrosion has occurred underneath the undamaged film of Viacryl.

Fig.10 The uniform appearance of glass samples whose upper parts had been immersed for nine days in Cital 12-12 at 40°C. The samples were then exposed to moist sulphur dioxide and it is evident that the Cital 12-12 has not affected the durability of the glass.

Fig.11 A prototype of the new method being developed for the conservation of stained glass.

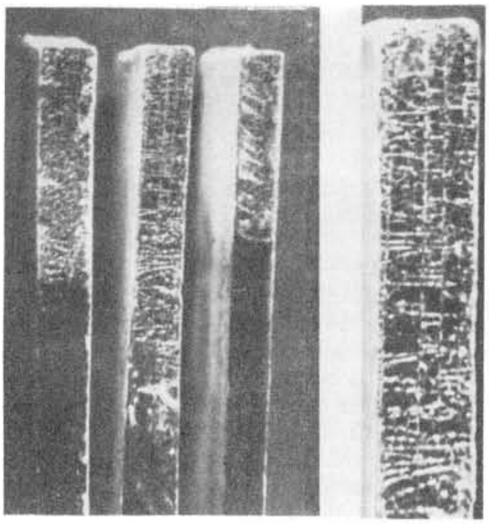

FIG 1 – Glass damaged by EDTA

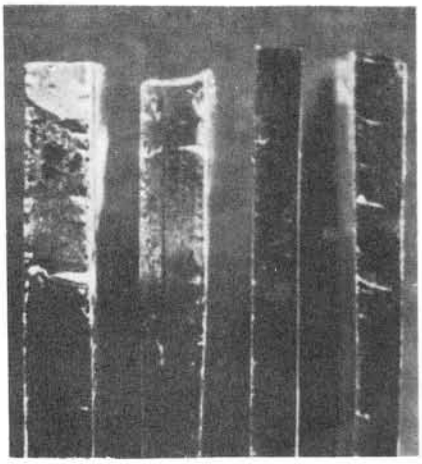

FIG 2 – Glass damaged by Calgon

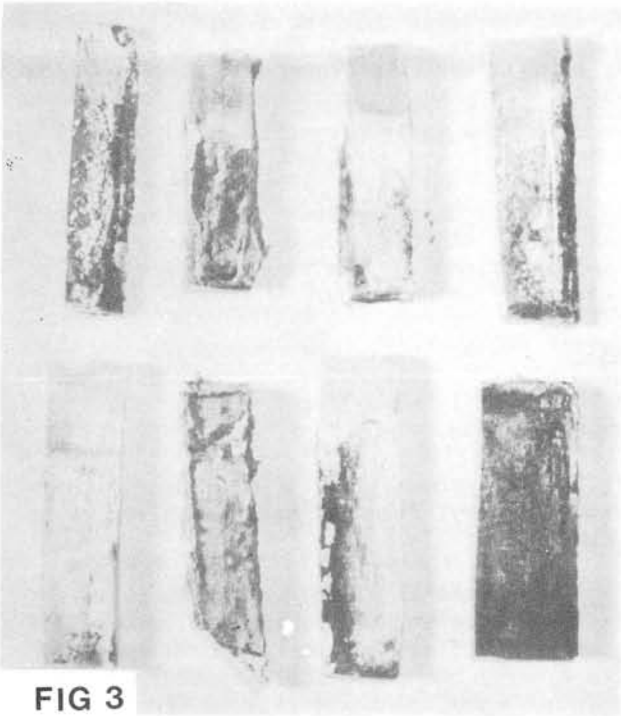

FIG 3

Effects of Calgon and EDTA on weathering

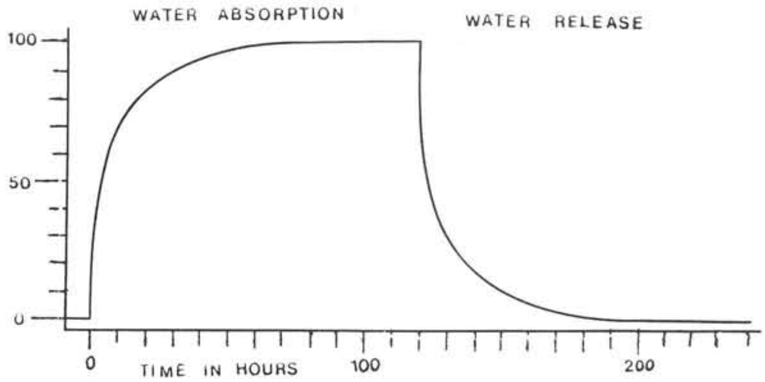

FIG 4 – Absorption of water by Viacryl resin

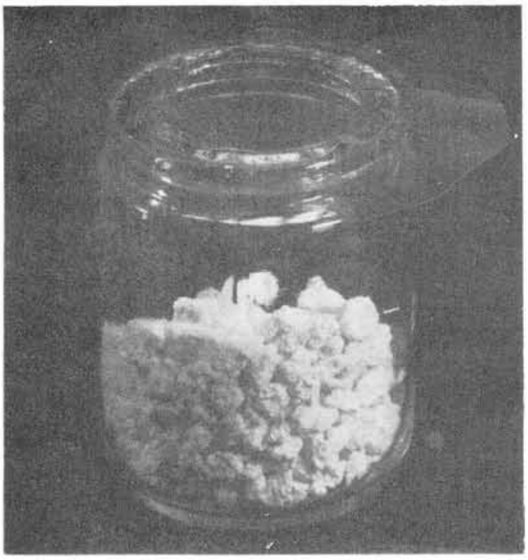

FIG 5 – Water permeation by Viacryl

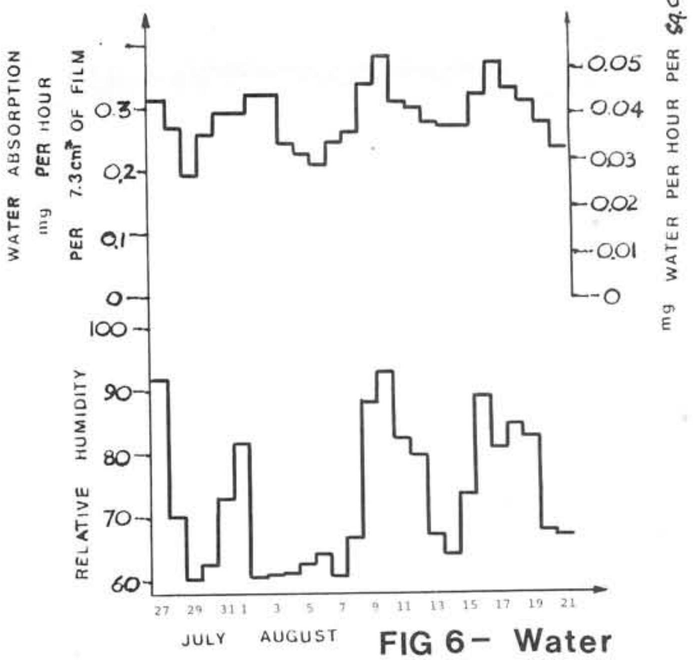

FIG 6 – Water permeation of Viacryl and the weather

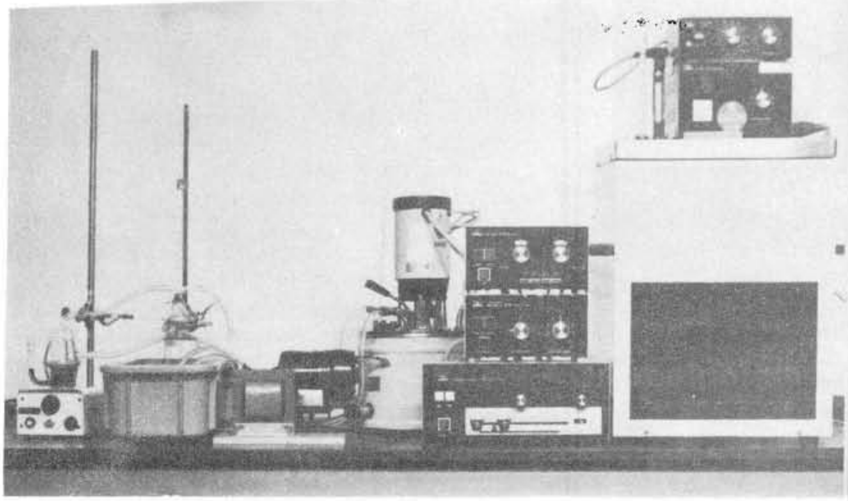
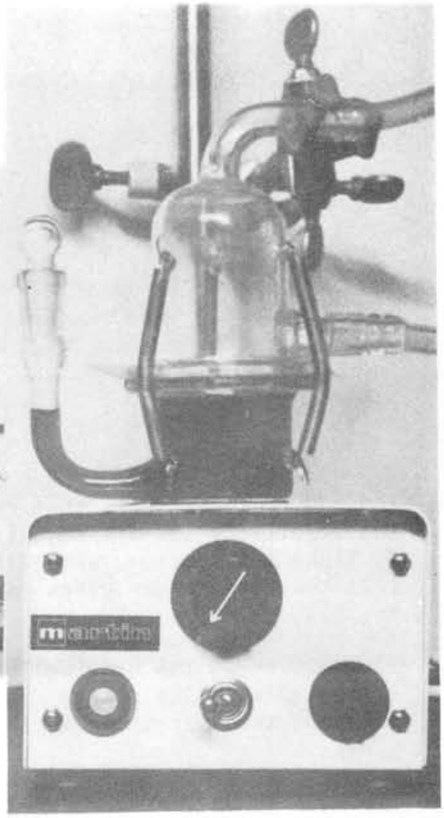

FIG 7 – The apparatus

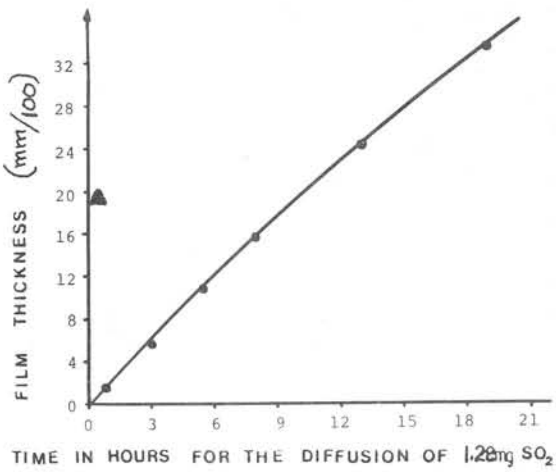

FIG 8 – Permeability of Viacryl to SO_2

FIG 9 – Corrosion under the Viacryl resin

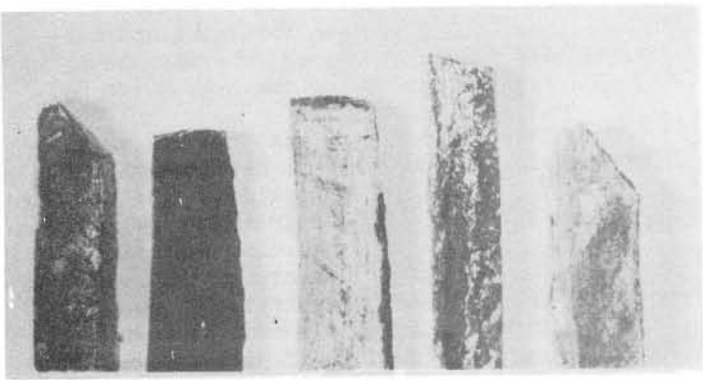

FIG 10 – Cital 12–12 does not affect the glass

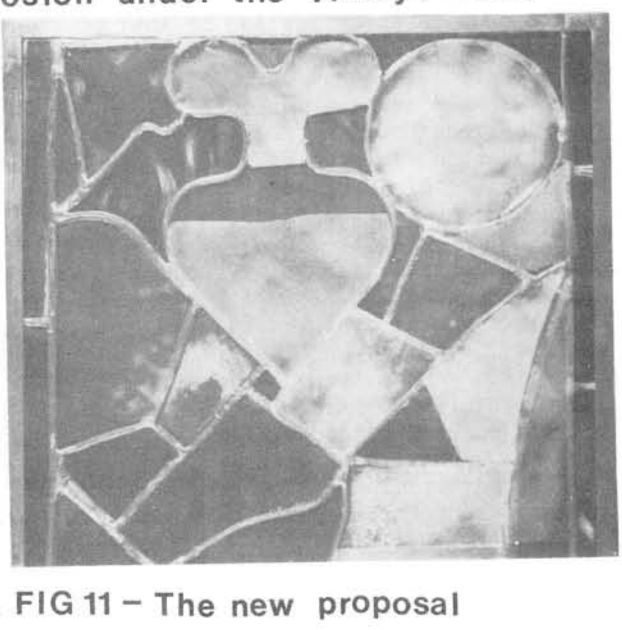

FIG 11 – The new proposal

4 CLEANING OF GLASS

In N.L. No.18, page 5 (Section 2) a translation was given of Dr W.P. Bauer's contribution to the 9th CVMA Colloquium (Paris, September 1975), on the effects which various methods of cleaning had on the surface of the glass. The lecture was accompanied by 12 slides and I expressed the hope that these important illustrations might be printed in the published account of the Colloquium.

The slides were not published but I have fortunately been able to borrow five of them, which are reproduced here as Figs. 12 to 16. I would remind readers that the glass was of the relatively low-silica, high-lime type from St Michael-in-Wachau, with a crusted surface. (All the details are given on p.5 of N.L. No.18).

Fig. 12 shows the original untreated surface of the glass. The opaque crust largely obscures some scratches in the surface of the glass.

Fig. 13 shows the surface of the glass after treatment with an alumina grit in the airbrasive apparatus (alumina grit 1/27, see Section 2 of N.L. No.21). The surface has been cleaned but it has also been roughened by the alumina grit. (RGN - if glass beads had been used in the airbrasive the surface would not have been rough like this.)

Fig. 14 Here the glass has been treated with J.M. Bettembourg's "Solution A" (with pyrophosphate) and the surface of the glass has not been attacked; in fact some scratches on the glass have been revealed.

Fig. 15 Here the glass has been treated with J.M. Bettembourg's "Solution B" (with EDTA); again, the glass has not been attacked and scratches have been revealed. (RGN - here we have what seems to be a conflict! Dr Bauer concludes that EDTA does not attack the glass, even after 48 hours, but Dr Ferrazzini concludes (see Fig.1 above) that EDTA will attack fractured surfaces. It is possible that the two glasses behave differently in the cleaning agents (we do not know the composition of Dr Ferrazzini's glass) and it is also possible that only clean fractured surfaces are attacked, and not the crusted surfaces which Dr Bauer studied!).

Fig. 16 shows the effect of airbrasion followed by hot hydrofluoric acid, and the glass is certainly attacked!

5 ABSTRACTS

245. ANON. "The corrosion of windows" (La corrosion des vitraux). Le Courrier du CNRS 1976 21 29-33.

This unsigned article is actually the result of collaboration between four distinguished French savants (Prof. R. Collongues, M J. Taralon, M J.M. Bettembourg and Prof. L. Grodecki) working in the fields of chemistry, conservation and art-history. It is therefore a highly-authoritative, well-balanced and wide-ranging summary of the present state of knowledge.

Much of it has appeared in previous News Letters (eg, Fig.4 is the same as Fig.6 of N.L. No.11 and Fig.5 is the same as Fig.1 of N.L. No.17, except that the distribution of phosphorus is shown instead of that of sulphur) but there are other fascinating illustrations. Fig.6 shows the formation of pits along a scratch which had been made at a previous restoration; results such as this are important in showing what really happens as a result of incorrect conservation procedures many years earlier.

The article starts by recounting the formation of the CVMA in 1952 and continues with a discussion of the cause of deterioration. It points out that corrosion phenomena cannot be generalised. French glass of the 12th century (25 assemblages) shows relatively little corrosion (especially the blue glass) but the windows have been subjected to many severe restorations. The many examples of 13th century French glass have exhibited more corrosion (even the blue glass) and some windows at Bourges have become totally obscured. (Readers should note that the captions to Figs. 1 and 2 have been reversed.) The rare 14th century French windows are in a better state of preservation whereas those of the 15th and 16th centuries are more variable.

The scientific studies of corrosion emphasise the importance of the composition of the glass and of the dangerous effects of moisture. Analyses are quoted for samples of glass from Amiens and from Evreux (see the results in N.L. No.21, analysis 27, p.11 and 23, p.10) and the type of corrosion (pitted or crusted) is related to the proportions of "modifying oxides". (RGN - the discussion of the effects of composition, by relating them to Stevel's "Y" factor (1948) would now be regarded as being out-of-date because it does not distinguish between "bridging and non-bridging oxygen atoms, eg, whether the modifying oxides are of the type RO or R_2O.)

They clearly show that the presence of sulphates in the crust is not necessarily evidence that sulphur dioxide is the primary agent of corrosion; water is the primary attacking agent and the sulphur dioxide merely converts the primary reactants into sulphates. This discussion is illustrated by excellent photomicrographs and electron microprobe "pictures" of sections of pits and it should be consulted by anyone who wants a first-rate summary of the state of knowledge in this field.

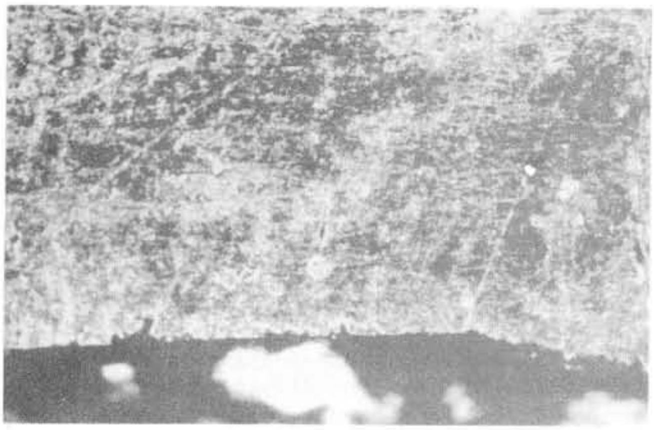

Fig. 12 Uncleaned

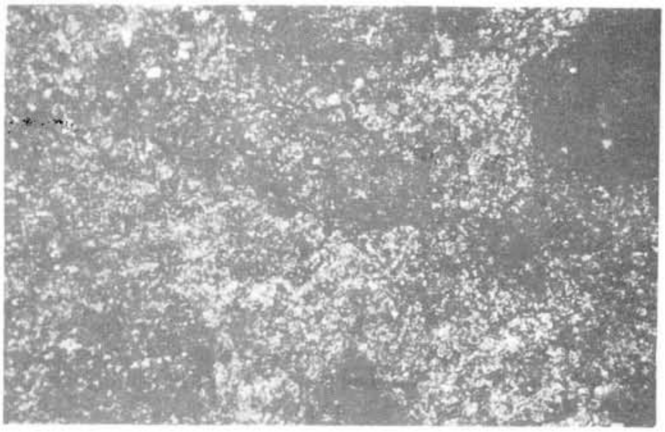

Fig. 13 Cleaned with Airbrasive

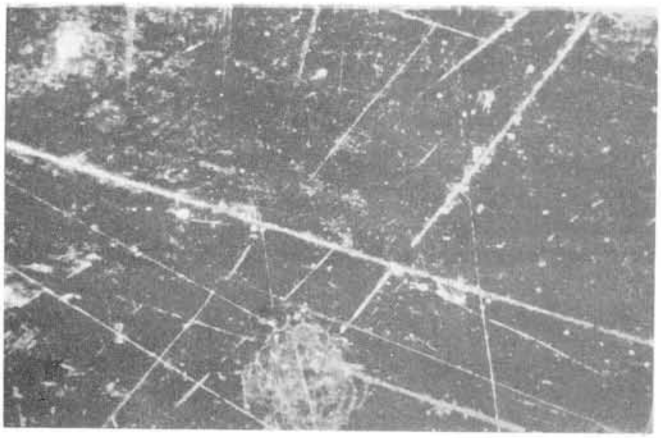

Fig. 14 Cleaned with Solution A

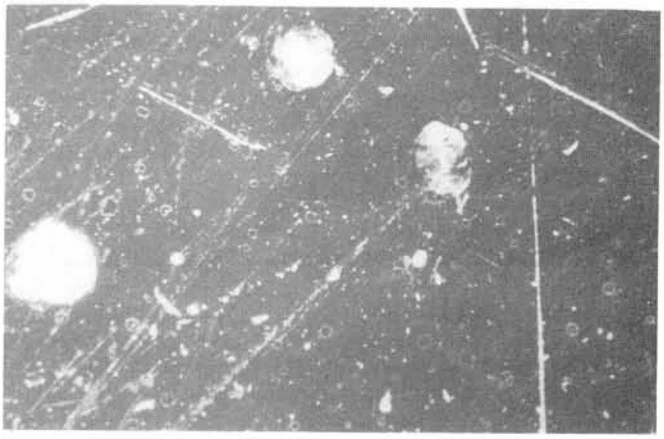

Fig. 15 Cleaned with Solution B

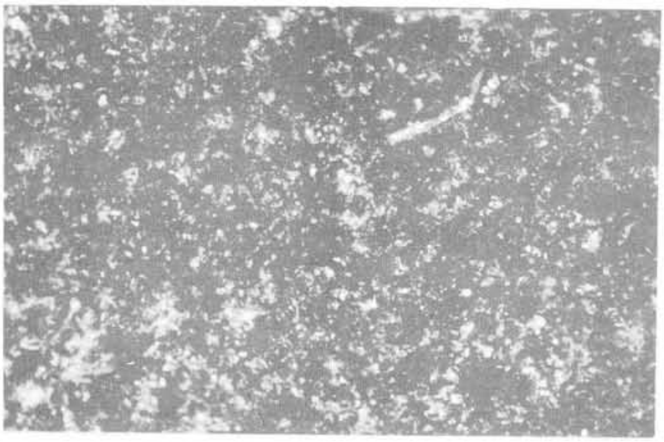

Fig. 16 Airbrasion and Hydrofluoric Acid

The restoration and conservation of medieval windows is discussed under four headings:- repair of the leads and of any breaks in the glass; cleaning; protection against atmospheric attack, and consolidation of loose paint. Re-leading is regarded as generally inevitable. Breaks in the glass are now edge-joined with silicone adhesives which are strong yet flexible. Cleaning of the glass is regarded as essential, despite claims in some quarters that the appearance of the glass is more beautiful if the crust is left in place, because the products of corrosion trapped under the crust cause further deterioration. Moreover, the individual pieces of coloured glass regain their true colours when the opacity of the crusts is removed.

The surface of the weathered glass, being deficient in the alkalies, is more durable than the original glass and hence any cleaning techniques should disturb this layer as little as possible. Glass-fibre brushes and the airbrasive are claimed to scratch the surface and give rise to pitting at a later date; ultra-sonic cleaning is not recommended because it may loosen paint and also predispose the glass to later deterioration; chemical solutions (see p.5 of N.L. No.18) are recommended because they remove any remaining insoluble salts without attacking the glass. (RGN - the whole question of cleaning seems to be much in dispute, see Figs. 1, 2, 14 and 15 of this News Letter!) The paintwork may be detached, friable, or porous and the first act of restoration should be the refixing of any loose paint by using Viacryl VC 363 diluted with ethyl acetate (see N.L. No.13, item 181E, p.9).

The cleaned glass can be protected against further weathering by an outer protective glazing, and studies of some systems are in progress. Plating procedures are not regarded as good because modern plating glasses do not exactly match the texture of the medieval surfaces and humidity or micro-organisms may penetrate the seal at the edge. A resin coating (Viacryl VC 363 - see N.L. No.20, item 220 on p.10) is recommended as a means of guaranteeing the exclusion of moisture (but this is challenged by Dr Ferrazzini in item 3 of this News Letter). The present collaboration between scientists and art-historians is international, really fundamental and totally interdisciplinary.

246. CRAMP, Rosemary (1975) "Window glass from the monastic site at Jarrow. Problems of interpretation" Journal of Glass Studies, 1975 17 88-96.

This paper is a further study of the very durable Saxon window glass found at Jarrow. The quarries are all extremely small, many being diamond-shaped with grozed sides about 20mm long. The colours are various shades of blue or green, and some are amber or red, but the majority are colourless. Very little lead was found on the site and hence it is not clear how these small quarries were glazed. None of the pieces bore any paint.

247. NEWTON, R.G. (1975) "The weathering of medieval glass" Journal of Glass Studies, 1975 17 161-168.

This is a general summary of the development of theories about weathering of glass in the last 20 years.

248. WEINBERG, Gladys Davidson (1975) "A medieval mystery: Byzantine glass production" Journal of Glass Studies, 1975 17 127-141.

Two medieval glass-melting sites were found in Corinth. One did not contain any remains of glass furnace pots and it seems that rectangular tank furnaces were used for a re-melting process, rather than for the primary melting of glass from batch materials. The other furnace site did have remains of cylindrical pots.

249. WERNER, A.E., BIMSON, M. and MEEKS, N.D. (1975) "The use of replica techniques and the scanning electron microscope in the study of ancient glass" Journal of Glass Studies, 1975 17 158-160.

This article describes the production of surface replicas of glass articles in order to help in the identification of forgeries. It was found that ancient weathered surfaces differ in a significant manner from those produced when forgeries are made.

250. LEE, Lawrence, SEDDON, George and STEPHENS, Francis "Stained Glass" Published by Mitchell Beazley, London 1976, 207 pages and 500 coloured illustrations, mostly by Sonia Halliday and Laura Lushington. £25.

This beautifully illustrated book contains everything that the ordinary reader would want to have on stained glass, and specialist readers would surely enjoy the book for the things it gives them about subjects other than their specialities. All of the famous windows are illustrated in colour and several cathedrals are shown in an "exploded" manner, with every window being visible.

It has been written in three parts, pages 8-63 being a general appreciation of stained glass; pages 64-175 provide a history of stained glass from the 11th to the 20th centuries; and pages 176-194 describe the making of a stained glass window and the conservation techniques in use at the Canterbury Glass Restoration Studio. The three main authors have been assisted by twelve consultants, of whom eight are Members of the Corpus Vitrearum. There is an excellent index and a four-page Gazetteer to the best glass in each country of the world. It is well worth the £25 price.

* * * * * * *

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.

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